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Cleavage of dinitrogen to yield a (*t*-BuPOCOP)molybdenum(IV) nitride†

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(*t*-BuPOCOP)MoI$_2$ (1; *t*-BuPOCOP = C$_6$H$_3$-1,3-[OP(*t*-Bu)$_2$]$_2$) has been synthesized from MoI$_3$(THF)$_3$. Upon reduction of 1 with Na/Hg under dinitrogen molecular nitrogen is cleaved to form [(*t*-BuPOCOP)Mo(I)(N)]$^-$. The origin of the N atom was confirmed using ^{15}N$_2$. Protonation of [(*t*-BuPOCOP)Mo(I)(N)]$^-$ results in the formation of a neutral species in which it is proposed that the proton has added across the Mo–P bond.

The catalytic reduction of N$_2$ to NH$_3$ at low temperature (22 °C) and pressure (1 atm) has been a long standing goal, both in terms of understanding how this transformation might be achieved in various nitrogenases,[1] but also in terms of creating an abiological catalytic system that could become a practical method of preparing ammonia (or other nitrogen-containing products) from dinitrogen.[2]

Two homogenous catalytic reductions of dinitrogen directly to ammonia employing protons and electrons are known. The first was reported in 2003.[3] The catalyst is a molybdenum complex that contains a hexaisopropylterphenyl-substituted triamidoamine ligand (Mo[HIPTN$_3$N]). The reaction is run in heptane with [2,6-lutidinium][BAr′$_4$] or [2,4,6-trimethylpyridinium]-[BAr′$_4$] (Ar′ = 3,5-(CF$_3$)$_2$C$_6$H$_3$) as the proton source and decamethylchromocene as the reducing agent. Seven to eight equivalents of ammonia are formed, with the remaining electrons being used to make dihydrogen. Eight of the proposed intermediates have been prepared and characterized crystallographically[4] and extensive calculations[5] support the proposed mechanism.[6]

A second example of the catalytic reduction of dinitrogen to ammonia employs a [Mo(L)(N$_2$)$_2$]$_2$(μ-N$_2$) complex (where L is a neutral "PNP pincer" ligand) in toluene.[7] Protons are added in the form of [2,6-lutidinium][OSO$_2$CF$_3$] and electrons are added in the form of cobaltocene. Approximately twelve equivalents of NH$_3$ are formed per molybdenum atom.

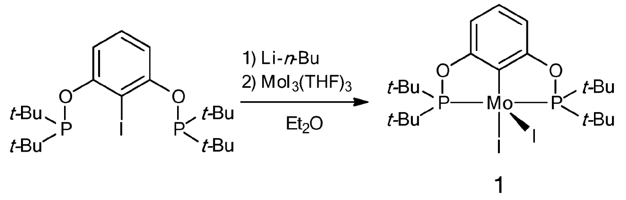
No mechanistic details for the [Mo(L)(N$_2$)$_2$]$_2$(μ-N$_2$) system have been elucidated, while mechanistic studies of the Mo[HIPTN$_3$N] system reveal that one or more intermediates prior to the formation of a nitride intermediate has some significant issues in terms of stability. Both systems have limited longevity due to ligand dissociation from the metal.

In view of the many "pincer" ligands that have been prepared in the last two decades[8] we became interested in preparing Mo complexes bearing an *anionic* "PCP" ligand as opposed to *neutral* "PNP" ligand in the hope that the PCP ligand would remain bound to the metal. An example of a "PCP" ligand which is bound to late transition metal complexes is the *t*-BuPOCOP (*t*-BuPOCOP = C$_6$H$_3$-1,3-[OP(*t*-Bu)$_2$]$_2$) anion. We found no examples of Mo complexes in the literature that contain a PCP ligand.

A *t*-BuPOCOP complex of molybdenum was prepared through lithiation of 1-iodo-2,6-[OP(*t*-Bu)$_2$]$_2$C$_6$H$_3$ and reaction of that lithium reagent with MoI$_3$(THF)$_3$ to give (*t*-BuPOCOP)MoI$_2$ (**1**, Scheme 1), a procedure similar to that employed to prepare a cobalt *t*-BuPOCOP complex.[9] Compound **1** was obtained as a yellow-brown solid in modest yield (46%). However, a diamagnetic impurity is present (10–15%), which is proposed to be (*t*-BuPOCOP)Mo(O)I (**2**), on the basis of NMR spectra and the fact that MoI$_3$(THF)$_3$ is known to decompose to give Mo=O species and 1,4-di-iodobutane.[10] An X-ray study of crystals of **1** was consistent with the presence of two cocrystallized square pyramidal species, but was plagued by an unsolvable disorder problem (see ESI†). All efforts to separate **1** and **2** by fractional crystallizaton failed.

Proton NMR spectra of **1** contain resonances (in a 2 : 1 : 18 : 18 ratio) consistent with diamagnetic **2** and one set of broad, paramagnetically shifted resonances that integrate (approximately) in the ratio 2 : 36 : 1 (see ESI). The largest paramagnetically shifted resonance is the *t*-butyl resonance at 18.14 ppm. Elemental analysis of this mixture is consistent with the sample of **1** containing 12% **2**.

Lithiation of 1-iodo-2,6-[OP(*t*-Bu)$_2$]$_2$C$_6$H$_3$ and reaction of that lithium reagent with MoCl$_3$(THF)$_3$ yielded a product with three major *t*-butyl resonances, along with a small resonance for (*t*-BuPOCOP)MoI$_2$, that we attribute to (*t*-BuPOCOP)MoCl$_2$ (at 23.08 ppm) and two geometrical isomers of (*t*-BuPOCOP)MoICl (at 24.35 and 17.42 ppm), in addition to (*t*-BuPOCOP)Mo(O)X impurities (see ESI).



Scheme 1

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† Electronic supplementary information (ESI) available: Experimental details, spectra, crystal parameters, data acquisition parameters and .cif files for complexes **3** (CCDC 856986) and **4** (CCDC 856987) along with a discussion of unsuccessful structural studies of **1**. See DOI: 10.1039/c2cc17634c

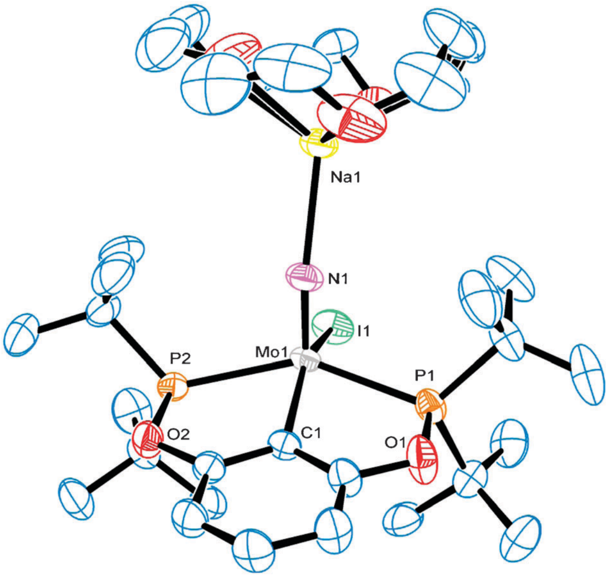


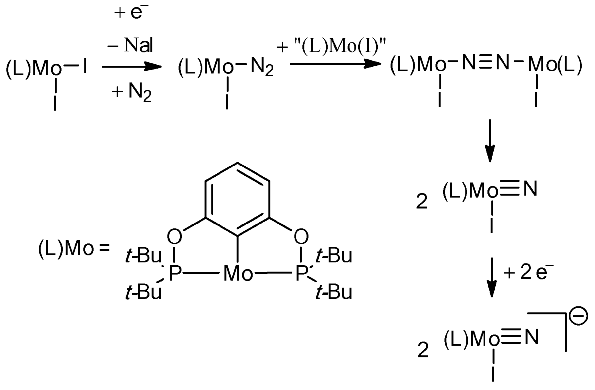
Fig. 1 Thermal ellipsoid representation of [(*t*-BuPOCOP)Mo(I)(N)][Na(15-crown-5)] (**3**) at 50% probability level.‡ H atoms and disordered atoms in the crown ether are omitted. Selected bond distances (Å) and angles (°): Mo1–C1 2.167(3), Mo1–P1 2.4314(8), Mo1–P2 2.4362(8), Mo1–I1 2.8523(3), Mo1–N1 1.659(2), N1–Na1 2.365(3), C1–Mo1–I1 149.55(7), P1–Mo1–P2 146.20(3), I1–Mo1–N1 106.67(9), N1–Mo1–Na1 151.72(16).

Finally, lithiation of 1-iodo-2,6-[OP(*t*-Bu)$_2$]$_2$C$_6$H$_3$ and reaction of that lithium reagent with MoBr$_3$(THF)$_3$ produced a mixture of (*t*-BuPOCOP)MoBr$_2$ (at 20.79 ppm) and two geometrical isomers of (*t*-BuPOCOP)MoIBr (at 22.92 and 16.66 ppm), in addition to (*t*-BuPOCOP)Mo(O)X impurities (see ESI†). So far no synthesis of a (*t*-BuPOCOP)MoX$_2$ species that avoids the use of THF, and therefore formation of (*t*-BuPOCOP)Mo(O)X, has been successful.

A THF solution of **1** (contaminated with **2**) was reduced with Na amalgam in the presence of 15-crown-5 under N$_2$. A dark brown solid was isolated in 57% yield. The ^{1}H NMR spectrum contained four resonances in the diamagnetic region in a 1 : 2 : 18 : 18 ratio. The ^{31}P{^{1}H} NMR spectrum contained one resonance. No resonances attributable to **2** were observed. An X-ray diffraction study confirmed that the product is [(*t*-BuPOCOP)Mo(I)(N)][Na(15-crown-5)] (**3**, Fig. 1). Crystal and data collection parameters can be found in ESI.†

Complex **3** is best described as having a pseudo square pyramidal structure (τ = 0.06)[11] analogous to the proposed structures of **1** and **2**, with which **3** is isoelectronic. The Mo1–N1 bond distance (1.659(2) Å) in **3** is within the typical range for a Mo nitrido bond. The N1–Na1 distance (2.365(3) Å) is characteristic of a relatively weak bonding interaction.[12] The ^{1}H NMR spectrum is consistent with **3** being a diamagnetic Mo(IV) complex analogous to **2**.

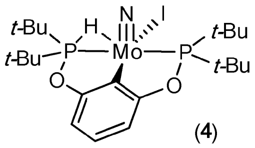
Synthesis of **3** under an ^{15}N$_2$ atmosphere yielded **3-^{15}N**. The nitride resonance is observed in the ^{15}N{^{1}H} NMR spectrum at 801.1 ppm relative to ammonia.[13] These data confirm gaseous N$_2$ as the source of the nitride in **3**. No ^{31}P-^{15}N coupling was observed, but a small J_{PN} is not unusual.[14] Compounds containing [(*t*-BuPOCOP)Mo(I)(N)]$^-$ were observed when two or more equivalents of KC$_8$ or Na naphthalenide were employed as reductants, but no [(*t*-BuPOCOP)Mo(I)(N)]$^-$ was observed using cobaltocene or decamethylchromocene as reducing agents.



Scheme 2 A mechanism of forming [Mo(*t*-BuPOCOP)(I)(N)]$^-$.

Several examples of dinitrogen cleavage in the presence of a transition metal species to give bis-μ-nitrido complexes[15] or μ-nitrido complexes[16] have been reported, but to our knowledge only Cummins and coworkers have reported homogeneous cleavage of N$_2$ to form a monotransition metal nitrido complex, as we have found here.[17] We propose that the key intermediate is a Mo(II)/Mo(II) complex, (I)(L)Mo(μ-N$_2$)Mo(L)(I), which cleaves to give a Mo(V) nitride, (I)(L)Mo(N), to which an electron is then added. Alternatively, the Mo(II)/Mo(II) complex could cleave after addition of two electrons. Bimetallic cleavage *via* a Mo–N–N–Mo intermediate is a common feature of each mechanism. A plausible mechanism for forming [Mo(*t*-BuPOCOP)(I)(N)]$^-$ is shown Scheme 2.

Complex **3** was protonated by [Et$_3$NH][BAr′$_4$] in benzene to give a diamagnetic yellow solid (**4**) in 64% isolated yield. The ^{1}H NMR spectrum of **4** showed no resonances attributable to Et$_3$N, BAr′$_4$, or 15-crown-5; the proton resonance (a doublet of doublets) was found at 3.94 ppm. The splitting pattern (J = 6, 133 Hz) arises from coupling of the proton to two inequivalent phosphorous nuclei (confirmed by ^{1}H{^{31}P} selective decoupling NMR experiments). However, a J_{HP} of 133 Hz is only a fraction of a typical J_{HP} in a phosphonium salt (~350 Hz). The ^{31}P{^{1}H} NMR spectrum contained two doublets of equal intensity with J_{PP} = 20 Hz. A similar experiment with **3-^{15}N** produced **4-^{15}N** in which the proton resonance is a double doublet with an additional splitting of 2.5 Hz (J_{HN}). This small J_{HN} coupling and the location of the ^{15}N resonance (945.0 ppm relative to NH$_3$) suggest there is no direct bonding between the hydrogen and nitrogen atoms. Therefore we are forced to propose that the proton is bridging between Mo and one P (Scheme 3), a structure that would be consistent with all NMR data. Although rare, examples of a proton bridging a Pd–P[18] or a Re–P[19] bond have been published.



(**4**)

Scheme 3

A crystal of **4** that was grown by slowly diffusing pentane vapor into a benzene solution proved to be a merohedral and racemic twin, disordered over three positions, only two of which were refined (see ESI†). The overall quality of the structure of **4** was poor. Therefore the H atom could not be located and the geometrical arrangement of non-H atoms around the Mo center was similar to that found in **3** (Fig. 1), *i.e.*, the Mo–P bond lengths were not statistically different.

A catalytic dinitrogen reduction system in which bimetallic cleavage of dinitrogen is part of the overall mechanism is potentially shorter and simpler than a scheme in which species of borderline stability, *e.g.*, a [HIPTN$_3$N]Mo–N=NH species in the Mo[HIPTN$_3$N] system, must be formed. However, the surprising failure to protonate the nitride in **3** to give a neutral Mo=NH species did not bode well for **3** behaving as a catalyst for dinitrogen reduction. The failure to form **3** employing cobaltocene or decamethylchromocene was also not promising. Therefore, we were not surprised to find that attempted dinitrogen reduction with **3** as a catalyst yielded only 0.34 equivalents of ammonia under Nishibayashi's conditions[7] and 0.30 equivalents under conditions employed for dinitrogen reduction by [HIPTN$_3$N]Mo complexes.[3] Catalytic reduction of dinitrogen to ammonia after all is still an extraordinarily rare event. We are continuing to probe the dinitrogen chemistry of Mo complexes that contain an anionic pincer ligand, especially those that contain Mo in an oxidation state of 3^+ or higher.

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Notes and references

‡ Crystal data for [(*t*-BuPOCOP)Mo(I)(N)][Na(15-crown-5)] (**3**): $C_{32}H_{59}IMoNNaO_7P_2$, M = 877.57, monoclinic, a = 11.1382(9) Å, b = 18.3038(15) Å, c = 19.6708(16) Å, α = 90.00°, β = 90.287(2)°, γ = 90.00°, V = 4010.3(6) Å^3, T = 150(2)K, space group $P2_1/n$, Z = 4, 91 396 reflections measured, 12 017 independent reflections (R_{int} = 0.0569). The final R_1 values were 0.0375 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0789 ($I > 2\sigma(I)$). The final R_1 values were 0.0612 (all data). The final $wR(F^2)$ values were 0.0889 (all data).

1 (*a*) B. K. Burgess and D. J. Lowe, *Chem. Rev.*, 1996, **96**, 2983–3011; (*b*) R. R. Eady, *Chem. Rev.*, 1996, **96**, 3013–3030; (*c*) B. E. Smith, *Adv. Inorg. Chem.*, 1999, **47**, 159–218; (*d*) D. Rehder, *Coord. Chem. Rev.*, 1999, **182**, 297–322; (*e*) Y. Zhao, S.-M. Bian, H.-N. Zhao and J.-F. Huang, *J. Integr. Plant Biol.*, 2006, **48**, 745–755.

2 (*a*) M. D. Fryzuk and S. A. Johnson, *Coord. Chem. Rev.*, 2000, **200–202**, 379–409; (*b*) M. Hidai and Y. Mizobe, *Chem. Rev.*, 1995, **95**, 1115–1133; (*c*) M. Hidai, *Coord. Chem. Rev.*, 1999, **185–186**, 99–108; (*d*) J. Chatt, J. R. Dilworth and R. L. Richards, *Chem. Rev.*, 1978, **78**, 589–625; (*e*) R. L. Richards, *Coord. Chem. Rev.*, 1996, **154**, 83–97; (*f*) R. L. Richards, *Pure Appl. Chem.*, 1996, **68**, 1521–1526; (*g*) T. A. Bazhenova and A. E. Shilov, *Coord. Chem. Rev.*, 1995, **144**, 69–145.

3 (*a*) D. V. Yandulov and R. R. Schrock, *Science*, 2003, **301**, 76–78; (*b*) R. R. Schrock, *Acc. Chem. Res.*, 2005, **38**, 955–962.

4 (*a*) D. V. Yandulov, R. R. Schrock, A. L. Rheingold, C. Ceccarelli and W. M. Davis, *Inorg. Chem.*, 2003, **42**, 796–813; (*b*) D. Yandulov and R. R. Schrock, *Inorg. Chem.*, 2005, **44**, 1103–1117.

5 S. Schenk, B. Le Guennic, B. Kirchner and M. Reiher, *Inorg. Chem.*, 2008, **47**, 3634–3650.

6 R. R. Schrock, *Angew. Chem., Int. Ed.*, 2008, **47**, 5512–5522.

7 K. Arashiba, Y. Miyake and Y. Nishibayashi, *Nat. Chem.*, 2011, **3**, 120–125.

8 *The Chemistry of Pincer Compounds*, ed. D. Morales-Morales and C. M. Jensen, Elsevier, Amsterdam, The Netherlands, 2007.

9 T. J. Hebden, A. J. St. John, D. G. Gusev, W. Kaminsky, K. I. Goldberg and D. M. Heinekey, *Angew. Chem., Int. Ed.*, 2011, **50**, 1873–1876.

10 F. A. Cotton and R. Poli, *Inorg. Chem.*, 1987, **26**, 1514–1518.

11 A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349–1356.

12 (*a*) S. Sarkar, A. R. Carlson, M. K. Veige, J. M. Falkowski, K. A. Abboud and A. S. Veige, *J. Am. Chem. Soc.*, 2008, **130**, 1116–1117; (*b*) R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.*, 1976, **32**, 751–767.

13 M. Witanowski, L. Stefaniak, S. Szymanski and H. Januszewski, *J. Magn. Reson.*, 1977, **28**, 217–226.

14 T. A. Betley and J. A. Peters, *J. Am. Chem. Soc.*, 2004, **126**, 6252–6254.

15 (*a*) J. A. Pool, E. Lobkovsky and P. J. Chirik, *Nature*, 2004, **427**, 527–530; (*b*) F. Akagi, T. Matsuo and H. Kawaguchi, *Angew. Chem., Int. Ed.*, 2007, **46**, 8778–8781; (*c*) H. Kawaguchi and T. Matsuo, *Angew. Chem., Int. Ed.*, 2002, **41**, 2792–2794; (*d*) I. Korobkov, S. Gambarotta and G. P. A. Yap, *Angew. Chem., Int. Ed.*, 2002, **41**, 3433–3436; (*e*) P. Berno and S. Gambarotta, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 822–824; (*f*) M. Hirotsu, P. P. Fontaine, A. Epshteyn, P. Y. Zavalij and L. R. Sita, *J. Am. Chem. Soc.*, 2007, **129**, 9284–9285; (*g*) A. Caselli, E. Solari, R. Scopelliti, C. Floriani, N. Re, C. Rizzoli and A. Chiesi-Villa, *J. Am. Chem. Soc.*, 2000, **122**, 3652–3670; (*h*) A. Zanotti-Gerosa, E. Solari, L. Giannini, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Am. Chem. Soc.*, 1998, **120**, 437–438; (*i*) G. K. B. Clentsmith, V. M. E. Bates, P. B. Hitchcock and F. G. N. Cloke, *J. Am. Chem. Soc.*, 1999, **121**, 10444–10445; (*j*) M. M. Rodriguez, E. Bill, W. W. Brennessel and P. L. Holland, *Science*, 2011, **334**, 780–783.

16 (*a*) I. Vidyaratne, P. Crewdson, E. Lefebvre and S. Gambarotta, *Inorg. Chem.*, 2007, **46**, 8836–8842; (*b*) M. D. Fryzuk, C. M. Kozak, M. R. Bowdridge, B. O. Patrick and S. J. Rettig, *J. Am. Chem. Soc.*, 2002, **124**, 8389–8397; (*c*) E. Solari, C. Da Silva, B. Iacono, J. Hesschenbrouck, C. Rizzoli, R. Scopelliti and C. Floriani, *Angew. Chem., Int. Ed.*, 2001, **40**, 3907–3909; (*d*) A. Caselli, E. Solari, R. Scopelliti, C. Floriani, N. Re, C. Rizzoli and A. Chiesi-Villa, *J. Am. Chem. Soc.*, 2000, **122**, 3652–3670; (*e*) Y.-C. Tsai, M. J. A. Johnson, D. J. Mindiola and C. C. Cummins, *J. Am. Chem. Soc.*, 1999, **121**, 10426–10427.

17 (*a*) J. S. Figueroa, N. A. Piro, C. R. Clough and C. C. Cummins, *J. Am. Chem. Soc.*, 2006, **128**, 940–950; (*b*) D. J. Mindiola, K. Meyer, J.-P. F. Cherry, T. A. Baker and C. C. Cummins, *Organometallics*, 2000, **19**, 1622–1624; (*c*) C. E. Laplaza, M. J. A. Johnson, J. C. Peters, A. L. Odom, E. Kim, C. C. Cummins, G. N. George and I. J. Pickering, *J. Am. Chem. Soc.*, 1996, **118**, 8623–8638; (*d*) C. E. Laplaza and C. C. Cummins, *Science*, 1995, **268**, 861–863.

18 (*a*) A. Albinati, F. Lianza, M. Pasquali, M. Sommovigo, P. Leoni, P. S. Pregosin and H. Rüegger, *Inorg. Chem.*, 1991, **30**, 4690–4692; (*b*) P. Leoni, M. Pasquali, M. Sommovigo, F. Laschi, P. Zanello, A. Albinati, F. Lianza, P. S. Pregosin and H. Rüegger, *Organometallics*, 1993, **12**, 1702–1713.

19 S. M. Reid, B. Neuner, R. R. Schrock and W. M. Davis, *Organometallics*, 1998, **17**, 4077–4089.