Synthesis and reactivity of an N-triphos Mo(0) dinitrogen complex

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The preparation and reactivity of a novel molybdenum dinitrogen complex supported by a nitrogen-centred tripodal phosphine ligand (N-triphos, $N(CH_2PPh_2)_3$, NP_3^{Ph}) is reported. Reaction of N-triphos with $[MoX_3(THF)_3]$ ($X=Cl, Br, I$) gave the Mo(III) complex $[MoX_3(\kappa^2-NP_3^{Ph})(THF)]$ (**1**), where bidentate N-triphos coordination was observed. Reduction of this complex in the presence of dppm (bis(diphenylphosphino)methane) gave the dinitrogen complex $[Mo(N_2)(dppm)(\kappa^3-NP_3^{Ph})]$ (**2**), which exhibits moderate dinitrogen activation. An additional hydride complex, $[Mo(H)_2(dppm)(\kappa^3-NP_3^{Ph})]$ (**4**), was produced either as a minor side product during the reduction step, or as a major product by direct hydrogenation of the dinitrogen complex **2**. The reactivity of the dinitrogen complex **2** with a range of Lewis acids was also investigated. At low temperatures, protic or borane Lewis acids (H^+ , BBr_3 and tris(pentafluorophenyl)borane (BCF)) were found to coordinate to the apical nitrogen atom of the N-triphos ligand, with no conclusive evidence of any functionalisation of the dinitrogen ligand. Alkali metal Lewis acid addition to **2** resulted in the unexpected rearrangement of the N-triphos ligand to form $[Mo(dppm)(PMePh_2)(PCP)][B(C_6F_5)_4]$ (**7**), where PCP, $[Ph_2PCNHCH_2PPh_2]$ is the carbenic ligand formed upon rearrangement from the reaction of **2** with $M[B(C_6F_5)_4]$ ($M=Li, Na$ or K). Single crystal X-ray diffraction of complexes **1**, **2**, **4** and **7** provided structural confirmation of the N-triphos molybdenum complexes described.

Introduction

Dinitrogen transition metal complexes are key intermediate targets in the development of more sustainable routes towards artificial nitrogen fixation. Many of these complexes have been inspired by the FeMo cofactor of nitrogenase enzymes that are able to facilitate the catalytic reduction of N_2 to NH_3 under ambient conditions.¹ The activation of dinitrogen via coordination to a transition metal centre was first reported over 50 years ago,² and since then, many examples of such complexes have been reported in the literature for a variety of transition metals.^{3–5} However, only a few examples of these dinitrogen complexes have shown significant dinitrogen activation along with subsequent activity towards the catalytic formation of ammonia by reductive protonation under ambient conditions.⁶ Multidentate ligand topologies have been prevalent in the design of these catalysts. The first example of a homogenous catalyst to show activity was reported by Schrock and incorporated a tetradentate tetraamine ligand supporting a Mo(III)- N_2 centre.⁷ Later ligand scaffolds from Peters and co-workers incorporated tripodal phosphine architectures that stabilised Fe(0)- N_2 complexes.^{8,9} The most active ammonia formation catalyst to date, reported by

Nishibayashi and co-workers, utilised a tridentate pincer phosphine/NHC ligand to stabilise a dimolybdenum, dinitrogen-bridged catalyst that transformed up to 230 equivalents of ammonia from dinitrogen.¹⁰

Despite these breakthroughs, there is still room for improving the activity of these homogeneous ammonia formation catalysts. A desire to enhance dinitrogen bond activation and to increase complex stability, and preventing catalytic decomposition, has inspired the design of further dinitrogen complexes that are stabilised by new multidentate ligand scaffolds. Branched triphosphine ligands (triphos) are prominent examples of such scaffolds. Their tripodal coordination imparts stability towards metal centres and ensures *cis* coordination sites for additional ligands, which can better enable catalytic transformations. Tuzek and co-workers have previously reported a range of molybdenum dinitrogen complexes using C-triphos ($R^1C(CH_2PR_2)_3$)^{11–13} and Si-triphos ($R^1Si(CH_2PR_2)_3$)^{14,15} ligands. Their complex design is based on the formation of an octahedral, pentaphosphine mono(dinitrogen) Mo(0) centre (figure 1). A chelating phosphine triphos arm is always *trans* to the coordinated dinitrogen which prevents the

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Figure 1: Previously reported molybdenum triphos dinitrogen complexes in comparison to the N-triphos complex presented in this work. Blue indicates reactive sites towards Lewis acids (LA) in both systems. E = C or Si.

formation of *trans* bis(dinitrogen) complexes that are typically susceptible to decomposition when employed for the formation of ammonia.¹⁶

Although triphos ligands are used extensively in coordination chemistry and catalysis, their synthesis can be challenging since it typically involves the preparation and reaction of highly sensitive metal phosphide reagents.¹⁷ In comparison, nitrogen-centred N-triphos derivatives ($\text{N}(\text{CH}_2\text{PR}_2)_3$) are readily prepared via a phosphorus-based Mannich reaction from a corresponding secondary phosphine.^{18,19} This route enables the easy tuning of the steric and electronic properties of the ligand at the phosphine substituents. Previous work from our group has investigated the coordination chemistry of these underexplored ligands and their catalytic applications for the hydrogenation of biomass-derived levulinic acid.^{20–24} We found that subtle changes in the phosphines' steric and electronic characteristics resulted in either κ^2 and κ^3 coordination modes of N-triphos.^{20,24}

Herein, we report the preparation of the first molybdenum dinitrogen complex supported by an N-triphos ligand scaffold. Inspired by Tuczek and co-workers' pentaphosphine C-triphos and Si-triphos $\text{Mo}(\text{O})\text{-N}_2$ complexes,^{11–15} we targeted a pentaphosphine mono(dinitrogen) complex combining the N-triphos ligand with an additional diposphine co-ligand, although the additional Lewis basic nitrogen centre of the N-triphos ligand in our work offers a different reactivity profile to any previous work (figure 1). The preparation of the N-triphos $\text{Mo}(\text{O})\text{-N}_2$ complex is discussed, along with its reactivity towards a range of Lewis acids.

Results and Discussion:

Coordination to $\text{Mo}(\text{III})$ Precursor: The phenyl-substituted N-triphos ligand, NP_3^{Ph} , was selected due to its ease of synthesis and ability to form stable κ^3 -coordination geometries with various low-oxidation state transition metal complexes.^{22,24} A range of $\text{NP}_3^{\text{Ph}}\text{-Mo}(\text{III})$ precursor complexes (scheme 1) were prepared as precursors in order to generate the $\text{Mo}(\text{O})\text{-N}_2$ species under reducing conditions (scheme 2).

Reaction of the NP_3^{Ph} ligand with $[\text{MoCl}_3(\text{THF})_3]$ in THF over several days resulted in the formation of the paramagnetic complex, $[\text{MoCl}_3(\kappa^2\text{-NP}_3^{\text{Ph}})(\text{THF})]$ (**1-Cl**). Crystallographic characterisation confirmed the structure of **1-Cl**, where the N-

Scheme 1: Synthesis of N-triphos molybdenum halide precursor complexes (**1**)

Figure 2: Crystal structure of $[\text{MoCl}_3(\kappa^2\text{-NP}_3^{\text{Ph}})(\text{THF})]$ (**1-Cl**)

triphos ligand coordinates in a bidentate fashion, with a coordinated THF molecule and the $\text{Mo}(\text{III})$ centre retaining the *meridional* chloride geometry (figure 2). $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy also eluded to this bidentate N-triphos structure, with just one singlet at -64 ppm observed (figure S1), relating to the free N-triphos arm (the coordinated N-triphos arms are likely too close to the paramagnetic centre to be observed by NMR spectroscopy).

As with the coordination of other tripodal ligands to $[\text{MoCl}_3(\text{THF})_3]$, there is an energetic barrier towards tridentate ligand coordination due to a *meridional* to *facial* rearrangement of the chloride ligands from the THF adduct complex to the tripod complex.^{25,26} The NP_3^{Ph} ligand was also reacted with both the bromide and the iodide precursor complexes, $[\text{MoX}_3(\text{THF})_3]$ $\text{X} = \text{Br}, \text{I}$, which have lower energetic barriers for the *mer* to *fac* halide rearrangement and therefore are more likely to encourage tridentate ligand coordination.²⁷ However, $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic characterisation was similar to the chloride complex, with single resonances of the uncoordinated N-triphos arm observed at -66 and -58 ppm for **1-Br** and **1-I** respectively (figures S2 and S3). Attempts to also prepare **1** in non-coordinating solvents (toluene or DCM) to encourage *facial* chloride and tridentate N-triphos coordination were unsuccessful, resulting in decomposition products.

Synthesis of N_2 complex: The halide N-triphos complex **1** (for $\text{X} = \text{Cl}, \text{Br}$, or I) was reduced under a nitrogen atmosphere (using either sodium amalgam or magnesium powder reducing agents) in the presence of a dppm

(bis(diphenylphosphino)methane) co-ligand to form the dinitrogen complex $[\text{Mo}(\text{N}_2)(\text{dppm})(\text{NP}_3^{\text{Ph}})]$ (**2**). This dppm co-ligand ensures the formation of a stable mono(dinitrogen) complex with octahedral geometry around the Mo centre (scheme 2).

Scheme 2: Synthesis of the mono(dinitrogen) complex, $[\text{Mo}(\text{N}_2)(\text{dppm})(\text{NP}_3^{\text{Ph}})]$ (**2**), by reduction of **1** ($\text{X}=\text{Cl}$, Br or I). Reducing agent = Na/Hg or Mg powder.

Figure 3: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of purified $[\text{Mo}(\text{N}_2)(\text{dppm})(\text{NP}_3^{\text{Ph}})]$ (**2**) (C_6D_6 , 161 MHz, 298 K).

Figure 4: Solid state IR spectrum of complex **2**

Complex **2** was characterised by multinuclear NMR, IR spectroscopy and single crystal X-ray crystallography. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** shows three distinctive multiplets at 7, 10 and 20 ppm (that arise due to second order coupling effects), relating to the three different phosphorus

environments within the pentaphosphine complex (figure 3). The presence of coordinated dinitrogen was confirmed by solid state IR spectroscopy, which showed a characteristic $\text{N}\equiv\text{N}$ stretch at 2027 cm^{-1} (figure 4), indicative of moderate dinitrogen activation. This value is at marginally lower wavenumbers compared to the reported C-triphos complex (employing phenyl substituted C-triphos and dppm) by Tuczek and co-workers ($\nu(\text{NN}) = 2035\text{ cm}^{-1}$),¹¹ indicating a similar degree of activation of dinitrogen. Crystals of complex **2**, suitable for single crystal X-ray diffraction, were obtained via vapour diffusion of hexane into a THF solution of the complex. The crystal structure (figure 5) further confirmed the solution state $^{31}\text{P}\{^1\text{H}\}$ spectroscopic assignments and the coordination of the dinitrogen molecule. The crystal structure shows steric protection of the coordinated dinitrogen: the space-filling model shows the extent to which the phenyl substituents on P3, P5, P51 and P53 envelope the dinitrogen coordination site (figure S30). The NN bond distance was found to be $1.114(4)\text{ \AA}$, and shows a clear elongation compared to free N_2 ($1.0975\text{ \AA}$),

Figure 5: Crystal structure of $[\text{Mo}(\text{N}_2)(\text{dppm})(\text{NP}_3^{\text{Ph}})]$ (**2**)

thus demonstrating NN bond activation.⁴

The $^{15}\text{N}_2$ -labelled isotopologue of **2**, $[\text{Mo}^{15}\text{N}_2](\text{dppm})(\text{NP}_3^{\text{Ph}})]$ (**2- ^{15}N**) was also prepared, either via displacement (exposing a solution of **2** to a $^{15}\text{N}_2$ atmosphere) or by performing the reduction of **1** under a $^{15}\text{N}_2$ atmosphere (analogous to scheme 2). In both cases, *in situ* characterisation by ^{15}N NMR spectroscopy showed broad signals at -28.2 and -39.4 ppm (in addition to a signal at -71.8 ppm , indicative of free $^{15}\text{N}_2$ gas) which correspond to the distal and proximal ^{15}N atoms of **2- ^{15}N** respectively (figure S8), and solution IR spectroscopy (in THF) showed an expected shift in the NN stretch to 1962 cm^{-1} , relative to **2** (2029 cm^{-1} in THF solution-figure S9). Attempts to isolate **2- ^{15}N** by work-up under an argon atmosphere were unsuccessful, owing to the possible instability of the dinitrogen complex under non-nitrogen atmospheres.

In addition to the formation of **2**, other side products were also formed during the reduction of **1** to form the dinitrogen complex. One of these side products could easily be identified as a bis(dinitrogen) complex, $[\text{Mo}(\text{N}_2)_2(\text{dppm})(\kappa^2\text{-NP}_3^{\text{Ph}})]$ (**3**), with bidentate coordination of the N-triphos ligand. Complex **3** was identified in the $^{31}\text{P}\{^1\text{H}\}$ NMR of the reduction mixtures, when the reduction was performed at lower temperatures. For such reductions, $^{31}\text{P}\{^1\text{H}\}$ NMR resonances in addition to those of **2** were observed at -29.0 (singlet), 10.3 (multiplet) and 39.0 (multiplet) ppm; the singlet at -29 ppm is indicative of an uncoordinated N-triphos arm, whereas the other two multiplet resonances indicate coordinated phosphine moieties (figure S10). Complex **3** is the kinetic product to the reduction, forming in significant quantities when the reduction was performed at colder temperatures (195 K); only very small amounts could be observed when the reduction of **1** was performed at room temperature. This kinetic product can be fully converted to thermodynamically stable **2** simply by heating, enforcing tridentate coordination of the N-triphos ligand to form the mono(dinitrogen) complex (scheme 3).

Scheme 3: Reactivity of **2**, showing the preparations of **3** and **4**

The other side product formed alongside **2** in the reduction of **1** was harder to identify, appearing as two additional singlet species in the crude reduction $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 24.1 and 32.9 ppm, in a respective 3:2 integral ratio, alongside **2** (and **3** if the reduction was performed at 195 K)-figure S11. The crude ^1H NMR spectrum of the reduction mixture showed the expected phenyl and methylene peaks associated with the dinitrogen complex **2** (expected for coordinated N-triphos^{Ph} and dppm), but the spectrum also showed a hydride-type resonance at -2 ppm (sextet)-figure S12. We therefore suspected that this side-product could be a hydride complex, which could be confirmed by hydrogenation of **2**. Subjecting dinitrogen complex **2** to a hydrogen (or deuterium) gas atmosphere resulted in the formation of a dihydride complex, $[\text{Mo}(\text{H})_2(\text{dppm})(\text{NP}_3^{\text{Ph}})]$ (**4**) (or $[\text{Mo}(\text{D})_2(\text{dppm})(\text{NP}_3^{\text{Ph}})]$ (**4-D**) for deuterium gas) (scheme 3).

Further characterisation of **4** (formed by hydrogenation of **2**) confirmed it as the side product from the original reduction; the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4** shows the aforementioned two

singlet resonances at 24.1 and 32.9 ppm, and the proton-coupled ^{31}P NMR spectrum shows these peaks as triplets, with coupling to two hydride ligands (figures S13 and S14). The ^1H NMR spectrum of **4** also shows the previously observed hydride resonance at -2 ppm, with a relative integral of 2, and sextet multiplicity, due to coupling to the 5 other coordinated phosphine moieties (figure S15). An additional T1 measurement of the ^1H NMR resonance at -2 ppm showed a relaxivity time of 348 ms, indicative of a metal-hydride resonance.²⁸ The IR spectrum of **4** shows loss of the NN stretch at 2027 cm^{-1} , and the appearance of a new Mo-H stretch at 2278 cm^{-1} (figure S16). Further confirmation of this hydride species was obtained by the deuterium gas labelling (formation of **4-D**, scheme 3), which showed a ^2H NMR multiplet resonance at -2 ppm for the deuteride ligands, and a shifted Mo-D stretch (relative to the Mo-H stretch) at 1613 cm^{-1} in the IR spectrum. Complex **4** was also characterised by single crystal XRD (figure 6); single crystals were obtained from a THF/hexane layer.

When formed as a side product to the formation of **2**, complex **4** could be removed from the crude reaction mixture by thoroughly washing the solid mixture with diethyl ether; **4** proved to be slightly more soluble in diethyl ether, enabling separation and subsequent purification of **2**. However, when the reduction was performed under an argon atmosphere

Figure 6: Crystal structure of the Mo dihydride complex $[\text{Mo}(\text{H})_2(\text{dppm})(\text{NP}_3^{\text{Ph}})]$ (**4**)

4 was exclusively formed. Despite conversion of **2** to **4** by hydrogenation, this process was irreversible, and **4** could not be converted back to **2**, even with thorough sparging with nitrogen gas (scheme 3).

The formation of **4** from the reduction of **1** is not an obvious progression. To rationalise this, a number of reductions were performed where possible sources of the hydride had been deuterated. Initially, we predicted the solvent was the hydride source, but reduction of **1** in $\text{d}_8\text{-THF}$

still gave formation of the hydride side-product, as indicated by ^1H NMR spectroscopy. We later thought that the ligands adopted in this system may be possible hydride sources – both N-triphos^{Ph} and dppm contain methylene backbones, which could be acidic and provide a hydride source. Employing the deuterio-analogues of these ligands (dppm- d_2 or N-triphos^{Ph}- d_6), with CD_2 methylene bridges rather than CH_2 methylene bridges, to the reductions (in d_8 -THF to avoid possible solvent H/D transfer) also resulted in the formation of the hydride complex **4** as a side product (and not the deuteride analogue **4-D**) (see table S1). We cannot currently explain the formation of **4** as a side product to the formation of **2**; a possible explanation may be due to minor contaminants in the dry solvent or nitrogen gas employed, even though we could detect no water impurities by checking the solvents with ^1H NMR spectroscopy.

Acid reactivity of $[\text{Mo}(\text{N}_2)(\text{dppm})(\text{NP}_3^{\text{Ph}})]$ (2**):** A series of protonation experiments were performed on complex **2** in order to investigate its potential activity towards catalytic nitrogen fixation. A hydrazido complex is a key intermediate within nitrogen fixation cycles and is known to form via protonation of a bound dinitrogen molecule. The previously reported similar C-triphos complex (employing phenyl-substituted C-triphos and dppm) did not exhibit reactivity at the dinitrogen ligand¹¹, and based on the IR stretching frequencies,

Scheme 4: Addition of triflic acid to dinitrogen complex **2**, to form $[\text{Mo}(\text{N}_2)(\text{dppm})(\text{H-NP}_3^{\text{Ph}})](\text{OTf})$ (**5**) (quantitative conversion by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic characterisation).

the N-triphos dinitrogen complex **2** shows a similar dinitrogen activation potential. Despite the structural similarities between our complex (**2**) and the previously reported C-triphos derivative, we hypothesised that the apical N-triphos atom may lead to interesting reactivity upon protonation of this complex (*ca.* figure 1). Incorporation of ancillary amine-containing ligands within transition-metal dinitrogen complexes has been previously explored by Mock and co-workers: they hypothesised that incorporation of pendant amines within the secondary coordination sphere could facilitate proton transfer towards the dinitrogen ligand.²⁹ Inclusion of a fixed amine site, such as in coordinated N-triphos, could therefore offer different reactivity upon protonation.

Addition of triflic acid to **2** at room temperature unfortunately resulted in complex decomposition, giving a series of unassignable resonances in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. Interestingly, however, addition of triflic acid to **2** at

195 K resulted in protonation at the apical nitrogen centre of the N-triphos ligand scaffold, forming $[\text{Mo}(\text{N}_2)(\text{dppm})(\text{H-NP}_3^{\text{Ph}})](\text{OTf})$ (**5**) (scheme 4). Surprisingly, the addition of excess acid (<5 eq) resulted in only the formation of **5**, with no evidence of additional protonation at the dinitrogen ligand occurring to form a hydrazido complex. A significant downfield shift in the three phosphorus resonances of **2** upon formation of **5** was observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, and this was particularly obvious for the two N-triphos signals (figure 7). This shift is the result of decreased shielding around the phosphines upon proton coordination to the ligand apical nitrogen centre. *In situ* low temperature infrared spectroscopy of the protonation of **2** was also performed, and the NN stretch was monitored (figure S18). On addition of HOTf, there was no observed change in the $\text{N}\equiv\text{N}$ stretch at 2027 cm^{-1} . Warming this mixture to room temperature resulted in the eventual decomposition of the protonated dinitrogen complex **5**. Protonation at the N-triphos apical nitrogen centre clearly alters electron density around the phosphines as evidenced by the shifts in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum which in turn will change the metal-backbonding towards both the phosphines and the dinitrogen ligand. It might therefore be expected to observe an increase in the NN stretching frequency in the spectrum of **5**, however, no significant change was observed in the *in situ* infrared spectra obtained. Repeated attempts to crystallise **5** were unsuccessful due to its temperature instability.

Previously reported examples of protonation at the N-triphos apical centre within transition metal complexes include

Figure 7: Stacked $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (202 MHz) of acid addition to dinitrogen complex **2**. Top to bottom: **2**, C_6D_6 , 298 K; addition of HOTf to form $[\text{Mo}(\text{N}_2)(\text{dppm})(\text{H-NP}_3^{\text{Ph}})](\text{OTf})$ (**5**), d_8 -THF, 195 K; addition of BBr_3 to form $[\text{Mo}(\text{N}_2)(\text{dppm})(\text{Br}_3\text{B-NP}_3^{\text{Ph}})]$ (**6-BBr3**), toluene, 195 K; addition of BCF to form $[\text{Mo}(\text{N}_2)(\text{dppm})(\text{C}_6\text{F}_5)_3\text{B-NP}_3^{\text{Ph}})]$ (**6-BCF**), toluene, 195 K.

the addition of HBF_4 to $[\text{M}(\text{CO})_3(\text{NP}_3^{\text{Ph}})]$ ($\text{M}=\text{Mo}^{30}, \text{W}^{24}$) which resulted in protonation at the ligand apical nitrogen centre to form cationic $\text{M}(\text{O})$ complexes $[\text{M}(\text{CO})_3(\text{H-NP}_3^{\text{Ph}})]^+$. The much stronger triflic acid is therefore even more likely to result in favourable N-triphos protonation, as proven by the formation of **5**. Unfortunately, no evidence of the hydrazido complex formation was observed on protonation of **2**; the more basic apical amine centre of N-triphos may inhibit its formation since

it is the preferential site of protonation. Furthermore, protonation of this apical amine centre may further deactivate bound dinitrogen by making the coordinated phosphines less electron donating, even though no observed change in the $\nu(\text{NN})$ infrared band was observed upon formation of **5**.

Lewis acidity of $[\text{Mo}(\text{N}_2)(\text{dppm})(\text{NP}_3^{\text{Ph}})]$ (2**):** In a further attempt to functionalise the coordinated dinitrogen of **2**, the reactivity with Lewis acidic boranes was investigated. Functionalisation of coordinated dinitrogen on Mo, W, Rh and Os complexes using aluminium based Lewis acids has previously been explored by Chatt and co-workers,³¹ and Tuzek and co-workers also reported the formation of $\text{Me}_3\text{Al-N}_2$ adduct complexes by the addition of trimethylaluminium to various molybdenum dinitrogen complexes with pentaphosphine ligand environments.^{14,32} With regards to borane Lewis acid functionalisation, recent promising work by both Szymczak and Etienne has shown that the addition of boranes to iron or molybdenum/tungsten dinitrogen complexes results in adduct formation of the borane to the dinitrogen ligand, enhancing dinitrogen activation and allowing for further dinitrogen functionalisation by protonation, borylation or silylation.^{33,34} We surmised that a similar addition of a strongly Lewis acidic borane could also result in adduct formation at the dinitrogen ligand of **2**. It may also be expected to form an adduct at the N-triphos nitrogen centre, which could act as a protecting group for this basic site, and therefore facilitate subsequent protonation selectively at the dinitrogen ligand site.

Scheme 6: Formation of Lewis pair adduct complexes, $[\text{Mo}(\text{N}_2)(\text{dppm})(\text{R}_3\text{B-NP}_3^{\text{Ph}})]$ (**6**), and attempted protonation to form the hydrazido species.

Dinitrogen complex **2** was reacted with the strong Lewis acids boron tribromide and tris(pentafluorophenyl)borane (BCF) which resulted in the formation of the Lewis pair adduct transition metal complexes $[\text{Mo}(\text{N}_2)(\text{dppm})(\text{R}_3\text{B-NP}_3^{\text{Ph}})]$ (**6**) ($\text{R}=\text{Br}$ **6-BBr₃**, $\text{R}=\text{C}_6\text{F}_5$ **6-BCF**) (scheme 6). Addition of the boranes to complex **2** at room temperature resulted in decomposition and unassignable $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, similar to the protonation reactions of **2**, however, addition of the boranes at 195 K resulted in the formation of **6**. A downfield shift of the three characteristic multiplet signals in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **6** were observed (again, a similar shift was observed for the formation of **5**) due to the decreased shielding of the phosphines upon adduct formation at the apical nitrogen site (figure 7). For both complexes,

heteronuclear $^{19}\text{F}\{^1\text{H}\}$ and ^{11}B NMR spectroscopy provided further insight and characterisation. In complex **6-BBr₃**, a singlet at -5.9 ppm was observed in the ^{11}B NMR spectrum, indicative of an amine-borane adduct. For complex **6-BCF**, a singlet at -4.7 ppm was observed in the ^{11}B NMR spectrum, again, indicative of an amine-borane adduct, whilst three broad, multiplet peaks in the ^{19}F NMR spectrum at -134.0, -157.9 and -163.0 ppm were observed, shifted characteristically upfield from free BCF due to increased shielding provided by the amine-borane interaction (figures S19 and S20). *In situ*, low temperature infrared spectroscopy was also performed for both **6-BBr₃** and **6-BCF**. Addition of either borane to **2** at 195 K resulted in no change in the NN stretch until the sample was warmed to room temperature, where decomposition of the adduct resulted in decreased intensity of the infrared stretching signal (figure S22). This behaviour is similar to complex **5**, where no change to $\nu(\text{NN})$ was also observed; the decreasing electron density around the phosphines, as shown by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, is expected to affect the NN stretch, but this change in frequency is likely small and not easily observed in the *in situ* IR spectra. Attempts to crystallise adduct complexes **6** for crystallographic characterisation were unsuccessful, owing to their temperature sensitivity.

We envisioned that the amine-borane adduct complexes **6** may facilitate subsequent protonation at the dinitrogen ligand, due to the now protected apical N-triphos nitrogen centre. Two equivalents of triflic acid were added to *in situ* generated **6** (both **6-BBr₃** and **6-BCF**) in fluorobenzene (more polar than toluene and a better solvent choice for protonations) at 233 K, and the reaction was monitored by low temperature NMR and *in situ* IR spectroscopy. Unfortunately, the ^1H NMR spectrum did not show any N-H signals indicative of a hydrazido complex, and the $^{31}\text{P}\{^1\text{H}\}$ NMR did not show any clear multiplet peaks, suggesting decomposition and loss of the characteristic pentaphosphine environment (figure S23). The *in situ* IR spectrum also showed little change to the NN stretch, with no significant new N-H stretches observed that may correspond to hydrazido complex formation (figure S24).

Due to the low temperature stability of **6** and the subsequent protonation products, further conclusive evidence could not be obtained to fully determine the occurrence of protonation at the dinitrogen ligand. It is likely that the parent dinitrogen complex **2** is not activated enough for further functionalization, even with borane protection of the apical amine of the N-triphos ligand backbone.

Alkali metal M^+ addition to $[\text{Mo}(\text{N}_2)(\text{dppm})(\text{NP}_3^{\text{Ph}})]$ (**2**):

Despite not indicating dinitrogen protonation reactivity, we did observe some interesting reactivity of complex **2** towards alkali metal Lewis acids. In a further attempt to functionalise the coordinated dinitrogen of complex **2** with other non-protic or non-borane-based Lewis acids, we turned to alkali metal salts, starting with Li^+ . Treatment of **2** with $[\text{Li}(\text{OEt}_2)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ at room temperature resulted in the formation of an unusual cationic molybdenum phosphine/carbene complex, $[\text{Mo}(\text{dppm})(\text{PMePh}_2)(\text{PCP})][\text{B}(\text{C}_6\text{F}_5)_4]$ (**7**), where PCP

(Ph₂PCNHCH₂PPh₂) is the new tridentate phosphine/carbene ligand formed upon rearrangement and cleavage of the N-triphos ligand (scheme 7). Addition of various equivalencies of Li⁺ (1-10 equivalents) also resulted in the formation of **7**, and the same reactivity was also observed for the other alkali metal analogue M[B(C₆F₅)₄] salts (M = Na or K). The formation of **7** was monitored by ³¹P{¹H} NMR spectroscopy: initial addition of the M⁺ salt resulted in the formation of an unidentified intermediate species that exhibited 3 multiplets at 20, 11 and -28 ppm in a 2:2:1 ratio, upfield shifted to the resonances of **2** (figure S26), but after 2-3 days, the ³¹P{¹H} NMR spectrum indicated the formation of **7** by 5 multiplet resonances, at 96, 32, 14, 2 and -107 ppm, relating to the 5 new phosphorus environments (figure S27). The infrared spectrum of both the unidentified intermediate and **7** shows loss of the NN stretch, which seems necessary for this transformation. Structural confirmation of **7** was ultimately provided by the X-ray crystal structure (figure 8).

From our previous coordination studies of N-triphos transition metal complexes, we typically observe this ligand class to form stable, chelating metal complexes, with either

Scheme 7: Reactivity of **2** with M[B(C₆F₅)₄] to form complex **7**. M = Li ([Li(OEt₂)₂]), Na or K, aromatic solvent = benzene, toluene or fluorobenzene.

Figure 8: Crystal structure of the cation of **7**, [Mo(dppm)(PMePh₂)(PCP)]⁺.

bidentate or tridentate N-triphos coordination only through the phosphine moieties.^{20–24} However, with the formation of **7**, we have now observed that the N-triphos ligand is susceptible

to ligand cleavage and rearrangement. Within **7**, one of the methylene bridges of the N-triphos ligand is now bonded to the metal centre through a metal-carbene interaction, with hydrogen atom transfer from the previous CH₂ group to both the apical nitrogen of the ligand and to another methylene bridge site, with subsequent cleavage of this N-C bond to form a PMePh₂ monophosphine ligand. The 'PCP' ligand in **7** that forms upon rearrangement is planar, and the crystal structure reveals a carbene Mo-C bond length of 1.984 (3) Å, which is similar to other Mo=CR₂ alkylidene complexes (the nearest similar structure reported, a Mo=C-P-C metallocycle complex, has a similar Mo-C bond length of 1.894(6) Å.³⁵

Although we have not yet elucidated a reaction pathway of **2** to **7**, the presence of a labile dinitrogen ligand in **2**, as well as the bulky, non-coordinating B(C₆F₅)₄ anion, seem to be significant for this transformation. Attempts to prepare **7** with other alkali metal salts with other anions (BPh₄ or PF₆) were unsuccessful. The role of M[B(C₆F₅)₄] is unknown, but we propose that there is an alkali-metal mediated oxidation of the molybdenum centre, with loss of the dinitrogen ligand and subsequent rearrangement of the N-triphos ligand. Addition of 1 equivalent of oxidizing agent (ferrocenium hexafluorophosphate) did not result in formation of **7**, suggesting this mechanism isn't a simple one electron oxidation. Further work is being undertaken to elucidate this mechanism and determining the role of the alkali metal in this reaction.

Conclusion: The first example of a molybdenum dinitrogen complex supported by the N-triphos ligand scaffold is reported and investigated for its dinitrogen activation potential via a series of protonation and borane-adduct forming experiments. A hydride species was found to form alongside the dinitrogen complex upon reduction but could also be formed by hydrogenation of the dinitrogen complex, further confirming its structure. The N-triphos ligand scaffold provides a similar extent of dinitrogen activation in comparison to the related C-triphos complex, but it does introduce a different reactivity profile with the additional apical amine site. The reactivity of the N-triphos molybdenum dinitrogen complex was investigated, and it was found that protic and borane Lewis acids coordinated only to the considerably more basic apical amine site of the coordinated N-triphos rather than functionalising the coordinated dinitrogen, which may be too sterically encumbered by surrounding phenyl groups. Formation of amine-borane adducts were observed upon addition of BBr₃ or BCF to the dinitrogen complex, protecting the apical nitrogen site. Evidence of further protonation at the dinitrogen ligand of these protected borane adduct complexes was inconclusive, although the parent dinitrogen complex may not be sufficiently activated. Reactivity of the dinitrogen ligand with M[B(C₆F₅)₄] (M=Li, Na, K) salts resulted in a new cationic molybdenum phosphine/carbene complex, with loss of coordinated dinitrogen, where the new chelating phosphine/carbene ligand is formed via a rearrangement of the N-triphos ligand and oxidation of the metal centre. Further

work is being undertaken to investigate this unusual transformation.

Overall, this system provides a useful model of reactivity towards general dinitrogen activation with N-triphos ligands that incorporate an apical amine site. However, there are some drawbacks to the current system: the temperature sensitivity of the reactivity studies results in difficult characterisation; the dinitrogen activation is only moderate, although this could be improved by incorporating more electron-donating phosphines; and the sterically demanding phenyl-substituted phosphine ligands may inhibit reactivity at the coordinated dinitrogen, so less sterically bulky phosphines could be substituted, that do not shield the dinitrogen ligand as much as in **2**. Further work is currently underway investigating the synthesis and reactivity of analogous complexes with varying phosphine substituents on both the N-triphos and the diphosphine ligands to improve the degree of dinitrogen activation.

Experimental:

General information: All manipulations were performed under a N₂ atmosphere using standard Schlenk line and glovebox techniques, unless otherwise stated. Dry solvents were obtained from an MBraun MB-SPS 800 Solvent Purification system, degassed by thoroughly sparging with nitrogen and stored over activated 3 Å molecular sieves. Deuterated solvents were purchased from Goss-Scientific, freeze-pump-thaw degassed, and stored over 3 Å molecular sieves. C₆D₆ and d₈-toluene were additionally dried over CaH₂ before storage. ¹⁵N₂ gases (Cambridge Isotope Laboratories, 98% ¹⁵N) were transferred from a breakseal flask using a Toepler pump. NP₃^{Ph},¹⁹ [MoBr₃(THF)₃],³⁶ [MoI₃(THF)₃]³⁶ and [Li(OEt₂)₂][B(C₆F₅)₄]³⁷ were prepared as described in the literature, and all other reagents were commercially available and were used as received. ¹H, ²H, ¹³C{¹H}, ³¹P{¹H}, ¹⁵N, ¹⁹F{¹H} and ¹¹B NMR spectra were recorded on Bruker AV-400, AV-500 or DRX-400 spectrometers. Chemical shifts are reported in ppm, using the residual proton impurities in the solvents for ¹H and ¹³C{¹H} NMR spectroscopy. ³¹P, ¹⁵N, ¹⁹F and ¹¹B chemical shifts were referenced (δ = 0) externally to 85% H₃PO₄ (aq), neat CH₃NO₂, CCl₄ and BF₃·OEt₂ respectively. Mass spectrometry analyses were conducted by the Mass Spectrometry Service, Imperial College London. Infrared spectra were recorded on a Perkin-Elmer Spectrum FT-IR spectrometer, with solution phase spectroscopy performed using an Omni-cell with NaCl plates. *In situ* infrared spectroscopy was performed using a Mettler Toledo ReactIR instrument at the University of Oxford. Elemental analyses were carried out by Mr. Stephen Boyer at London Metropolitan University. X-ray diffraction analysis was carried out by both S.L. Apps and Dr. Andrew White of the Department of Chemistry at Imperial College London. Details of the single-crystal X-ray diffraction analysis can be found in the Supporting Information.

[MoX₃(κ²-NP₃^{Ph})(THF)] (1): An equimolar suspension of [MoX₃(THF)₃] (X = Cl, Br or I, typical amount 0.500 – 1.00 g) and

NP₃^{Ph} in THF (20 mL) was stirred for up to 5 d at 298 K. The resulting dark red/brown solution was concentrated to 5 mL before the addition of hexane (30 mL) to precipitate the product. The resulting suspension was filtered, and the orange/brown solid was washed with hexane (2 x 10 mL) and dried *in vacuo*.

[MoCl₃(κ²-NP₃^{Ph})(THF)]: [MoCl₃(THF)₃] (300 mg, 0.722 mmol, 1.02 eq) was reacted with NP₃^{Ph} (438 mg, 0.716 mmol, 1 eq) in THF for either 5 d at 298 K, or 2 d at 323 K. Orange/brown solid, yield = 500 mg, 90%. ³¹P{¹H} NMR (C₆D₆, 162 MHz, 298 K) δ: -65.0 (s). ES-MS (positive ion): *m/z* calcd. for C₃₉H₃₆Cl₃MoNP₃Na ([M+Na]⁺) 837.010, found 837.008. Anal. Calcd. for C₃₉H₃₆Cl₃MoNP₃ (found): C, 57.55 (57.82); H, 4.46 (4.34); N, 1.72 (1.86). Single yellow/orange crystals suitable for X-ray diffraction were obtained by vapour diffusion of a concentrated solution of [MoCl₃(NP₃^{Ph})] in THF with hexane.

[MoBr₃(κ²-NP₃^{Ph})(THF)]: [MoBr₃(THF)₃] (500 mg, 0.911 mmol) was reacted with NP₃^{Ph} (557 mg, 0.911 mmol) in THF at 298 K for 3 d. Yield = 780 mg, 90%. ³¹P{¹H} NMR (C₆D₆, 162 MHz, 298 K) δ: -65.0 (s). ES-MS (positive ion): *m/z* calcd. for C₃₉H₃₇Br₃MoNP₃Na ([M+H]⁺) 948.872, found 948.874. Anal. Calcd. for C₃₉H₃₆Br₃MoNP₃ (found): C, 49.45 (49.36); H, 4.01 (3.83); N, 1.60 (1.48)

[MoI₃(κ²-NP₃^{Ph})(THF)]: [MoI₃(THF)₃] (990 mg, 1.44 mmol) was reacted with NP₃^{Ph} (863 mg, 1.41 mmol) in THF (20 mL). The THF solution was brought to dryness to yield a dark red/brown solid instead of precipitation from solution with hexane. Yield = 1.30 g, 87%. ³¹P{¹H} NMR (C₆D₆, 162 MHz, 298 K) δ: -58.4. Anal. Calcd. for C₃₉H₃₆I₃MoNP₃ (found): C, 43.04 (43.33); H, 3.33 (3.72); N, 1.29 (1.18).

[Mo(N₂)(dppm)(NP₃^{Ph})] (2): Complex **2** can be prepared by either a sodium amalgam (<1% wt Na in Hg) or a magnesium powder reduction of [MoX₃(NP₃^{Ph})] for X = Cl, Br or I. An equimolar suspension of [MoI₃(κ²-NP₃^{Ph})(THF)] (758 mg, 0.697 mmol) and bis(diphenylphosphino)methane (268 mg, 0.697 mmol) in THF (15 mL) was decanted into a separate flask containing the reducing agent (excess, > 2.09 mmol) at 273 K. The mixture was stirred under a constant flow of N₂ at 273 K for 1 h, then at 293 K for 16 h. The orange suspension was separated from the reducing agent and salts by cannula filtration, and the resulting orange/red solution was concentrated to 5 mL *in vacuo*. Et₂O (20 mL) was added to precipitate the product, which was isolated by filtration and washed thoroughly with Et₂O (5 x 10 mL) and dried *in vacuo*. The orange residue was redissolved in benzene (15 mL), the solution filtered and then the product re-precipitated with Et₂O (30 mL). The orange solid was isolated by filtration and washed with Et₂O (5 x 15 mL) and hexane (2 x 15 mL) and dried *in vacuo*. Yield = 432 mg, 55%. Single crystals suitable for X-ray diffraction were grown by vapour diffusion of hexane into a THF solution of the complex. ¹H NMR (C₆D₆, 400 MHz, 298 K): 7.52–7.48 (t, 8H, *J*_{HH}=6.8 Hz, phenyl), 7.28–7.25 (t, 4H, *J*_{HH}=6.7 Hz, phenyl), 7.03–6.88 (m, 26H, phenyl), 6.79–6.76 (t, 6H, *J*_{HH}=6.8 Hz, phenyl), 6.54–6.51 (t, 4H, *J*_{HH}=7.2 Hz, phenyl), 5.47–5.39 (dt, 1H, ²*J*_{HH}=15.0 Hz, ⁴*J*_{HH}=7.8 Hz, NCH₂P-*trans*-N₂), 5.19–5.12 (dt, 1H, ²*J*_{HH}=16.8 Hz, ⁴*J*_{HH}=8 Hz, NCH₂P-*trans*-N₂), 4.46–

4.42 (m, 2H, PCH_2P), 4.23–4.17 (m, 4H, $\text{NCH}_2\text{P-trans-dppm}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 161 MHz, 298 K): δ : 20.7–19.5 (m, 2P, m , $\text{NP}_3\text{-cis-N}_2(\text{P}_a)$), 10.1–9.5 (m, 1P, $\text{NP}_3\text{-trans-N}_2(\text{P}_b)$), 8.1–6.7 (m, 2P, $\text{dppm}(\text{P}_c)$). IR (ATR, solid, 298 K, cm^{-1}) 2027 (s, ν_{NN}). ES-MS (positive ion): m/z calcd. for $\text{C}_{66}\text{H}_{64}\text{MoN}_4\text{P}_5$ ($[\text{M}+\text{MeCN}+\text{H}]^+$) 1165.2873, found 1165.2878. Anal. Calcd. for $\text{C}_{64}\text{H}_{58}\text{MoN}_3\text{P}_5$ (found): C, 68.63 (67.26); H, 5.22 (5.20); N, 3.75 (2.92). Loss of N_2 is expected upon combustion, hence the discrepancy in the values.

[Mo($^{15}\text{N}_2$)(dppm)(NP_3^{Ph})] (2- $^{15}\text{N}_2$**):**

*By displacement of $^{14}\text{N}_2$ for $^{15}\text{N}_2$ from **2**:* To a J.Y. NMR tube charged with **2**, $[\text{Mo}(\text{N}_2)(\text{dppm})(\text{NP}_3^{\text{Ph}})]$ (10 mg, 0.0089 mmol) was added in $\text{d}_8\text{-THF}$ (0.5 mL). The tube was freeze-pump-thaw degassed before subjected to a $^{15}\text{N}_2$ atmosphere. The sample was characterized by ^{15}N NMR spectroscopy over the period of 7 d. ^{15}N NMR ($\text{d}_8\text{-THF}$, 51 MHz, 298 K): -28.2 (broad s, distal), -39.4 (s, proximal). IR (solution cell, THF, 298 K, cm^{-1}): 1962 (m, $\nu_{15\text{N}-15\text{N}}$)

By reduction under $^{15}\text{N}_2$ atmosphere: To a J.Y. flask charged with **1** (**1-Br**, 80 mg, 0.0845 mmol), bis(diphenylphosphino)methane (32 mg, 0.0845 mmol) and Mg powder (20 mg, excess) was added THF (10 mL) and the mixture was freeze-pump-thaw degassed and backfilled with $^{15}\text{N}_2$ (1 atm, ~ 1 mmol). The mixture was stirred at 298 K for 2 d, before an aliquot was taken for NMR characterization, revealing the formation of **2- $^{15}\text{N}_2$** (alongside **4** as a side product). ^{15}N NMR (THF, 51 MHz, 298 K): -28.2 (broad s, distal), -39.4 (s, proximal). IR (solution cell, THF, 298 K, cm^{-1}): 1962 (m, $\nu_{15\text{N}-15\text{N}}$)

[Mo(H) $_2$ (dppm)(NP_3^{Ph})] (4**):**

*By hydrogenation of **2**:* To a J.Y. NMR tube charged with **2**, $[\text{Mo}(\text{N}_2)(\text{NP}_3^{\text{Ph}})(\text{dppm})]$ (15 mg, 0.013 mmol), was added C_6D_6 (0.5 mL). The solution was freeze-pump-thaw degassed 3 times, then subjected to a hydrogen atmosphere and characterised *in situ* by NMR and IR spectroscopy. ^1H NMR (C_6D_6 , 400 MHz, 298 K): 7.65–7.60 (m, 8H, phenyl), 7.27–7.21 (m, 12H, phenyl), 6.93–6.86 (m, 18H, phenyl), 6.78–6.74 (t, 12 H, $J_{\text{HH}} = 7.5$ Hz, phenyl), 5.10–5.06 (t, 2H, $^2J_{\text{HH}} = 8.9$ Hz, $\text{CH}_2\text{-dppm}$), 4.09 (s, 6H, $\text{CH}_2\text{-NP}_3$), -1.91– -2.31 (h, 2H, $^3J_{\text{HP}} = 32$ Hz, Mo-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 161 MHz, 298 K): δ : 33.0 (s, 2P, dppm), 24.1 (s, 3P, NP_3). IR (ATR, C_6D_6 solution, 298 K cm^{-1}) 2278 (s, ν_{MoH}).

*By reduction of **1** under Ar:* This reaction was performed under an argon atmosphere, and all solvents were sparged with argon before use. A solution of $[\text{MoBr}_3(\kappa^2\text{-NP}_3^{\text{Ph}})(\text{THF})]$ (266 mg, 0.260 mmol) and bis(diphenylphosphino)methane (100 mg, 0.260 mmol) in THF (10 mL) was added to a freshly prepared sodium amalgam (<1 wt%, 84 mg Na in ~ 20 g Hg) at 273 K. The reaction mixture was brought to room temperature and stirred under an argon atmosphere for 16 h. The resulting red suspension was decanted by cannula away from the amalgam, and the resulting suspension was cannula filtered. The red/orange solution was concentrated *in vacuo* and Et_2O was added to precipitate the product. The orange residue was washed with Et_2O (3 x 5 mL) and dried *in vacuo*. This method yielded only enough product for NMR characterisation, as above.

[Mo(N_2)(dppm)(H- NP_3^{Ph})]OTf (5**):** To a Schlenk flask containing $\text{d}_8\text{-THF}$ was added HOTf (7.0 μL , 0.078 mmol), and the mixture cooled to 195 K. This solution was decanted into a Schlenk flask charged with $[\text{Mo}(\text{N}_2)(\text{NP}_3^{\text{Ph}})(\text{dppm})]$ (45 mg, 0.039 mmol) at 195 K. An aliquot of the yellow/brown solution was transferred into an NMR tube at 195 K, and characterised by NMR spectroscopy at 195 K. $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{d}_8\text{-THF}$, 202 MHz, 195 K): δ : 31.4–30.4 (m, 2P, dppm), 23.9–23.3 (m, 1P, $\text{NP}_3\text{-trans-N}_2$), 10.6–9.5 (m, 2P, $\text{NP}_3\text{-cis-N}_2$).

[Mo(N_2)(dppm)($\text{Br}_3\text{B-NP}_3^{\text{Ph}}$)] (6-BBr₃**):** To a J.Y. NMR tube charged with $[\text{Mo}(\text{N}_2)(\text{dppm})(\text{NP}_3^{\text{Ph}})]$ (30 mg, 0.027 mmol) was added toluene (0.5 mL). The solution was cooled to 195 K before the addition of BBr_3 (7.0 mg, 0.027 mmol). The tube was sealed and kept at 195 K for heteronuclear NMR spectroscopic characterisation. ^1H NMR ($\text{d}_8\text{-toluene}$, 500 MHz, 195 K): 5.81 (m, 1H, $\text{CH}_2\text{-NP}_3$), 4.99 (m, 1H, $\text{CH}_2\text{-NP}_3$), 4.54 (m, 2H, $\text{CH}_2\text{-dppm}$), 4.09 (m, 4H, $\text{CH}_2\text{-NP}_3$). The phenyl peaks cannot be assigned due to overlap with the toluene solvent. $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{d}_8\text{-toluene}$, 202 MHz, 195 K): 32.3–30.4 (m, 2P, $\text{NP}_3\text{-cis-N}_2$), 24.7–23.4 (m, 1P, $\text{NP}_3\text{-trans-N}_2$), 10.4–8.6 (m, 2P, dppm). ^{11}B NMR ($\text{d}_8\text{-toluene}$, 160 MHz, 195 K): -5.9 (s).

[Mo(N_2)(dppm)((C_6F_5) $_3\text{B-NP}_3^{\text{Ph}}$)] (6-BCF**):** To a J.Y. NMR tube charged with $[\text{Mo}(\text{N}_2)(\text{dppm})(\text{NP}_3^{\text{Ph}})]$ (15 mg, 0.013 mmol) and tris(pentafluorophenyl)borane (7.0 mg, 0.013 mmol) was added cold (195 K) toluene (0.5 mL). The tube was sealed and kept at 195 K for heteronuclear NMR spectroscopic characterisation. $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{d}_8\text{-toluene}$, 202 MHz, 195 K): 33.4–31.2 (m, 2P, $\text{NP}_3\text{-trans-dppm}$), 23.4–22.1 (m, 1P, $\text{NP}_3\text{-cis-N}_2$), 10.8–9.1 (m, 2P, dppm). ^{11}B NMR ($\text{d}_8\text{-toluene}$, 160 MHz, 195 K): -4.7 (s). $^{19}\text{F}\{^1\text{H}\}$ NMR ($\text{d}_8\text{-toluene}$, 470 MHz, 195 K): -134.0 (d, *ortho*), -157.8 (t, *meta*), -163.0 (t, *para*).

[Mo(dppm)(PMePh $_2$)(PCP)][B(C_6F_5) $_4$] (7**):** To a Schlenk flask charged with **2** (20 mg, 0.017 mmol) and $[\text{Li}(\text{OEt})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (14 mg, 0.017 mmol) was added PhF (2 mL). The reaction was stirred for 3 d at 298 K. The mixture was filtered, and the solvent was removed *in vacuo* to yield an orange/brown solid. The solid residue was dissolved in C_6D_6 for NMR spectroscopic characterization. Single crystals suitable for X-ray diffraction were grown by slow vapour diffusion of hexane into a fluorobenzene solution of **7** over the course of 3 weeks. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz, 195 K): 95.6–95.3 (m, 1P), 32.3–31.8 (m, 1P), 14.8–14.1 (m, 1P), 2.6–1.9 (m, 1P), -106.6– -107.1 (m, 1P). $^{11}\text{B}/^{19}\text{F}$ NMR are consistent with the $[\text{B}(\text{C}_6\text{F}_5)_4]$ counterion. ES-MS (positive ion): m/z calcd. for $\text{C}_{64}\text{H}_{58}\text{MoNP}_5$ ($[\text{M}]^+$) 1093.2311, found 1093.2311. Anal. Calcd. for $\text{C}_{88}\text{H}_{58}\text{BF}_{20}\text{MoNP}_3$ (found): C, 59.68 (58.19); H, 3.30 (3.48); N, 0.79 (0.94).

Author Contributions

PWM and NJL designed the project, SLA carried out all synthetic and characterization work, AJPW and SLA performed the X-ray crystallographic work and analysis, and all the authors wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

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