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

Samantha L. Apps[a], Andrew J. P. White[a], Philip W. Miller[a]*, Nicholas J. Long[a]*

Department of Chemistry, Imperial College London, London SW7 2AZ, UK

Email: philip.miller@imperial.ac.uk; n.long@imperial.ac.uk

Contents:

1. Additional experimental procedures
    1.1 Additional synthetic procedures
        1.1.1 [Mo(N$_2$)$_2$(dppm)(κ^2-NP$_3^{Ph}$)] (3)
        1.1.2 [Mo(D)$_2$(dppm)(NP$_3^{Ph}$) (4-D)
        1.1.3 N-triphos^{Ph}-d$_6$
        1.1.4 Attempts to determine source of hydride to form (4)
        1.1.5 Attempted protonation of [Mo(N$_2$)(dppm)((C$_6$F$_5$)$_3$B-NP$_3^{Ph}$)](6-BCF)
        1.1.6 **Attempted protonation of [Mo(N$_2$)(dppm)(Br$_3$B-NP$_3^{Ph}$)] (6-BBr$_3$)**
    1.2 *In situ* IR spectroscopic characterisation
        1.2.1 [Mo(N$_2$)(dppm)(H-NP$_3^{Ph}$)]OTf (5)
        1.2.2 [Mo(N$_2$)(dppm)((C$_6$F$_5$)$_3$B-NP$_3^{Ph}$)](6-BCF)
        1.2.3 [Mo(N$_2$)(dppm)(Br$_3$B-NP$_3^{Ph}$)](6-BBr$_3$) and protonation
2. Additional NMR and IR Spectra
    2.1 Complex (1)
    2.2 Complex (2)
    2.3 Complex (4)
    2.4 Complex (5)
    2.5 Complex (6)
    2.6 Complex (7)
3. Crystallographic Information
4. References

1. Additional experimental

1.1 Additional synthetic procedures

Additional general information: D_2 gas (Cambridge Isotope Laboratories, 98% ^{15}N) was transferred from a breakseal flask using a Toepler pump and dried over 3 Å molecular sieves before use. Dppm-d_2 was prepared according to literature procedure.[1]

1.1.1 **[Mo(N$_2$)$_2$(dppm)(κ^2-NP$_3^{Ph}$)] (3):** Complex **3** was generated *in situ* as a mixture with complex **2**, in the preparation of complex **2** using a magnesium powder reducing agent at 195 K. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): 4.72-4.67 (t, 2H, $^2J_{HH}$=8.5 Hz, CH_2-dppm), 3.76 (s, 4H, CH_2-NP_3 coordinated), 3.07 (s, 2H, CH_2-NP_3 uncoordinated). The phenyl peaks cannot be uniquely assigned in this mixture due to overlap of phenyl peaks for **2**. $^{31}P\{^1H\}$ NMR (C_6D_6, 161 MHz, 298 K) δ: 39.5-38.4 (m, 2P, coordinated-NP_3), 10.8-9.7 (m, 2P, dppm), -29.1 (s, 1P, uncoordinated-NP_3) (see figure S10).

1.1.2 **[Mo(D)$_2$(dppm)(NP$_3^{Ph}$)] (4-D):** To a J.Y. NMR tube charged with [Mo(N$_2$)(NP$_3^{Ph}$)(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 D_2 gas atmosphere (1 atm) and characterised *in situ* by NMR and IR spectroscopy. ^{2}H NMR (d_8-THF, 400 MHz, 298 K): -2.11- -2.46 (m, Mo-*D*). $^{31}P\{^1H\}$ NMR (C_6D_6, 161 MHz, 298 K): δ 33.0 (s, 2P, dppm), 23.8 (s, 3P, NP_3). IR (ATR, C_6D_6 solution, 298 K, cm^{-1}) 1613 (s, υ_{MoD}).

1.1.3 **N-triphos^{Ph}-d$_6$:** Prepared according to adapted literature procedures.[2] To a Schlenk flask charged with paraformaldehyde-d_2 (0.250 g, 7.80 mmol) was added diphenylphosphine (1.45 g, 7.80 mmol). The mixture was heated to 393 K for 3 h until homogeneous, and then cooled to room temperature. MeOH (5 mL) was added and the solution was stirred for 5 minutes before the addition of a methanolic ammonia solution (2M, 1.30 mL, 2.60 mmol). The mixture was heated for 2 h at 333 K, resulting in the precipitation of a white solid. The solid was isolated by filtration, washed with MeOH (3 x 5 mL) and dried *in vacuo*. Yield = 0.738 g, 45 %. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ: 7.37-7.34 (t, 12H, J = 6.8 Hz, phenyl), 7.29-7.21 (m, 18H, phenyl). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz, 298 K) δ: -29.4. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 298 K): 137.9 (d, J_{CP} = 12.3 Hz, phenyl), 133.3 (d, J_{CP} = 18.3 Hz, phenyl), 128.5 (d, J_{CP} = 18.8 Hz, phenyl), 59.4 (br m, N$\underline{C}D_2$P).

1.1.4 Attempts to prepare **4-D** by reductions of **1** with deuterated versions of the ligands (dppm-d_2 or N-triphos^{Ph}-d_6) were also performed, to determine the source of hydrogen that forms the hydride complex **4** as a side product to the reduction to form dinitrogen complex **2**. Table 1 summarises the various combinations tried, all of which gave hydride peaks in the ^{1}H NMR spectrum after reduction, showing formation of **4** and not **4-D**.

Solvent	Complex **1** prepared	Reduction of **1**, in	Possible hydride	^{1}H NMR signal at

	with ligand:	combination with ligand:	source investigated	δ = - 2ppm
THF	NP_3^{Ph}	dppm	-	Y
d_8-THF	NP_3^{Ph}	dppm	solvent	Y
d_8-THF	NP_3^{Ph}	dppm-d_2	dppm	Y
d_8-THF	NP_3^{Ph}-d_6	dppm	NP_3^{Ph}	Y
d_8-THF	NP_3^{Ph}-d_6	dppm-d_2	NP_3^{Ph} + dppm	Y

Table S1. Combinations tried in reductions to form the mixture of **2** and **4**, to investigate possible sources of the hydride to form **4** as side product.

1.1.5 **Attempted protonation of [Mo(N_2)(dppm)((C_6F_5)$_3$B-NP_3^{Ph})](8-BCF):** To a Schlenk flask charged with **2,** [Mo(N_2)(dppm))(NP_3^{Ph})] (20 mg, 0.017 mmol) and tris(pentafluorophenyl)borane (9.0 mg, 0.017 mmol) was added PhF at 233 K. The solution was stirred at this temperature for 5 minutes before the addition of HOTf (4.0 μL, 0.034 mmol, 2 eq). The resulting suspension was transferred to a J.Y. NMR tube and characterised *in situ* by NMR spectroscopy at 233 K (the spectrum was showed no assignable peaks, likely due to poor solubility in toluene),

1.1.6 **Attempted protonation of [Mo(N_2)(dppm)(Br_3B-NP_3^{Ph})] (8-BBr_3):** To a Schlenk flask charged with **2**, [Mo(N_2)(dppm)(NP_3^{Ph})] (20 mg, 0.017 mmol) was added PhF , and the mixture was cooled to 233 K. BBr_3 (2.0 μL, 0.017 mmol, 1 eq) was added to the solution and stirred for 5 minutes before the addition of HOTf (4.0 μL, 0.036 mmol, 2 eq). The resulting suspension was transferred to a J.Y. NMR tube and characterised in situ by NMR spectroscopy at 233 K. The following broad resonances were observed, but were too ambiguous to fully assign. $^{31}P\{^1H\}$ NMR (fluorobenzene, 202 MHz, 233 K): 22.5-17.9 (m, 2P), -3.3- -5.5 (m, 1P), -6.1- -9.1 (m, 2P)- see figures S23 and S24.

1.2 In situ IR spectroscopic characterisation

These experiments were performed at the University of Oxford with the assistance of Gemma Trott, in collaboration with Prof. Charlotte Williams. The experiment was performed under inert conditions, with a Mettler Toledo ReactIR instrument. The probe was inserted inside the reaction vessel for the duration of the experiment.

1.2.1 **[Mo(N_2)(dppm)(H-NP_3^{Ph})]OTf (5):** To a Schlenk flask charged with **2,** [Mo(N_2)(NP_3^{Ph})(dppm)] (50 mg, 0.044 mmol) was added THF (3 mL) and the orange suspension was cooled to 195 K in a dry ice/acetone bath. HOTf (4 µL,1 eq → 20 eq) was sequentially added to the cooled solution, and after the addition of 20 eq HOTf, the solution was slowly brought to room temperature. The solution was characterised *in situ* by IR spectroscopy for the entire duration of the experiment (1.5 h)- figure S18.

1.2.2 **[Mo(N_2)(dppm)((C_6F_5)$_3$B-NP_3^{Ph})] (6-BCF):** To a Schlenk flask charged with **2**, [Mo(N_2)(NP_3^{Ph})(dppm)] (50 mg, 0.044 mmol) was added toluene (5 mL) and the orange suspension was cooled to 195 K and maintained at this temperature. 1 equivalent of tris(pentafluorophenyl)borane (23 mg, 0.044 mmol) dissolved in cold (195 K) toluene (1 mL) was added to the mixture, and after 20 minutes, the solution was slowly brought to room temperature. The solution was characterised *in situ* by IR spectroscopy for the entire duration of the experiment (1.5 h), but no NN stretches could be observed due to poor solubility of the complexes in toluene.

1.2.3 **[Mo(N_2)(dppm)(Br_3B-NP_3^{Ph})] (6-BBr_3), with subsequent protonation:** To a Schlenk flask charged with **2**, [Mo(N_2)(NP_3^{Ph})(dppm)] (50 mg, 0.044 mmol) was added PhF (8 mL) and the orange suspension was cooled to 233 K and maintained at this temperature. BBr_3 (4.0 µL, 0.044 mmol, 1 eq) was added to the suspension and after 5 minutes, HOTf (8.0 µL, 0.088 mmol, 2 eq) was added to the mixture. Additional HOTf (total 6 eq, 24 µL total) was added sequentially to the mixture, and after 30 minutes, the reaction mixture was brought to room temperature. The mixture was characterised *in situ* by IR spectroscopy for the entire duration of the experiment (2 h) – figure S22 and S24.

2. Additional NMR and IR spectra

2.1 Complex (1), [$MoX_3(\kappa^2\text{-}NP_3^{Ph})(THF)$]

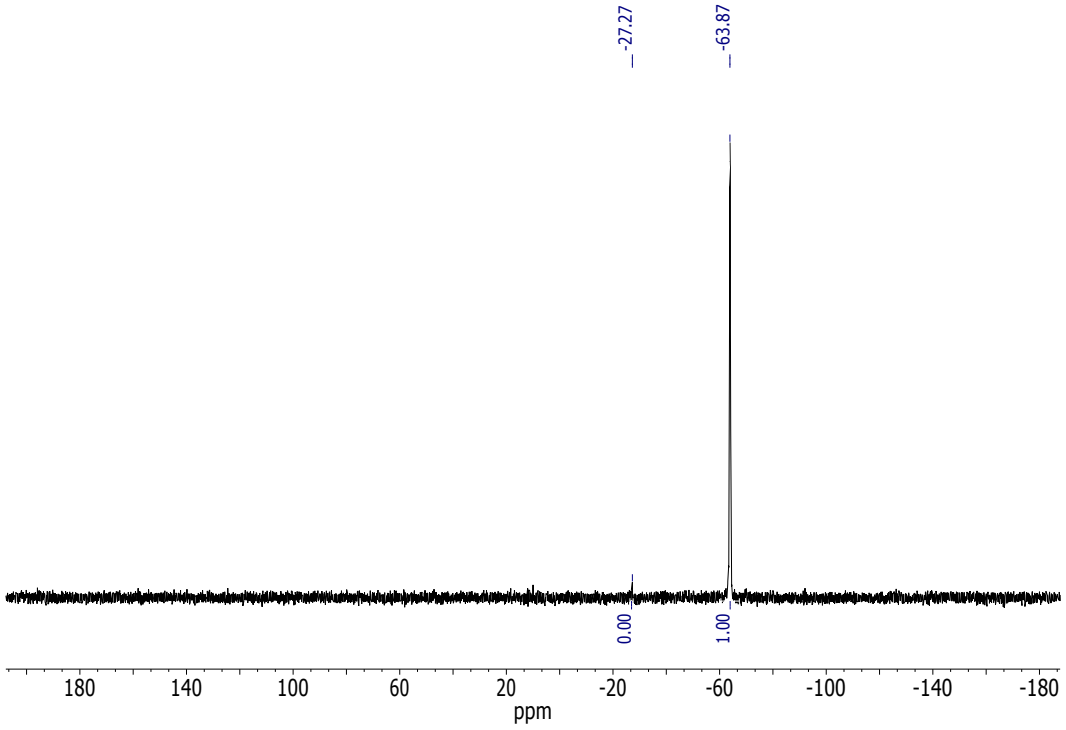

Figure S1: $^{31}P\{^1H\}$ NMR spectrum of purified **1-Cl**, d_8-THF, 298 K, 161 MHz. Minor peak at -27 ppm relates to minor free ligand (NP_3^{Ph}) impurity

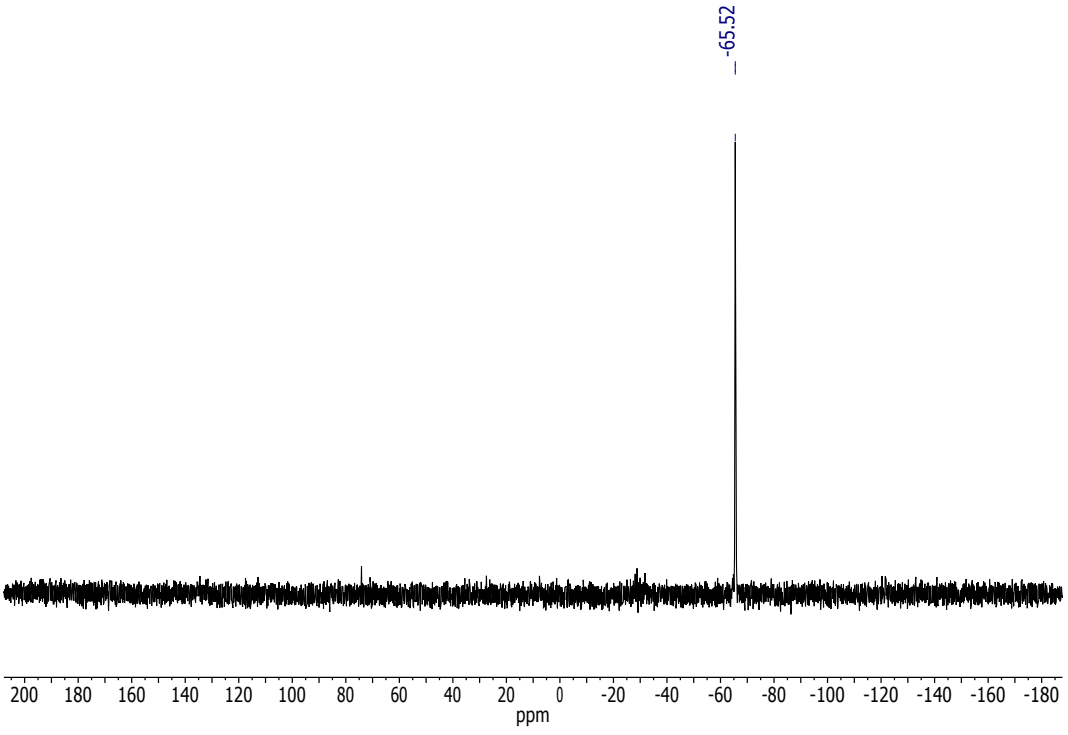

Figure S2: $^{31}P\{^1H\}$ NMR spectrum of purified **1-Br**, d_8-THF, 298 K, 161 MHz

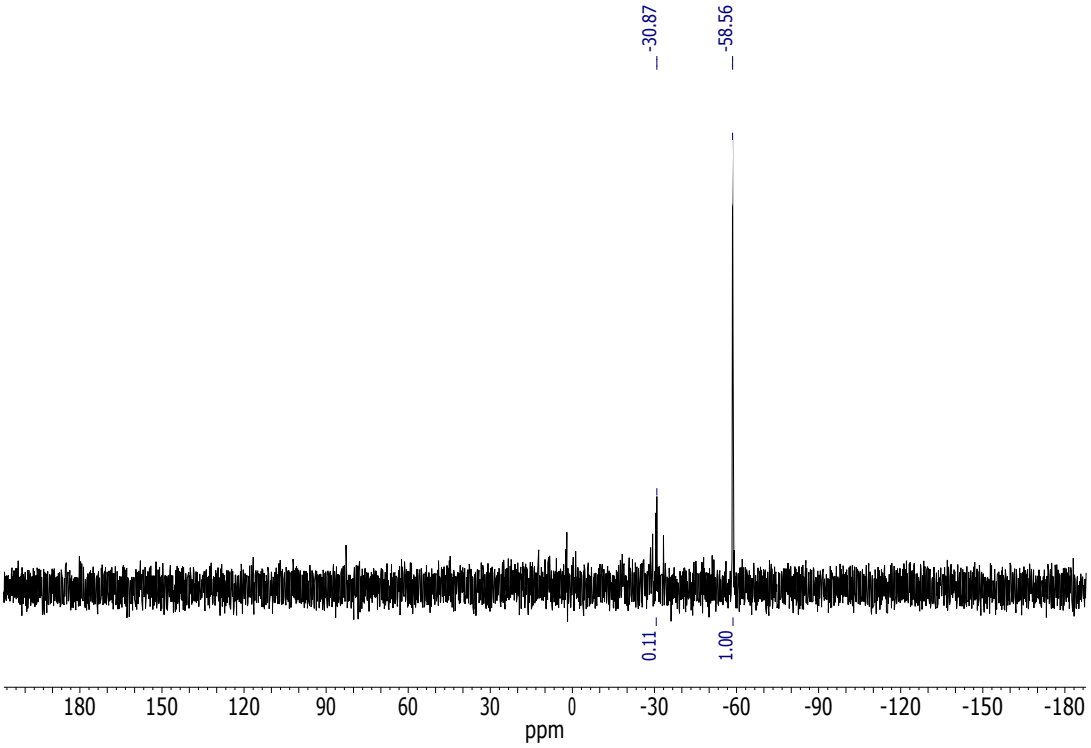

Figure S3: $^{31}P\{^{1}H\}$ NMR spectrum of purified **1-I**, d_8-THF, 298 K, 161 MHz. Minor peak at -31 ppm relates to minor free ligand (NP_3^{Ph}) impurity

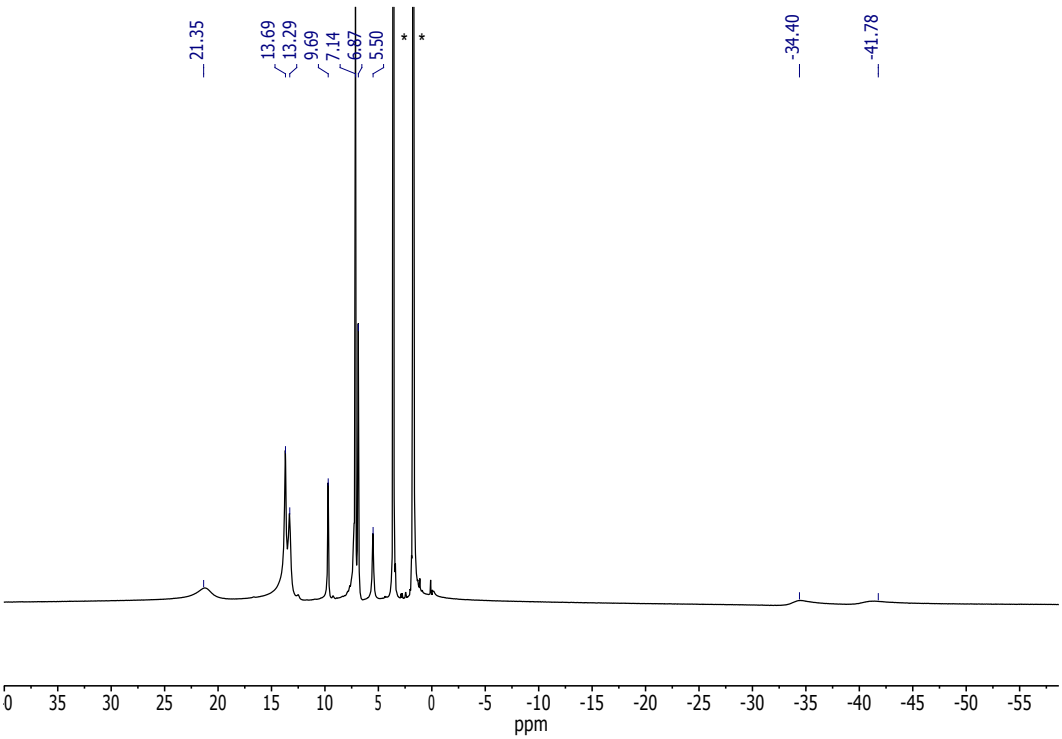

Figure S4: ^{1}H NMR spectrum of **1-Cl**, d_8-THF, 298 K, 400 MHz. *d_8-THF solvent peak.

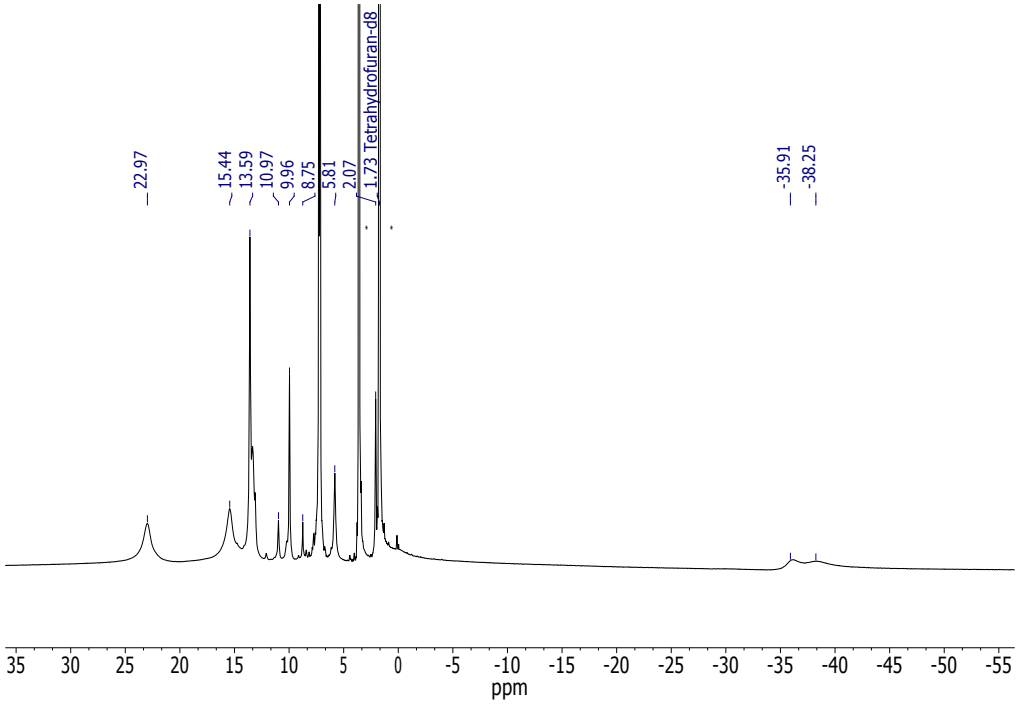

Figure S5: ^{1}H NMR spectrum of **1-Br**, d_8-THF, 298 K, 400 MHz. *d_8-THF solvent peak.

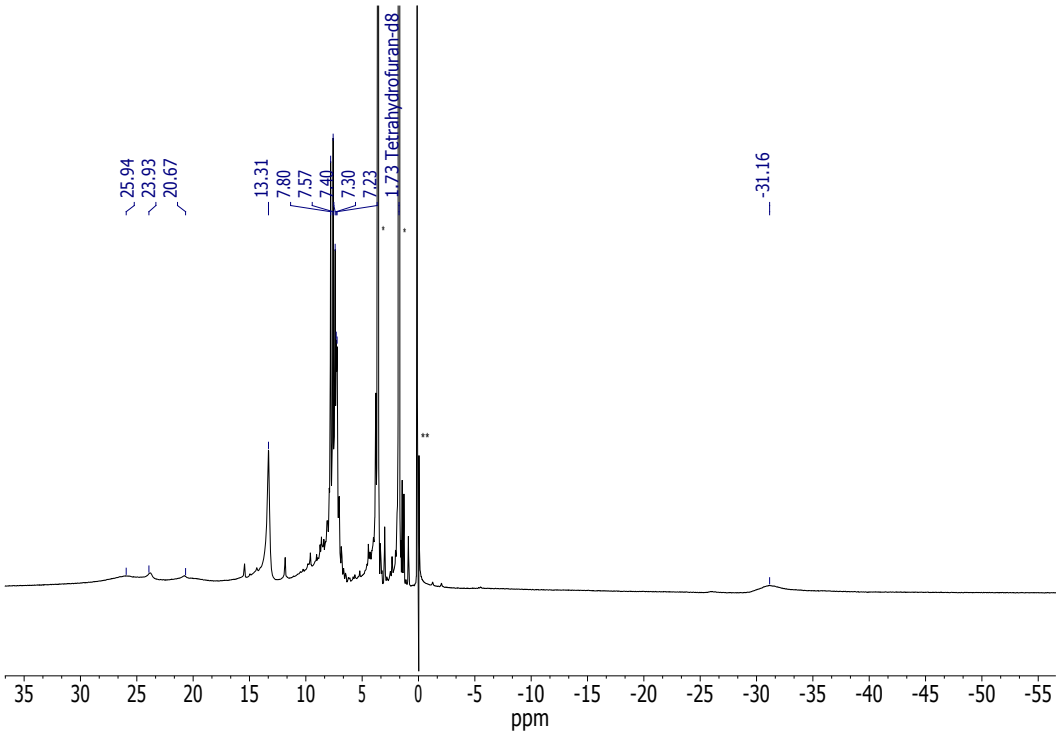

Figure S6: ^{1}H NMR spectrum of **1-I**, d_8-THF, 298 K, 400 MHz. *d_8-THF solvent peak, **silicone grease.

2.2 Complex (2), [Mo(N_2)(dppm)(NP_3^{Ph})]

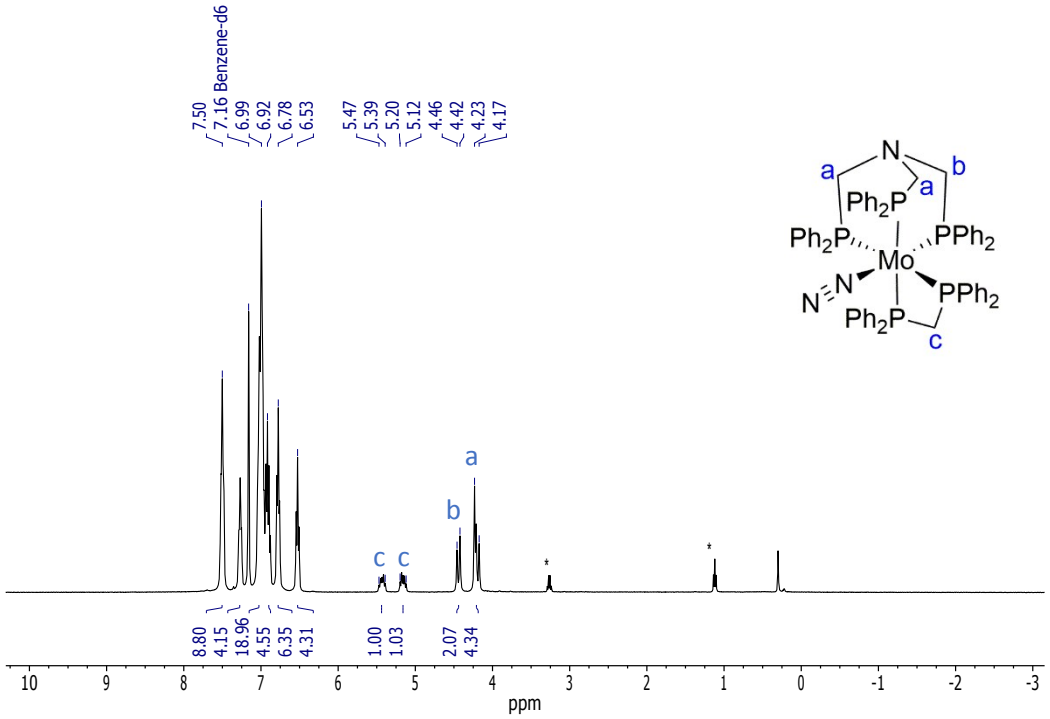

Figure S7: ^{1}H NMR spectrum of **2**, C_6D_6, 298 K, 400 MHz. *residual solvent traces, **grease. Non-phenyl peak assignments are annotated.

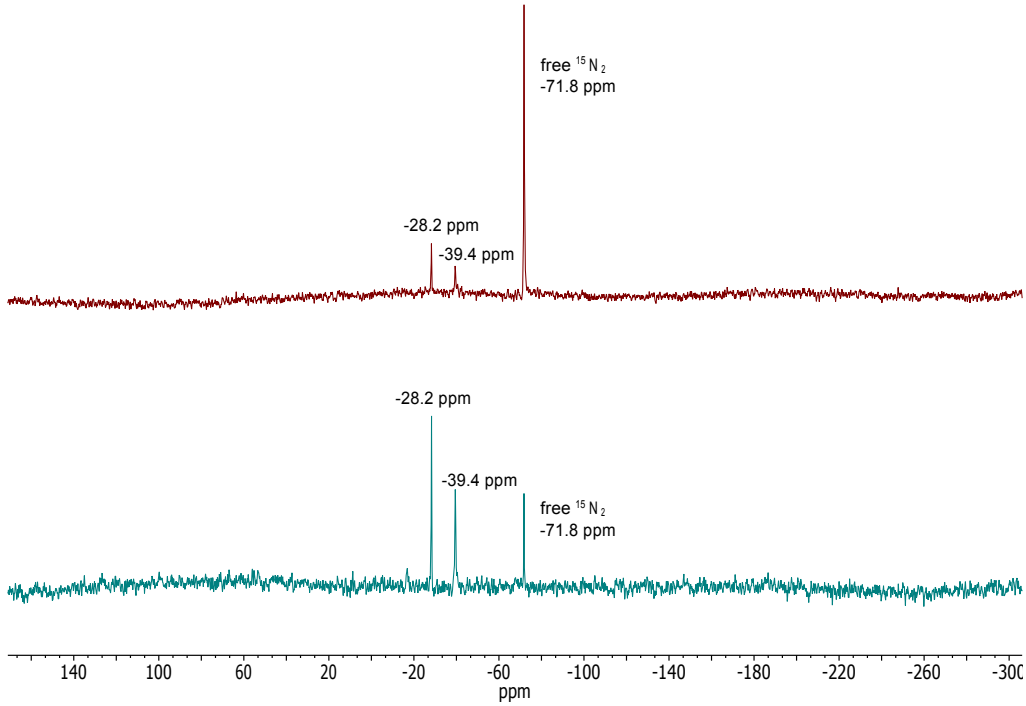

Figure S8: ^{15}N{^{1}H} NMR spectrum of **2-^{15}N**, d_8-THF, 298 K, 51 MHz. Top: when formed by displacement from $^{14}N_2$ complex, bottom: when formed by reduction under $^{15}N_2$ atmosphere. δ = -71.8 ppm is free $^{15}N_2$ gas, present in the NMR samples.

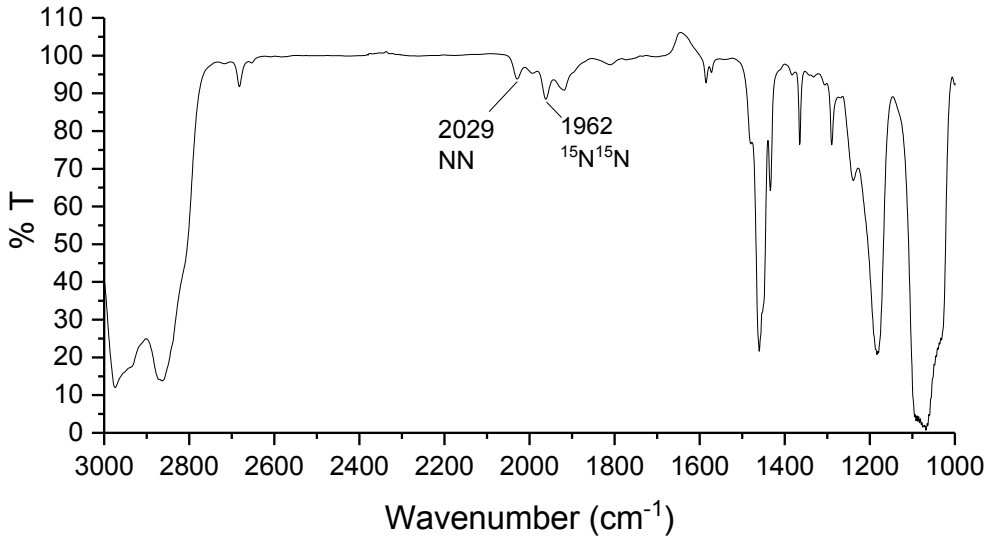

Figure S9: Solution IR spectrum (THF) of **2** and **2-^{15}N**. Small amounts of **2** were present due to exchange with the $^{14}N_2$ glovebox atmosphere in which the solution IR sample was prepared. Large/intense peaks are due to the solvent (THF).

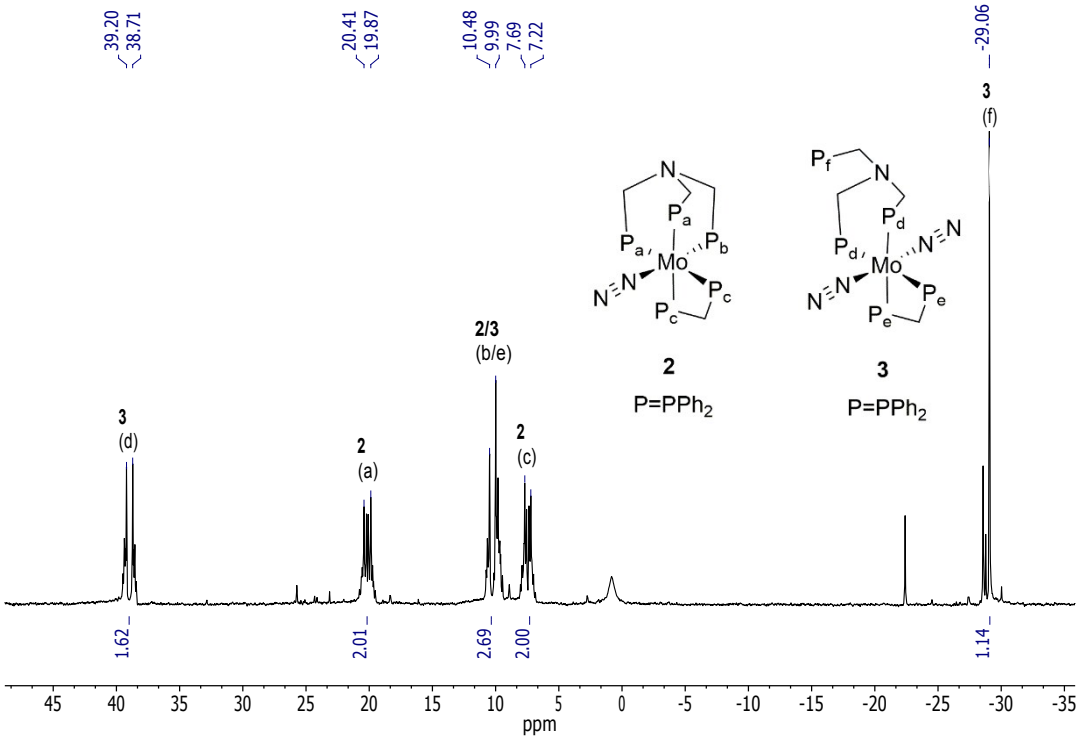

Figure S10: $^{31}P\{^{1}H\}$ NMR spectrum of the crude reduction mixture forming **2** and **3**, formed by Mg reduction of **1** at 195 K C_6D_6, 298 K, 161 MHz.

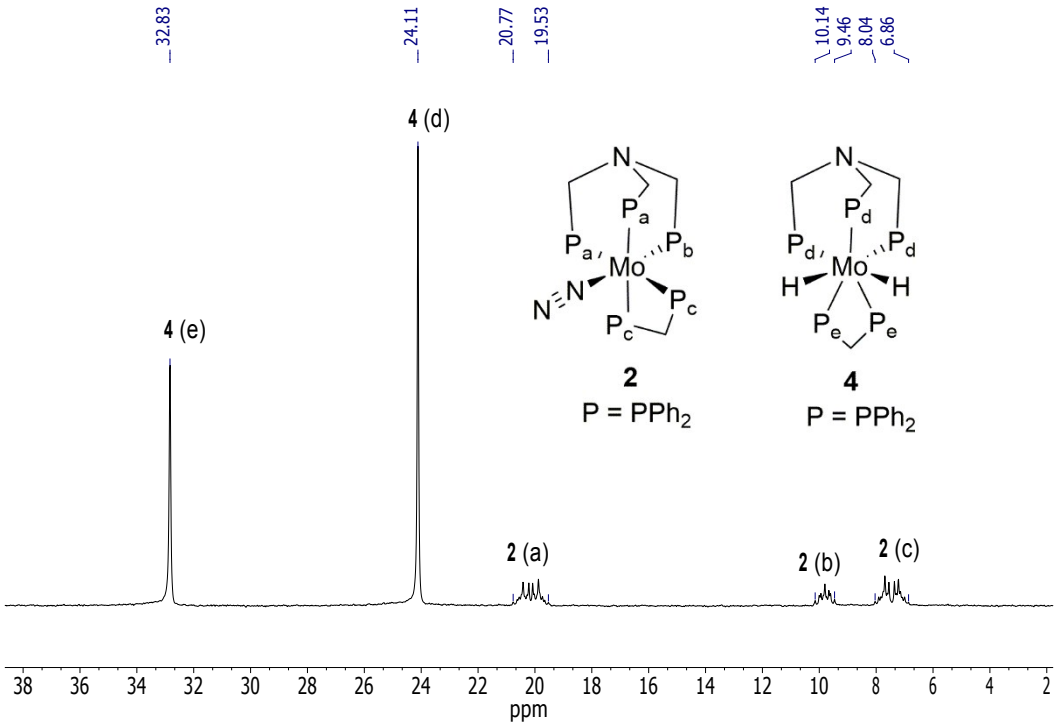

Figure S11: $^{31}P\{^{1}H\}$ NMR spectrum of the crude reduction mixture, showing **2** and **4**, C_6D_6, 298 K, 161 MHz.

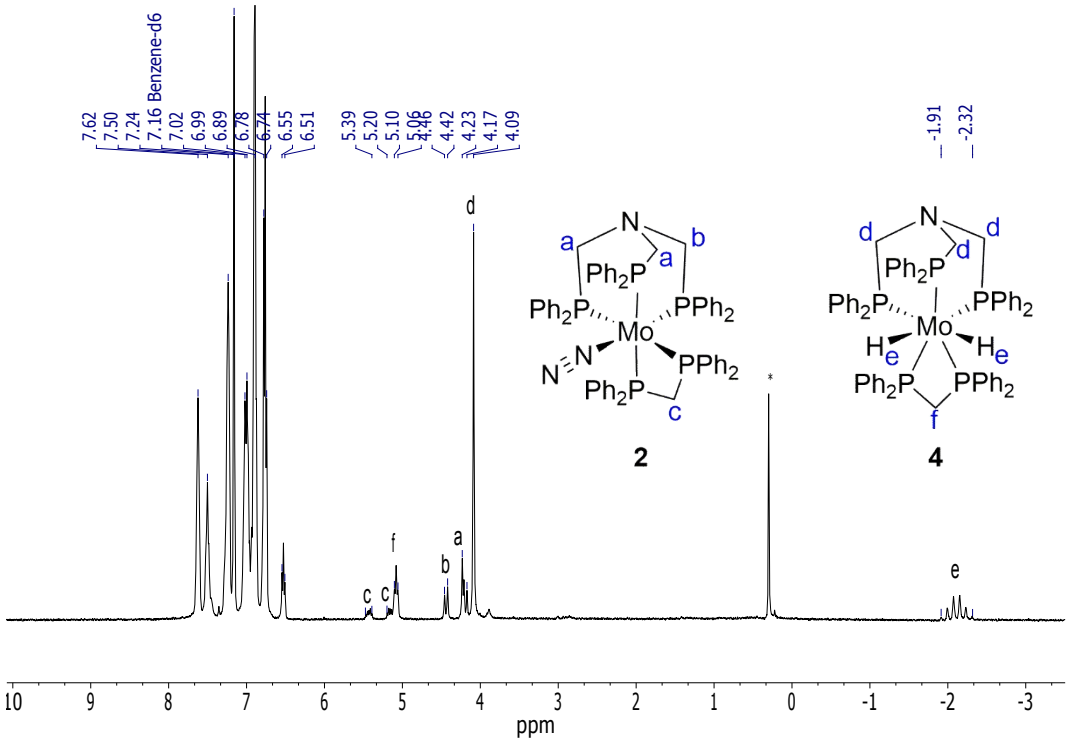

Figure S12: ^{1}H NMR spectrum of the crude reduction mixture, showing **2** and **4**, C_6D_6, 298 K, 400 MHz. *silicone grease.

2.3 Complex (4), $[Mo(H)_2(dppm)(NP_3^{Ph})]$

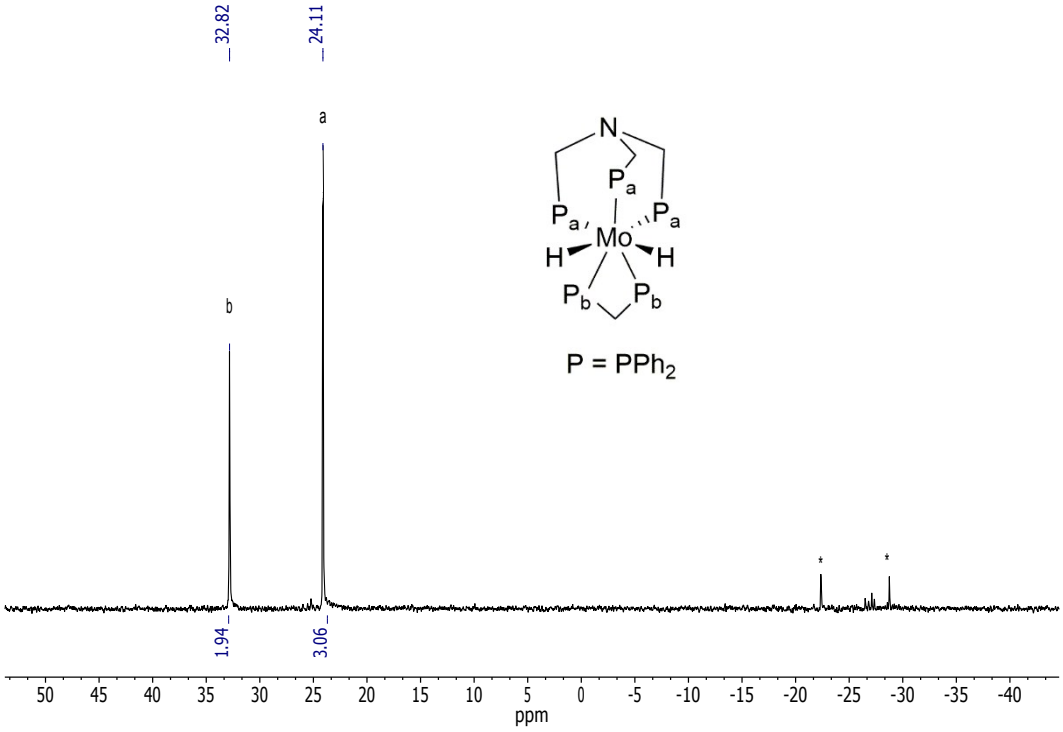

Figure S13: $^{31}P\{^{1}H\}$ NMR spectrum of **4**, C_6D_6, 298 K, 161 MHz. *free ligand impurities.

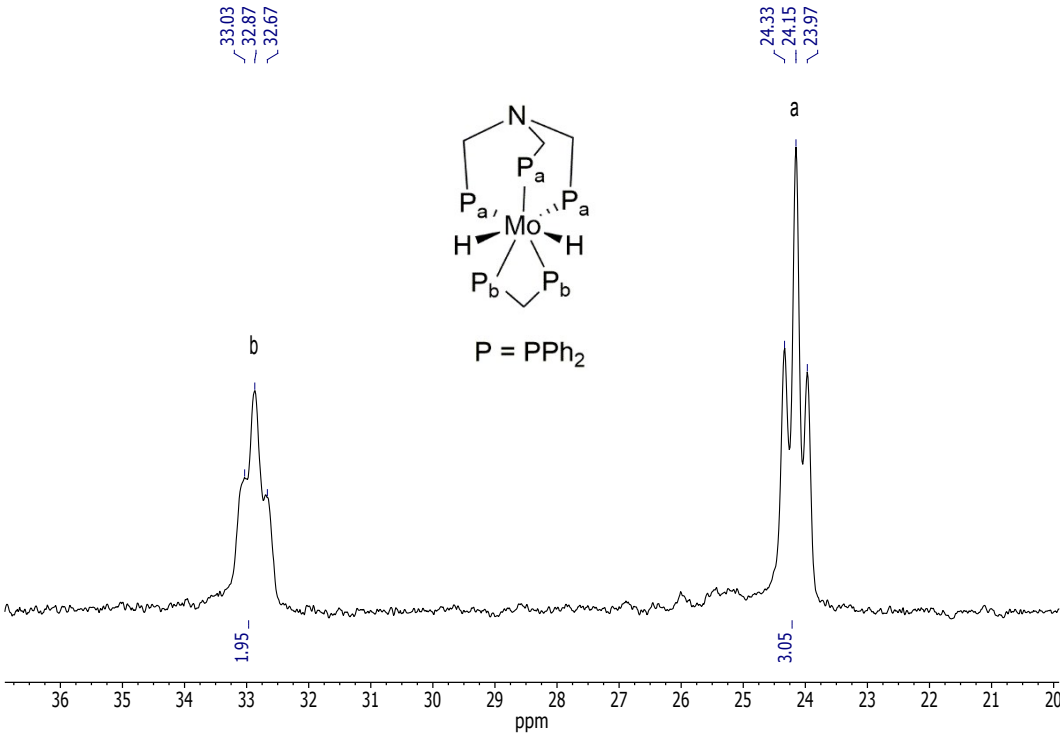

Figure S14: Proton-coupled ^{31}P NMR spectrum of **4**, C_6D_6, 298 K, 161 MHz

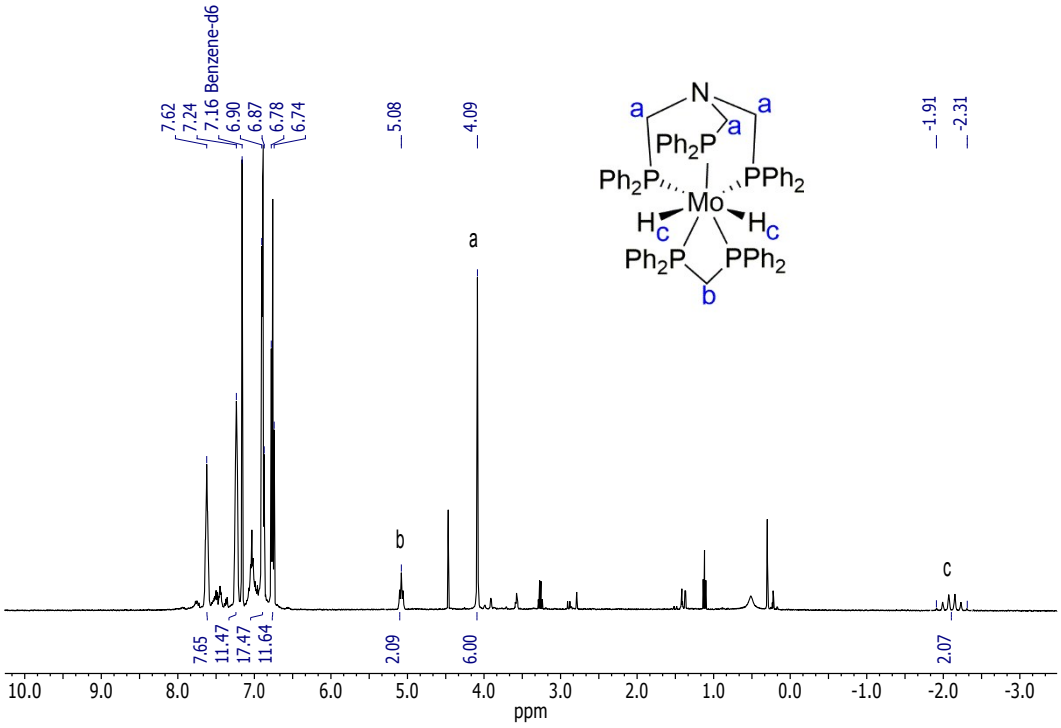

Figure S15: ^{1}H NMR spectrum of **4**, C_6D_6, 298 K, 400 MHz. Impurity peaks (e.g. residual solvent traces, grease) are unlabelled. Non-phenyl peak assignments are annotated.

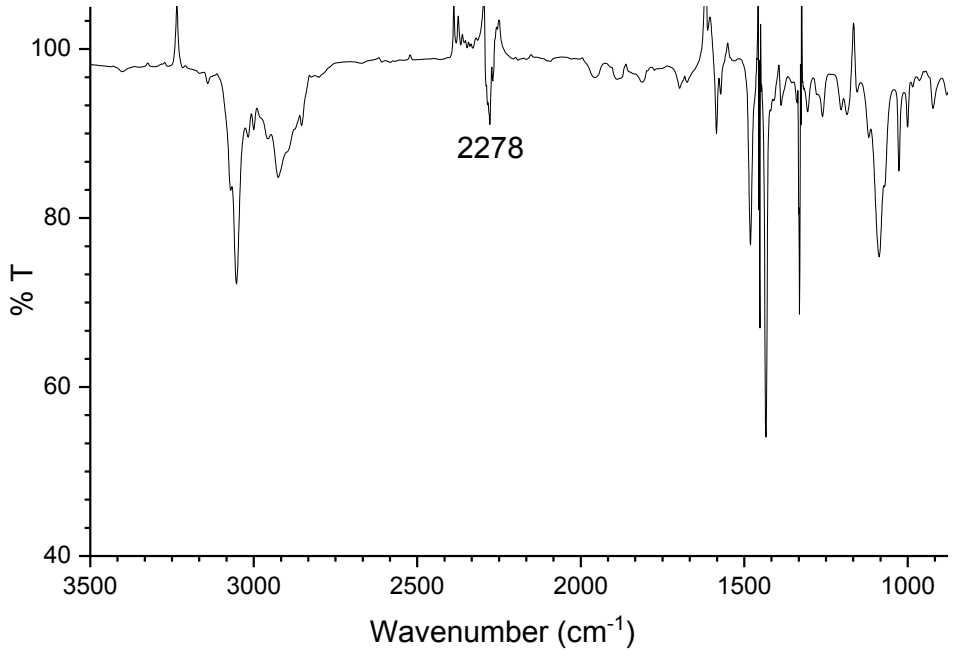

Figure S16: IR spectrum of **4** (solution, C_6D_6, 298K)

2.4 Complex (5), [Mo(N_2)(dppm)(H-NP_3^{Ph})](OTf)

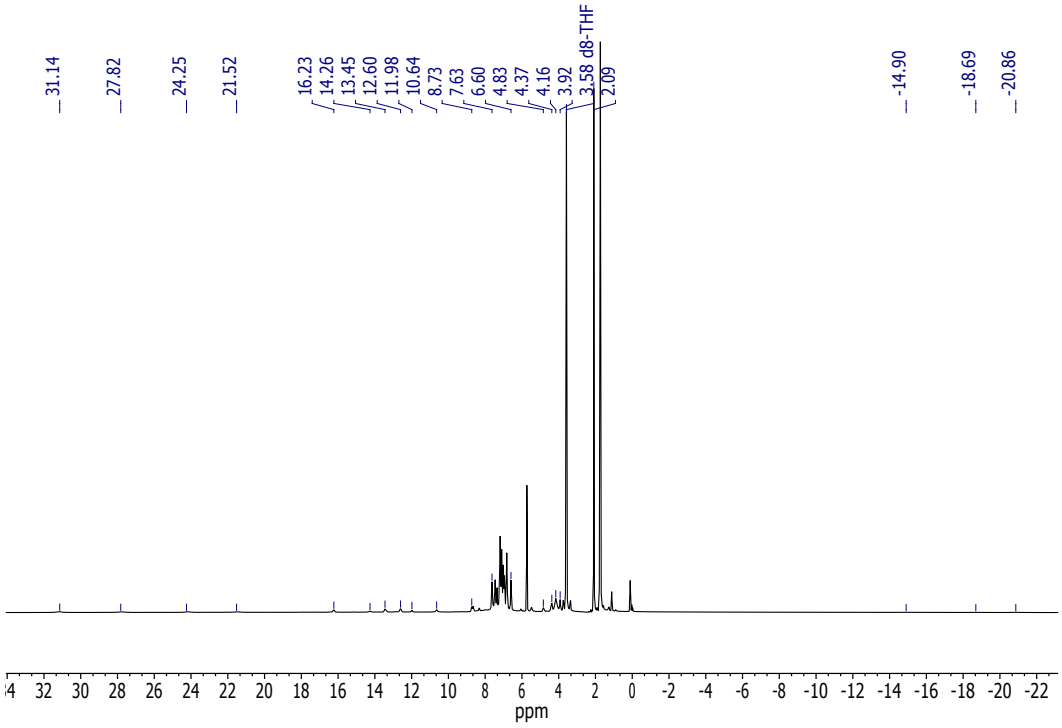

Figure S17: ^{1}H NMR spectrum of **5**, d_8-THF, 195 K, 500 MHz

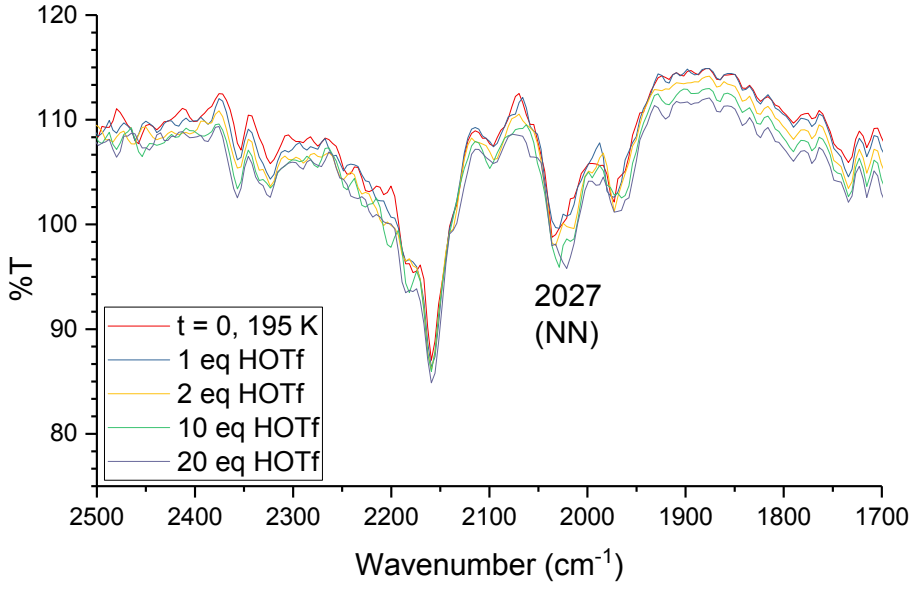

Figure S18: *In situ* solution IR spectrum of the formation of **5** in THF at 195 K (using ReactIR set-up). Almost no change to the NN stretch at 2027 cm^{-1} was observed.

2.5 Complex (6), [Mo(N_2)(dppm)(R_3B-NP_3^{Ph})]

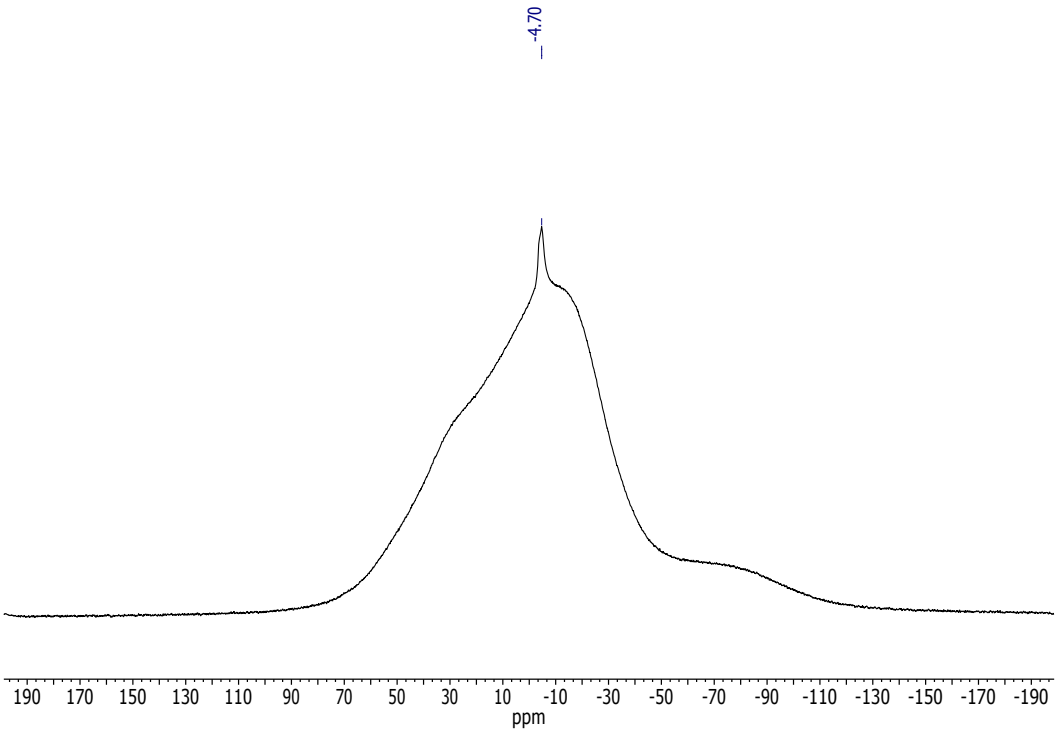

Figure S19: ^{11}B NMR spectrum of **6-BCF**, toluene, 195 K, 160 MHz

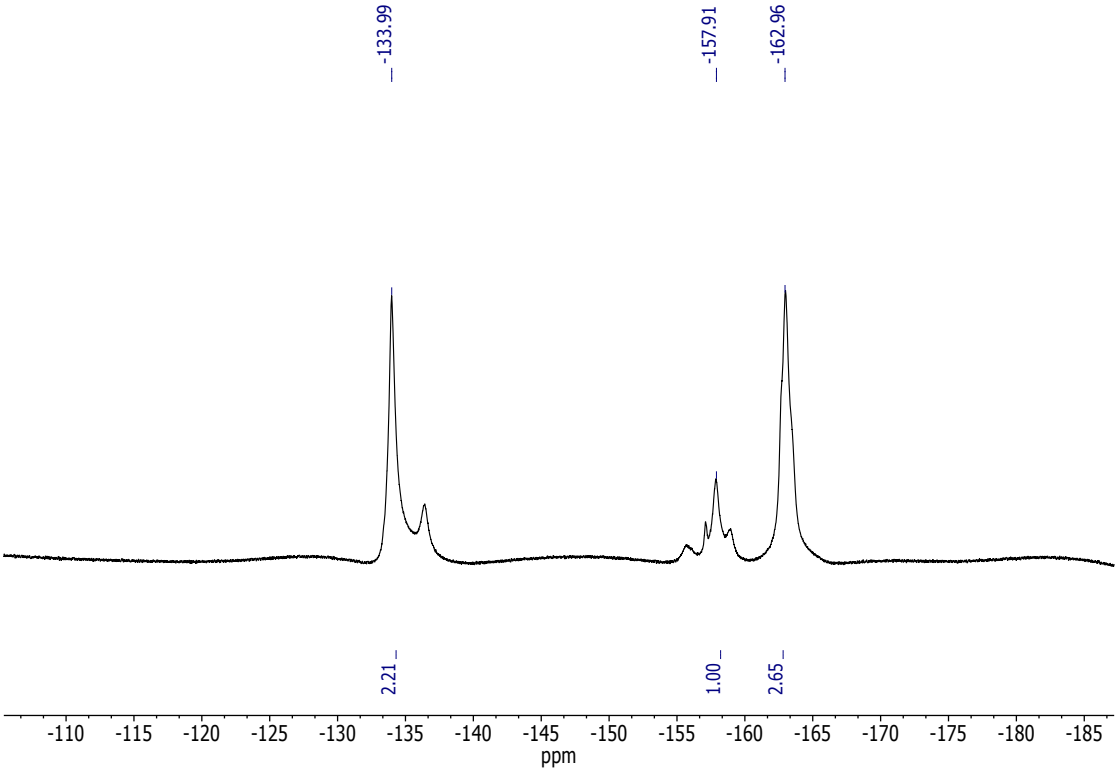

Figure S20: ^{19}F{^{1}H} NMR spectrum of **6-BCF**, toluene, 195 K, 470 MHz

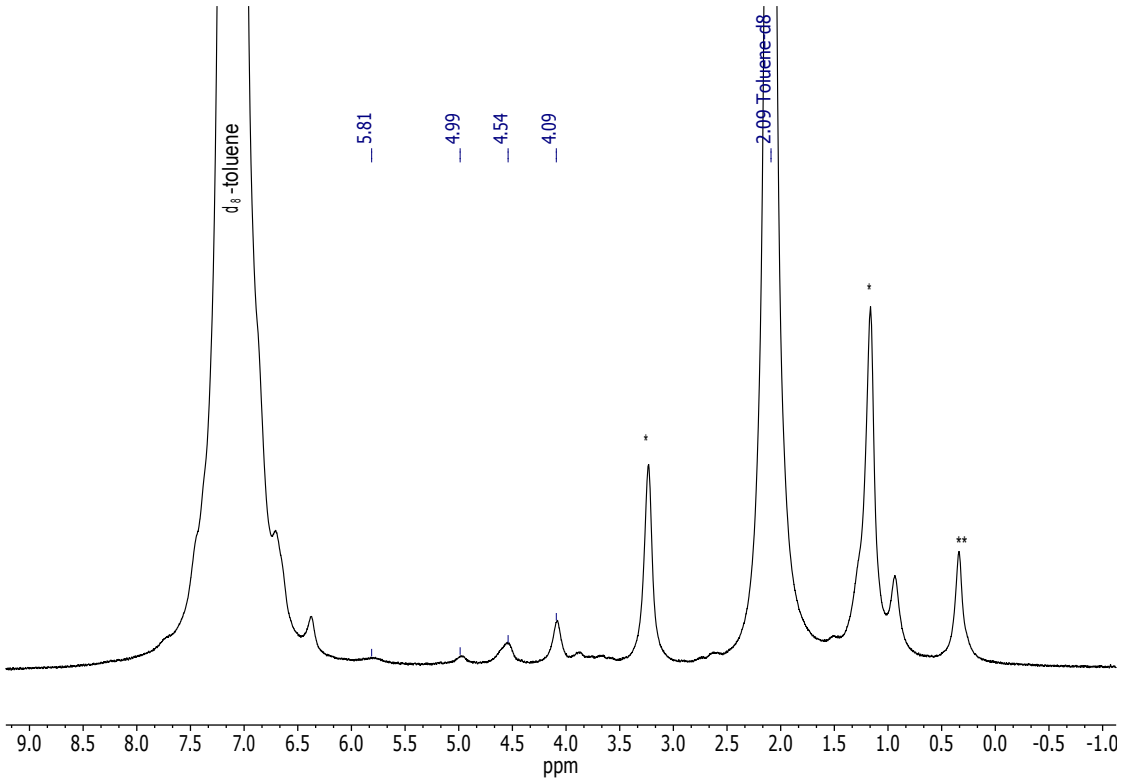

Figure S21: ^{1}H NMR spectrum of **6-BBr$_3$**, d$_8$-toluene, 195 K, 500 MHz. *diethyl ether impurity, **residual grease. Broadened spectrum due to poor solubility in toluene and precipitate in the NMR tube. Annotated signals refer to methylene bridge protons.

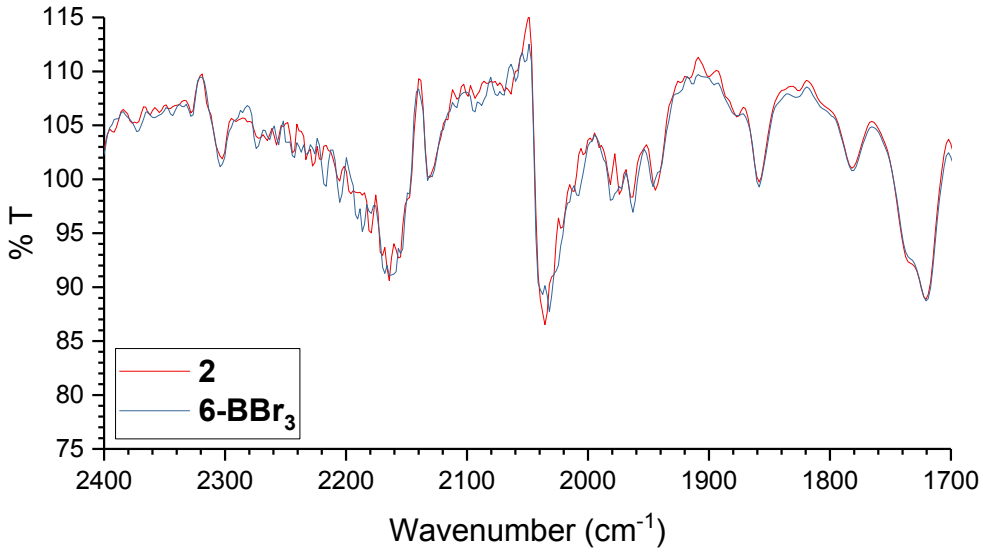

Figure S22: *In situ* solution IR spectrum of the formation of **6-BBr$_3$** in PhF at 233 K (using ReactIR set-up). Almost no change to the NN stretch at 2027 cm^{-1} was observed.

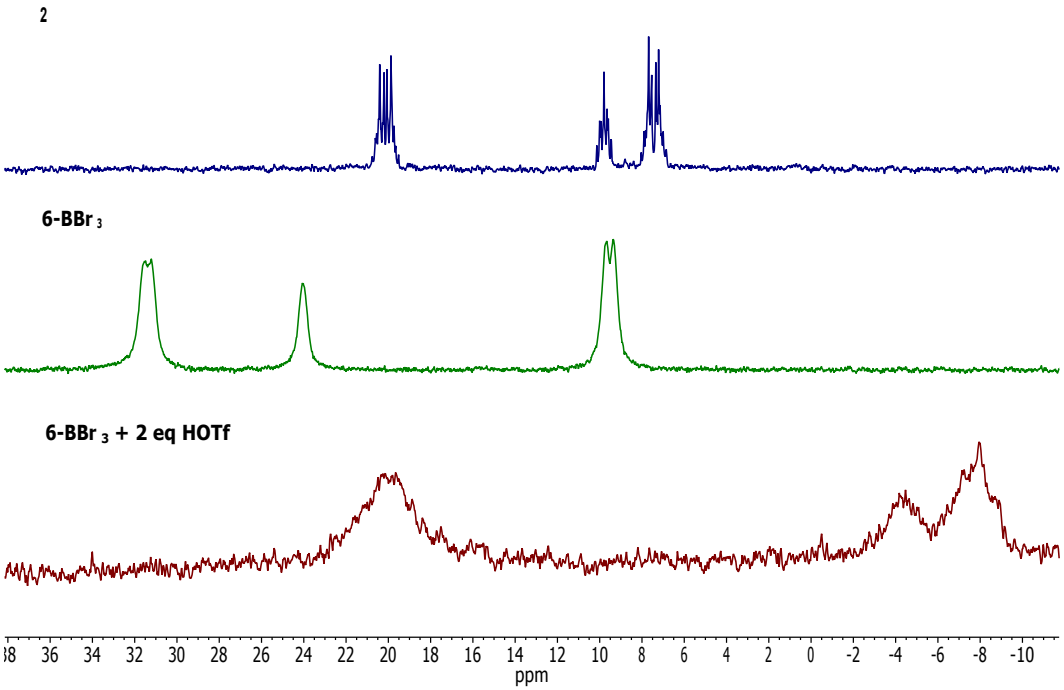

Figure S23: $^{31}P\{^{1}H\}$ NMR spectra of the attempted protonation of **6-BBr$_3$** by addition of 2 eq HOTf (bottom, stacked relative to the $^{31}P\{^{1}H\}$ NMR spectra of **2** in C_6D_6 and **6-BBr$_3$** in d_8-toluene), fluorobenzene, 233 K, 202 MHz.

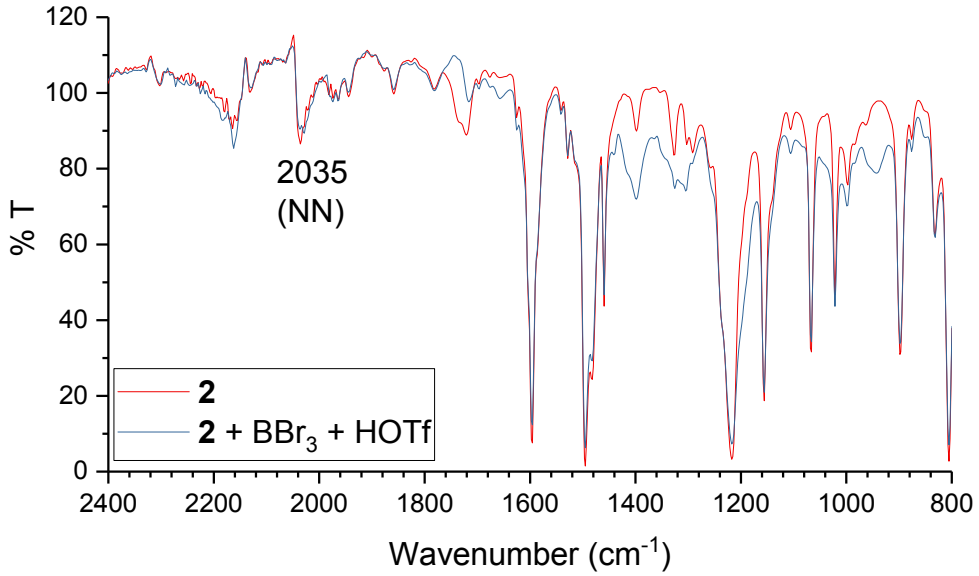

Figure S24: *In situ* infrared spectra of [Mo(N_2)(dppm)(NP_3^{Ph})] (**2**), with the addition of BBr_3 and HOTf (6 equivalents) in fluorobenzene. The strong absorbances near the baseline are attributed to the solvent (fluorobenzene), as no background could be recorded within the experimental setup.

2.6 Complex (7), [Mo(dppm)(PMePh$_2$)(PCP)][B(C$_6$F$_5$)$_4$]

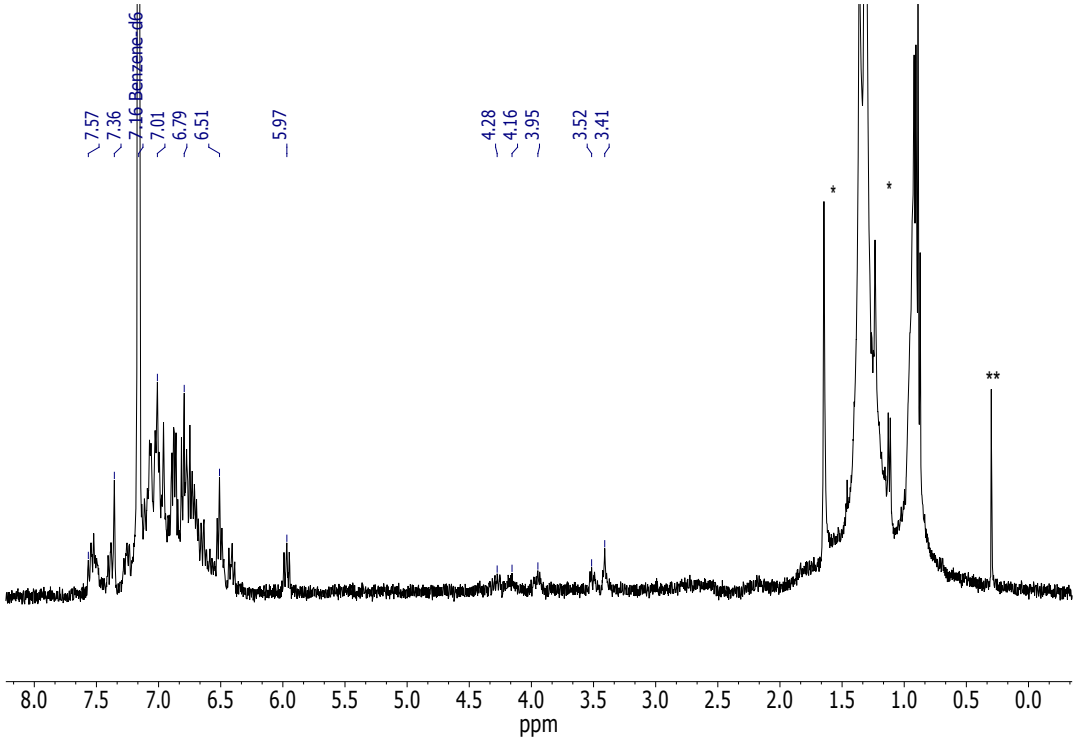

Figure S25. ^{1}H NMR spectrum of **7** (C$_6$D$_6$, 500 MHz, 298 K). *solvent impurities (hexane), ** grease.

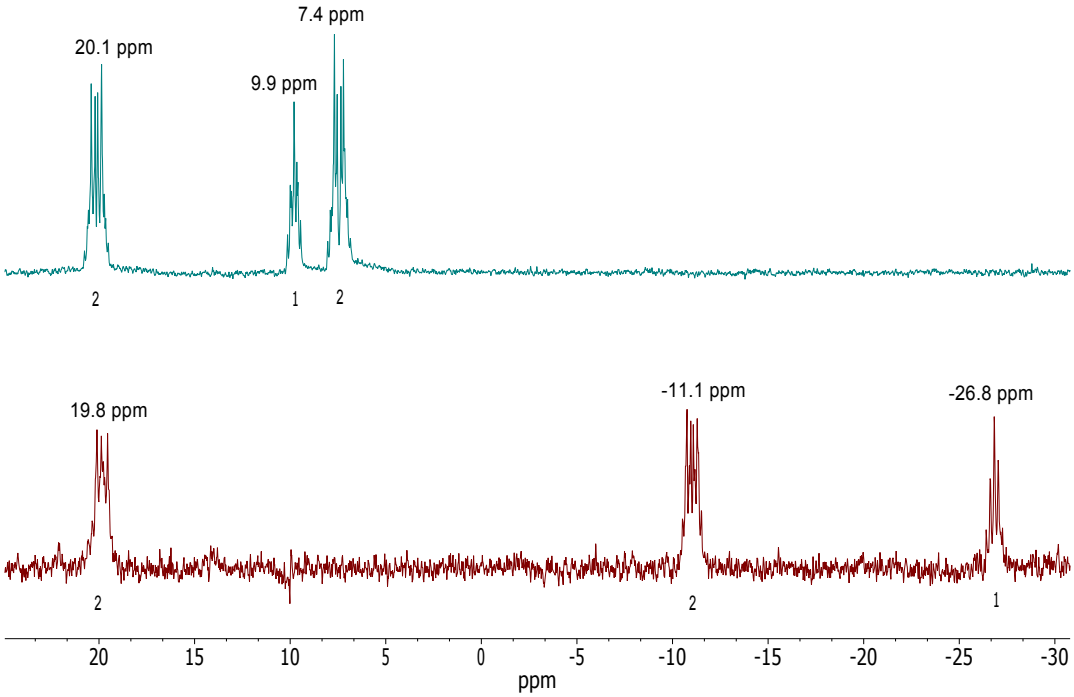

Figure S26. Stacked ^{31}P{^{1}H} NMR spectra of **2** (top) and the intermediate to **7**, formed from initial addition of M[B(C$_6$F$_5$)$_4$] to **2** (bottom). Chemical shifts are denoted above the peaks, relative integrals below. C$_6$D$_6$, 162 MHz, 298 K.

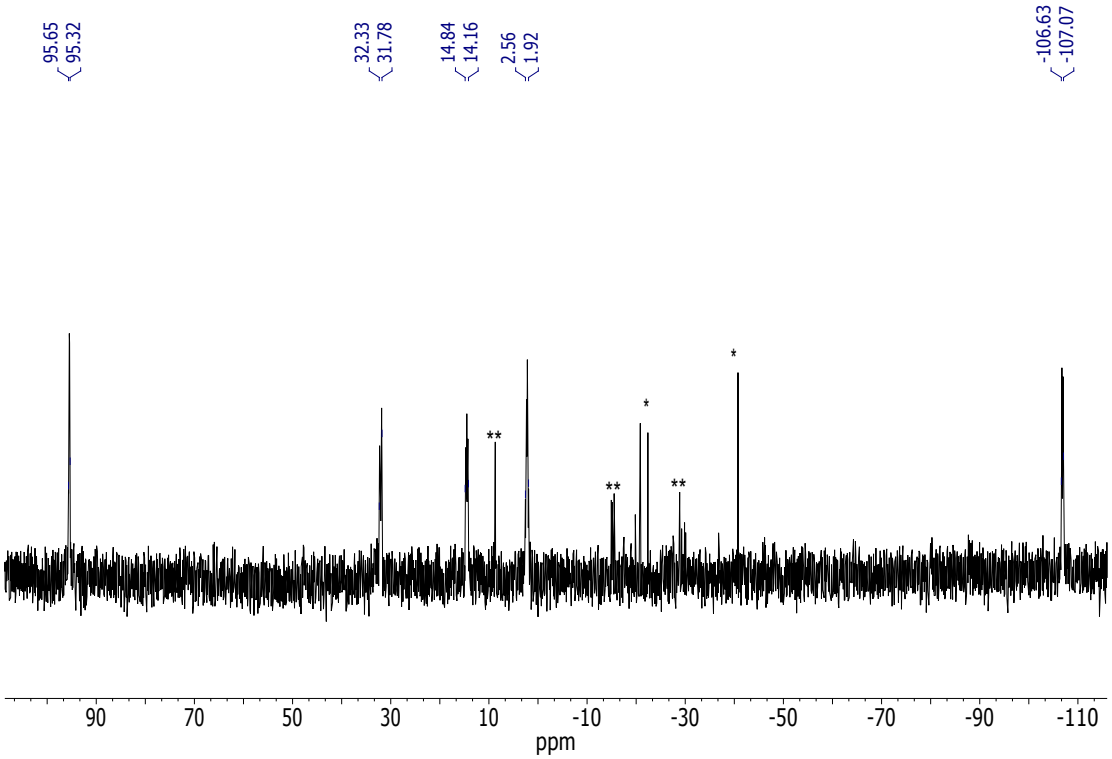

Figure S27. $^{31}P\{^{1}H\}$ NMR spectrum of **7** (C_6D_6, 202 MHz, 298 K). *free ligand impurities, **unknown minor impurities.

3. Crystallographic data

Data were collected using Agilent Xcalibur PX Ultra A diffractometer and the structures were refined using the SHELXTL and SHELX-2013 program systems, with refinement against F^2.[3,4] CCDC 1581753-1581755 and 1849359.

data	**1-Cl**	**2**	**4**	**7**
chemical formula	$C_{43}H_{44}Cl_3MoNOP_3$	$C_{64}H_{58}MoN_3P_5$	$C_{64}H_{60}MoNP_5$	$C_{64}H_{58}MoNP_5$, $C_{24}BF_{20}$
solvent	$3(C_4H_8O)$	-	$0.3(C_6H_{14})$, $0.2(C_4H_8O)$	C_6H_5F
M (g mol^{-1})	1102.30	1119.92	1134.19	1867.05
T/K	173	173	173	173
Crystal appearance	yellow shards	red blocky needles	red needles	red plates
space group	P-1 (no. 2)	$P2_1/c$ (no. 14)	*Pbca* (no. 61)	$P2_1/n$ (no. 14)
a (Å)	13.5291(5)	20.2089(4)	23.2167(3)	13.1523(4)
b (Å)	14.7971(5)	10.65052(16)	18.8351(2)	40.9129(12)
c (Å)	15.8920(5)	25.2105(4)	25.8766(3)	15.2959(4)
α (deg)	70.463(3)	90	90	90
β (deg)	86.734(3)	104.6516(19)	90	92.818(2)
γ (deg)	64.591(4)	90	90	90
V (Å^3)	2694.21(19)	5249.74(16)	11315.5(2)	8220.8(4)
Z	2	4	8	4
ρ_{calcd} (g cm^{-3})	1.359	1.417	1.332	1.509
radiation used	Cu-Kα	Cu-Kα	Cu-Kα	Mo-Kα
λ (Å)	1.54184	1.54184	1.54184	0.71073
μ (mm^{-1})	4.553	3.833	3.554	0.354
$2\theta_{max}$ (deg)	148	148	148	56
measured reflections	10292	10121	11040	16056
R_{int}	0.0325	0.0324	0.0403	0.0291
reflections[a] $[\|F_o\|>4\sigma(\|F_o\|)]$	8283	8288	8652	12592
parameters	667	658	648	1113
R_1 (obs)[a]	0.0355	0.0335	0.0390	0.0552
wR_2 (all)[b]	0.0917	0.0852	0.0930	0.1119
CCDC	1581753	1581754	1581755	1849359

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$

Table S2: The crystallographic data for compounds **1-Cl, 2**, **4** and **7**.

4.1 The X-ray crystal structure of 1-Cl: The O60-, O70-, and O80-based included thf solvent molecules in the structure of **1-Cl** were all found to be disordered, and in each case two orientations were identified, of *ca*. 64:36, 53:47 and 79:21% occupancy respectively. The geometries of each pair of orientations were optimised, the thermal parameters of adjacent atoms were strained to be similar, and only the non-hydrogen atoms of the major occupancy orientations were refined anisotropically (those of the minor occupancy orientations were refined isotropically).

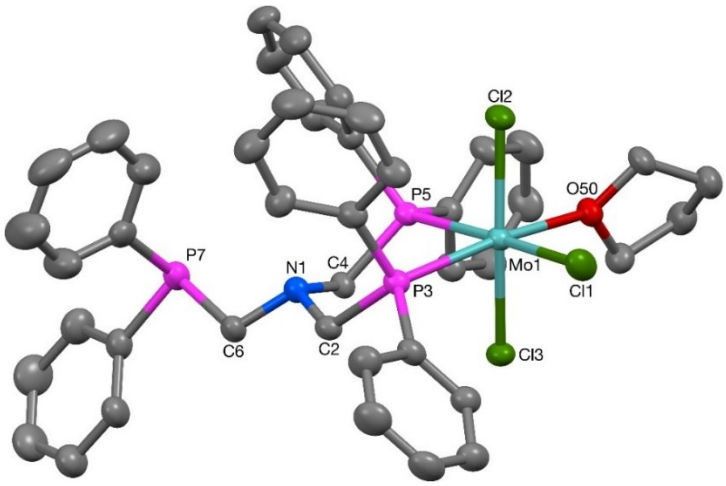

Figure S28: The crystal structure of **1-Cl** (50% probability ellipsoids).

4.2 The X-ray crystal structure of 2

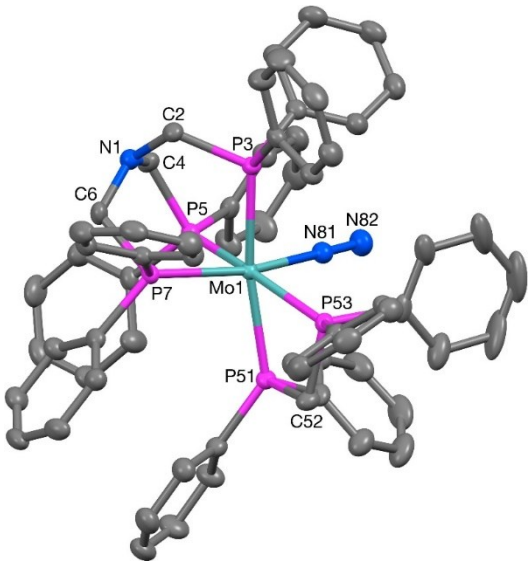

Figure S29: The crystal structure of **2** (50% probability ellipsoids).

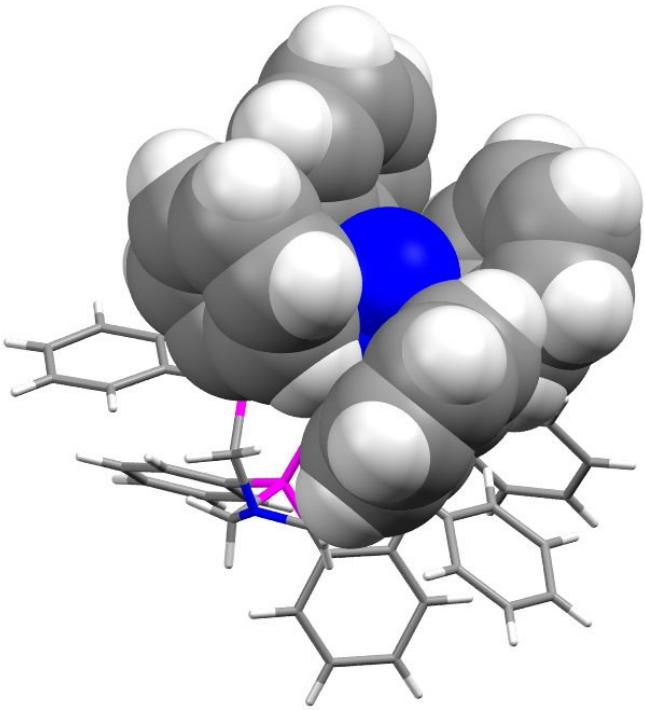

Figure S30: The crystal structure of **2** showing space-filling model of the sterically protecting phenyl rings around the dinitrogen ligand (in blue).

4.3 The X-ray crystal structure of 4: The included solvent in the structure of **4** was found to be highly disordered, and the best approach to handling this diffuse electron density was found to be the SQUEEZE routine of PLATON.[5] This suggested a total of 180 electrons per unit cell, equivalent to 22.5 electrons per asymmetric unit. Before the use of SQUEEZE the solvent most resembled a mixture of hexane (C_6H_{14}, 50 electrons) and thf (C_4H_8O, 40 electrons) in an approximate 3:2 ratio, and a combination of 0.3 hexane molecules and 0.2 thf molecules corresponds to 23 electrons, so this was used as the solvent present. As a result, the atom list for the asymmetric unit is low by $0.3(C_6H_{14}) + 0.2(C_4H_8O) = C_{2.6}H_{5.8}O_{0.2}$ (and that for the unit cell low by $C_{20.8}H_{46.4}O_{1.6}$) compared to what is actually presumed to be present. The two Mo–H hydrogen atoms were located from ΔF maps and refined freely.

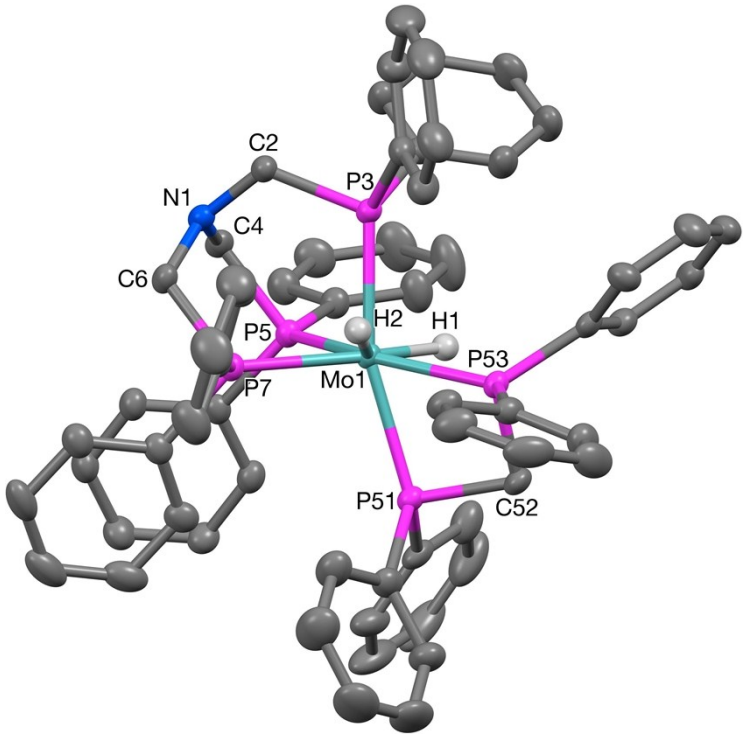

Figure S31: The crystal structure of **4** (50% probability ellipsoids).

4.4 The X-ray crystal structure of 7:

The included fluorobenzene solvent molecule in the structure of **7** showed only minimal disorder around the fluorine atom, which did not need to be modelled. The N-H hydrogen atom was located from Δ*F* maps, and refined with a fixed N-H bond of 0.90(2) Å.

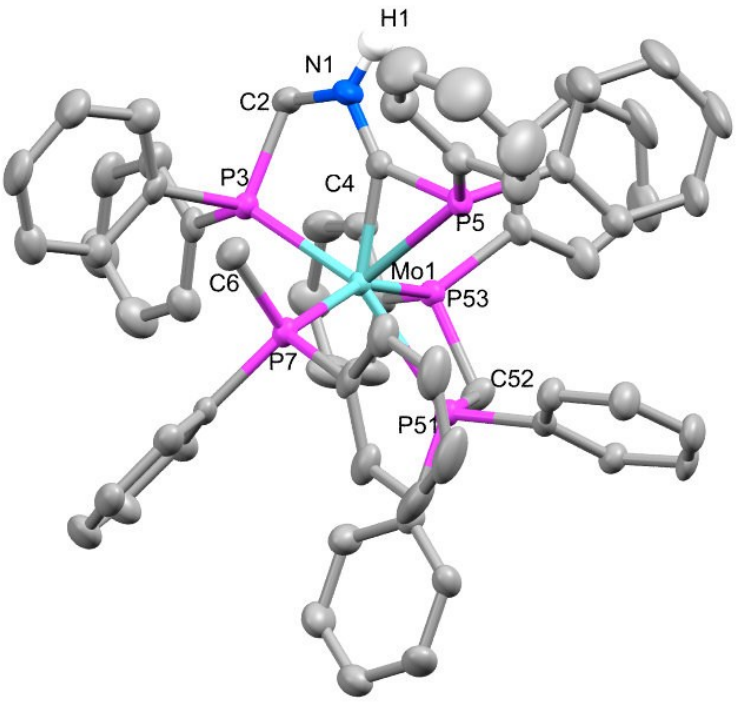

Figure S32: The crystal structure of **7** (50% probability ellipsoids).

4. References

1. Wong, T. Y. H., Barnabas, A. F., Sallin, D., James, B. R., *Inorg. Chem.*, 1995, **34**, 2278-2286

2. Markl G., Jin G., *Tetrahedron Lett.,* 1981, **22**, 1105-1108

3. SHELXTL v5.1, Bruker AXS, Madison, WI, 1998.

4. SHELX-2013, G.M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.

5. A.L. Spek (2003, 2009) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands. See also A.L. Spek, *Acta. Cryst.*, 2015, **C71**, 9-18.