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FEATURE ARTICLE

Reductive cleavage and related reactions leading to molybdenum–element multiple bonds: new pathways offered by three-coordinate molybdenum(III)

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Three-coordinate molybdenum(III) complexes comprise a new class of reactive-yet-isolable substances. Related to a well known class of metal–metal triple bonded dimers, the monomeric molybdenum(III) complexes supported by sterically-demanding *N-tert*-alkylanilide ligands offer previously unavailable synthetic routes to molybdenum–element multiple bonds. Terminal nitride, phosphide and carbide functionalities have been prepared from reactions with dinitrogen, white phosphorus and carbon monoxide, respectively.

Introduction

Professor Malcolm H. Chisholm of Indiana University has championed the chemistry of compounds containing Mo≡Mo and W≡W triple bonded moieties since the early 1970s.[1] For the most part, the compounds of interest have supporting amide (*e.g.* NMe_2) or alkoxide (*e.g.* OBu^t) ligands. Although chromium(III) does not exhibit a similar tendency to form unbridged metal–metal triple bonds, it was shown in seminal work by Bradley's group that the complex $Cr(NPr^i_2)_3$ **1** exists in discrete monomeric form.[2] Moreover, the compound manifests a trigonal-planar coordination geometry, along with a high-spin (quartet) ground state. Thus an interesting dichotomy arose between the chemistry of chromium(III), on the one hand, and that of molybdenum(III) and tungsten(III) on the other. The successful synthesis of a discrete monomeric molybdenum(III) entity would bridge this gap, and hints that such a species might be accessible *via* implementation of bulky amide ligands can be found in reported attempts at the synthesis of $Mo[N(SiMe_3)_2]_3$ **2**.[3] Note, indeed, that the hexamethyldisilazide ligand is known to support three-coordination for the 3d metals Sc through Co in the 3+ oxidation state, and that the remarkable amide $U[N(SiMe_3)_2]_3$ **3** is a monomer.[4]

Against the foregoing backdrop, we set out to explore complexes of the new amide ligand N(R)Ar [$R = (CD_3)_2CH_3$, $Ar = 3,5\text{-}C_6H_3Me_2$], and related derivatives.[5] Use of the $C(CD_3)_2CH_3$ substituent was deemed worthwhile as a ^2H NMR spectroscopic handle, and the choice of substituents was prompted by a desire to (i) avoid β-hydrogens, (ii) combine one roughly spherical substituent with one roughly planar substituent for efficient intramolecular packing, and (iii) use hydrocarbon-only building blocks so as to avoid decomposition pathways to which silylamides are prone, such as cyclometallation or N–Si bond cleavage.[6]

A ready synthesis of deuterated *N-tert*-butylanilides was found to consist of [$^2H_6$]acetone condensation with the desired substituted aniline, followed by treatment of the resulting imine with methyllithium.[5] The most widely successful ligand to date is that derived from deprotonation of *N*-[$^2H_6$]-*tert*-butyl-3,5-dimethylaniline with *n*-butyllithium. Crystallization from ether affords the white etherate $Li[N(R)Ar](OEt_2)$, which is suitable for reaction with transition metal halides.

Synthesis and characterization of three-coordinate complexes

Following the lead of Bradley's synthesis of $Cr(NPr^i_2)_3$ **1** from chromium(III) chloride and lithium diisopropylamide,[2] it was elected to investigate the reaction of $MoCl_3(THF)_3$[7] with $Li[N(R)Ar](OEt_2)$.[5] In this endeavour, the presence of a deuterium label in the ligand led to rapid identification of appropriate conditions for the synthesis of $Mo[N(R)Ar]_3$ **4**, the compound exhibiting a single ^2H NMR peak at δ *ca.* 64.[8] Various conditions were sampled, with the result that a 2:1 lithium amide to molybdenum chloride stoichiometry was deemed optimal (ostensibly to speed conversion to products) and that diethyl ether solvent gave the best results. The desired compound, $Mo[N(R)Ar]_3$ **4**, has been obtained in 60–80% isolated yield as a lipophilic orange–red crystalline substance.[9] Other variously substituted anilide ligands including the 'parent' $-N(Bu^t)Ph$,[9] the adamantyl-substituted derivatives –N(1-Ad)Ar and –N(2-Ad)Ar, and the mono-fluorinated derivative $-N(R)(4\text{-}C_6H_4F)$[10] have all provided corresponding three-coordinate tris-anilide complexes of Mo^{III} following the standard protocol developed for **4**.[9]

An important feature of the characterization of **4** is the fact, substantiated by X-ray crystallography,[9] that it exists in the solid as discrete mononuclear complexes with no short intermolecular contacts. As such, **4** and related derivatives constitute the first definitive examples of three-coordinate molybdenum. The geometry at molybdenum is trigonal planar. Thus, although Mo≡Mo triple bonds are known to be *ca.* 80 kcal mol^{-1} (1 cal = 4.184 J),[11] the substituents are sufficiently large in the present case to obviate dimerization.[12] A representative structure[9] is that of $Mo[N(R)Ar]_3$ **4**, shown in Fig. 1.

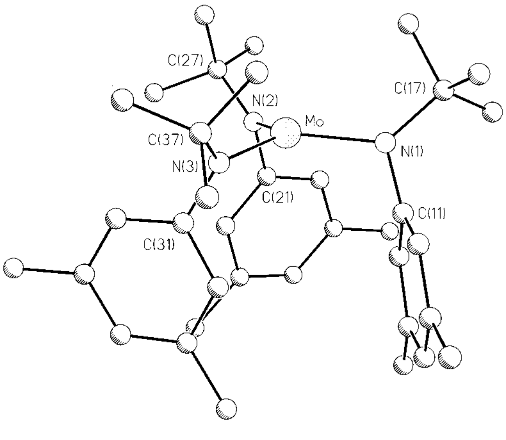

Fig. 1 Ball and stick representation of $Mo[N(R)Ar]_3$ **4**, from X-ray coordinates.[9] The Mo–N distances average 1.967(7) Å, and the sum of N–Mo–N angles is 357.7(3)°.

The X-ray crystallography studies show that the intramolecular packing conformation is one with the three $3,5\text{-}C_6H_3Me_2$ substituents on one side of the trigonal plane and the three Bu^t groups on the other side. Another conformation that would maximize the in-plane N to Mo π bonding is a 'two-up, one-down' arrangement of substituents; investigation of this alternative by molecular mechanics suggests that it is higher in energy by *ca.* 6 kcal mol^{-1} than the observed conformation.[12] Solution NMR spectra of Mo[N(R)Ar]$_3$ **4** are consistent with preservation of the pseudo-C_3 symmetric structure, with only a single –N(R)Ar environment being observed down to *ca.* −40 °C. EXAFS data collected at 10 K on frozen toluene solutions likewise were consistent with the pseudo-C_3 symmetric conformation.[9]

Also critical to an appreciation of the tris-anilide molybdenum(III) complexes is the fact that they are high spin, with all three d electrons unpaired. This is known from both solution and solid-state magnetic susceptibility studies, with μ_{eff} for the complexes being close to the spin-only value.[9] Symmetry arguments and computational studies[13] agrees that this should be the case, and indicate that the half-occupied orbitals possess σ (d$_{x^2}$) and π (d$_{xz}$, d$_{yz}$) symmetry with respect to the pseudo-C_3 axis. This is an interesting point to be recalled later in the bonding discussion pertaining to very stable nitrido complexes, *e.g.* N≡Mo[N(R)Ar]$_3$ **5**.

With regard to the properties of **4**, it should be noted that despite its coordinative unsaturation no reaction is observed with pyridine, triethylphosphine, or tetrahydrofuran (benzene, 25 °C). Thus, the compound is not a Lewis acid. If this result is to be attributed to electronic effects, then a reluctance to go low-spin (making the d$_{z^2}$ orbital available) can be invoked. Otherwise, it can be suggested that the pyridine, PEt$_3$, and THF molecules are too large to access the molybdenum center. That more electron-deficient complexes such as Ti[N(R)Ar]$_3$ **6** display an η^3 bonding mode for the N(R)Ar ligand,[14] while the molybdenum complexes display strictly the η^1 bonding mode, can be taken as evidence that the Mo complexes are not overly electron-poor.

Reactions furnishing the nitrido linkage

Theoretical work has placed the N≡Mo bond dissociation enthalpy (BDE) at *ca.* 165 kcal mol^{-1}, nearly 75% of the value for the N≡N triple bond of dinitrogen.[13] This being the case, it is not surprising that many reactions have been found which, in effect, transfer a nitrogen atom to Mo[N(R)Ar]$_3$ **4**, giving rise to N≡Mo[N(R)Ar]$_3$ **5**. Compound **5** can thus be regarded as a thermodynamic sink in systems containing **4** and sources of a nitrogen atom. Also, **4** can be regarded as an example of an 'azophilic' complex, in much the same way that fragments poised to form strong bonds to oxygen [*e.g.* Ta(OSiBu$^t_3$)$_3$] **7** are regarded as oxophilic.[15] The notion of the extreme stability of **5** is further substantiated by electrochemical studies showing that the complex is highly resistant to both oxidation and reduction.

Geometric and electronic structure issues related to diamagnetic **5** are reminiscent of the discussion given above for **4**. A representative structure is that of NMo[N(Bu^t)Ph]$_3$ **8**, shown in Fig. 2.[9] As in the case of **4**, the aryl groups are close-packed on one side of the molecule, while the Bu^t groups now form a protective 'pocket' about the Mo≡N triple bond. The three d electrons unpaired in **4** are involved in **5** in making the σ and π bonds to the nitrido nitrogen, bonds which have the same symmetry as the orbitals (d$_{z^2}$, d$_{xz}$ and d$_{yz}$) utilized in **4** for the unpaired electrons. Thus it can be seen that the molybdenum–anilide bonding is essentially unperturbed on going from **4** to **5** (a notion substantiated by bond length considerations), and that the conformation of the Mo[N(R)Ar]$_3$ fragment also remains essentially constant. Little reorganization is required for addition of a nitrogen atom to **4**.

During initial purifications of **4** by recrystallization (OEt$_2$, −40 °C), it was noted that solutions became purple if under N$_2$, but retained the orange–red color of **4** if maintained in an argon atmosphere. Solid **4** can be manipulated under N$_2$ without any observable decompostion, and 0.05 M solutions of **4** stored under N$_2$ at room temperature degrade only slowly (*ca.* 5% per day). Naturally it was surmised that the purple color was due to N$_2$ chemistry, favored at low temperature either due to enhanced solubility of N$_2$ or to other entropic factors. In fact, at the time a purple N$_2$-bridged dimolybdenum(III) amido complex was already known, namely (μ-N$_2$)[Mo(Bu^{t}Me$_2$SiNCH$_2$CH$_2$)$_3$N]$_2$ **9**.[16] Thus, the purification process for **4** was developed to involve exclusion of N$_2$. The full details of the reaction of **4** with N$_2$[9] were not elucidated until after **5** had already been characterized in full in the context of a nitrous oxide N–N cleavage reaction.[8]

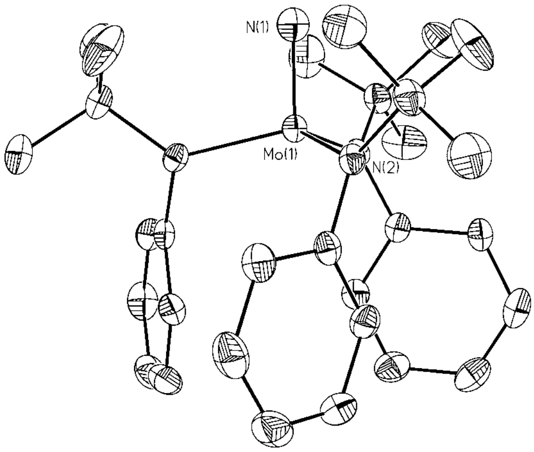

Fig. 2 Thermal ellipsoid representation of N≡Mo[N(Bu^t)Ph]$_3$ **8** from an X-ray study.[9] The Mo–N$_{\text{nitride}}$ bond resides on a crystallographic threefold axis. Ellipsoids are at the 35% probability level. The Mo–N$_{\text{nitride}}$ bond length is 1.658(5) Å, while the Mo–N$_{\text{amide}}$ bond length is 1.979(2) Å.

Nitrous oxide

The existence of molybdenum(VI) nitrido-tris-amide complexes such as NMo(NPh$_2$)$_3$[17] **10** was an early indicator that **4** should function as an N-atom acceptor. This raised the question: what molecule might serve, with a minimum of reorganization, as a nitrogen-atom donor? One answer that came to mind was nitrous oxide, since loss of its terminal nitrogen atom would yield nitric oxide. The latter, while admittedly reactive, is a viable diatomic gas plausible as a leaving group in an N-atom transfer reaction. A problem with the selection of nitrous oxide as an N-atom donor was that literature precedent showed clearly that reducing metal complexes react with N$_2$O to give exclusive N–O bond cleavage, liberating N$_2$ as a stable byproduct.[18] This is why nitrous oxide is sometimes referred to as 'a clean oxidant'. Furthermore, on thermodynamic grounds one expects N–O bond cleavage, given that the N–O bond is the weaker by *ca.* 75 kcal mol^{-1} of the two bonds in the molecule.[19]

Experiments showed that solutions of **4** react smoothly with nitrous oxide (⩾4 equiv.), **4** being converted rapidly (⩽5 min, 25 °C) to a 1 : 1 mixture of nitride **5** and the similarly diamagnetic nitrosyl derivative (ON)Mo[N(R)Ar]$_3$ **11** with no observable intermediates [eqn. (1)].[8] Various conditions were sampled, and in no case was the ratio of nitride : nitrosyl perturbed from 1 : 1. Careful analysis of the reaction mixtures ruled out the presence of the (at the time unknown) oxo complex, Mo(O)[N(R)Ar]$_3$ **12**, which would have been produced if **4** has deoxygenated nitrous oxide. (As described below, brown paramagnetic oxo complex **12** can be synthesized independently.[20])

$$\underset{\mathbf{4}}{\text{Mo[N(R)Ar]}_3} \xrightarrow{\text{N}_2\text{O}} \underset{\mathbf{5}}{\text{N}{\equiv}\text{Mo[N(R)Ar]}_3} + \underset{\mathbf{11}}{\text{O=N=Mo[N(R)Ar]}_3} \qquad (1)$$

An independent synthesis of nitrosyl **11** was achieved by simple treatment of a solution of **4** with nitric oxide [eqn. (2)].[8]

$$\underset{\mathbf{4}}{\text{Mo[N(R)Ar]}_3} \xrightarrow{\text{NO}} \underset{\mathbf{11}}{\text{O=N=Mo[N(R)Ar]}_3} \qquad (2)$$

The yellow, diamagnetic compound was produced in high yield, its synthesis being reminiscent of Bradley's classic synthesis of $(ON)Cr[N(SiMe_3)_2]_3$ **13**.[21] The synthesis and characterization of **11** in pure form permitted unambiguous assignment of its contribution to the NMR spectra from the N_2O reactions. Furthermore, the rapid and efficient combination of nitric oxide with **4** raised the possibility that free NO may be involved in the mechanism for nitrous oxide N–N bond cleavage by **4**. A second possibility is that the mechanism involves bimetallic activation of nitrous oxide, an appealing possibility that neatly accounts for the observed 1 : 1 ratio of **5** : **11**. The data in hand, however, are insufficient to pinpoint the mechanism of the splitting reaction. Definitive kinetic data will have to be acquired by stopped-flow techniques in order to settle the issue.

Characterization of nitride **5** was required for a complete interpretation of the data from nitrous oxide reactions with **4**. Interestingly, a clean route to **5** was discovered that involves treatment of **4** with mesityl azide.[8] This reaction, like the N_2O reaction, is unusual in comparison with known reactions of the substrate with reducing metal compounds. Normally, reductants elicit N_2 elimination from organoazides, giving metal imido derivatives.[22] Here, as demonstrated with a ^{15}N-labeling study, abstraction of the terminal nitrogen atom occurred, giving high-yield conversion to pale yellow **5**. As in the case of the N_2O activation reaction, the mechanism of mesityl azide N–N bond cleavage by **4** remains to be elucidated in detail. A key issue here is whether the N–N bond breaks before or after the N–C bond. The issue of a bimetallic activation mechanism is not important for the case of mesityl azide, since no evidence was found for the formation of the putative aryldiazenido complex $MesN{=}NMo[N(R)Ar]_3$. Based on subsequent synthetic studies, the latter is expected to be a stable, diamagnetic complex.

Dinitrogen

Having characterized nitride **5**, $N{\equiv}Mo[(R)Ar]_3$, a more detailed interpretation of the behavior of **4** in the cold under N_2 (1 atm) became possible.[23] Catalina Laplaza noticed that the purple solutions (presumed to contain $(\mu\text{-}N_2)\{Mo[N(R)Ar]_3\}_2$, **14**) lost the purple color upon standing for a couple of hours at 25 °C, and that peaks for nitride **5** were dominant in corresponding NMR spectra. This raised the exciting possibility that **4** was able to directly bind and split N_2, under mild conditions, and in the absence of any added reagents! Accordingly it was found that **4** could be converted in good yield to **14** by storage of a toluene solution under N_2 at −40 °C for 3–5 days. Subsequent warming to room temperature gave quantitative conversion to nitride **5** with the first-order kinetics and a $t_{1/2}$ of *ca.* 30 min.[23]

Subsequent work has included extensive characterization of the intermediate purple dinitrogen complex **14**, with its N–N bond length of 1.19(2) Å (EXAFS) and ν_{NN} of 1630 cm^{-1} (Raman).[9] The dinitrogen ligand bridges the two molybdenum centers in the typical[24] linear, end-on fashion, and the relatively high symmetry of the complex renders it paramagnetic, with a triplet ground state. It exhibits a single ^2H NMR signal at δ *ca.* 14. Isotopic labeling studies with $^{15}N_2$ permitted determination of a temperature-dependent primary kinetic isotope effect on the splitting reaction (conversion of **14** to **5**),[9] the magnitude of which was in accord with predictions based on the observed Raman ν_{NN} of $(\mu\text{-}^{15}N_2)\{Mo[N(R)Ar]_3\}_2$ and the diatomic oscillator approximation.[9]

The mechanism of dinitrogen cleavage by **4** has now also been studied in considerable detail by theoretical methods.[13] The important steps are [eqn.(3)] binding of dinitrogen by **4** to

$$\underset{\textbf{4}}{Mo[N(R)Ar]_3} + N_2 \rightleftharpoons \underset{\textbf{15}}{N_2Mo[N(R)Ar]_3} \qquad (3)$$

give the low-spin 1 : 1 adduct, $(N_2)Mo[N(R)Ar]_3$ **15**, [eqn. (4)] trapping of **15** by a second equiv. of **4** to give dinuclear **14**, and [eqn. (5)] unimolecular fission of **14** at the N–N bond *via* a

$$\underset{\textbf{4}}{Mo[N(R)Ar]_3} + \underset{\textbf{15}}{N_2Mo[N(R)Ar]_3} \longrightarrow \underset{\textbf{14}}{(\mu\text{-}N_2)[Mo\{N(R)Ar\}_3]_2} \qquad (4)$$

$$\underset{\textbf{14}}{(\mu\text{-}N_2)[Mo\{N(R)Ar\}_3]_2} \longrightarrow 2\ \underset{\textbf{5}}{N{\equiv}Mo[N(R)Ar]_3} \qquad (5)$$

zigzag (not linear) transition state to produce 2 equiv. of nitride **5**.

Experimentally we have not yet been able to observe the 1 : 1 adduct **15** directly, and we postulate that the binding of N_2 by **4** is rapid and reversible with only small equilibrium concentrations of **15** being present under 1 atm of N_2. To observe **15** directly, experiments are currently underway wherein **4** is being monitored by NMR and IR under large dinitrogen pressures. Theoretical studies predict that **15** will feature an end-on interaction between Mo and the N_2, and this is in accord with the structure of recently reported $N_2Mo(Me_3SiNCH_2CH_2)_3N$ **16**,[25] which has been shown (in contrast to **15**) not to be labile.

Although the reductive cleavage of dinitrogen to nitride by well-defined transition metal complexes in homogeneous solution was unprecedented prior to 1995,[23] it can be expected that more examples of this remarkable reaction type will eventually come to light. A very recent example comes from the labs of Floriani,[26] and it involves the use of niobium calixarene complexes. It is reasonable to speculate that the development of robust complexes capable of N_2 reductive cleavage will eventually result in applications in catalysis, the ultimate goal being the development of a homogeneous analog of the Haber–Bosch process.[27] The real obstacle to this type of application, currently, rests in the low reactivity of the very stable metal–nitrido functional group—*e.g. ca.* 165 kcal mol^{-1} for the $Mo{\equiv}N$ bond in $NMo[N(R)Ar]_3$.[13]

Nitrogen atom transfer

Intermetal nitrogen atom transfer is a reaction type known for less than a decade, and it has the attractive feature of providing a means for breaking a metal–nitrogen triple bond under mild conditions in homogeneous solution.[28] Although such reactions—in which a neutral N atom passes completely from one metal to another with breaking of one $M{\equiv}N$ triple bond and formation of a new one—have been proposed to proceed by μ_2-N atom-bridged intermediate complexes,[29] experimental verification of this has come only recently.[10]

A question one might ask concerns the degree to which the spectator ligands in a nitrido metal complex attenuate the affinity of the metal fragment for the N atom. In an experiment[30] designed to compare alkoxides with anilides, $Mo[N(R)Ar]_3$ was treated with Chisholm's alkoxynitride complex, $NMo(OBu^t)_3$, **17**.[31] Reaction of **4** with **17** [eqn. (6)] led to formation of a blue

$$\underset{\textbf{4}}{Mo[N(R)Ar]_3} + \underset{\textbf{17}}{N{\equiv}Mo(OBu^t)_3} \longrightarrow \underset{\textbf{18}}{(Bu^tO)_3Mo{=}N{=}Mo[N(R)Ar]_3} \qquad (6)$$

intermediate, presumed to be $(Bu^tO)_3Mo(\mu\text{-}N)Mo[N(R)Ar]_3$, **18**.[30] Conducting the reaction in benzene at 25 °C in the absence of N_2 led to formation of nitride **5** along with 0.5 equiv. of the well known metal–metal triple-bonded dimer,[11] $Mo_2(OBu^t)_6$, **19** [eqns. (7) and (8)]. Thus, N-atom transfer was sub-

$$\underset{\textbf{18}}{(Bu^tO)_3Mo{=}N{=}Mo[N(R)Ar]_3} \rightleftharpoons \underset{\textbf{5}}{N{\equiv}Mo[N(R)Ar]_3} + \underset{\textbf{20}}{\text{'}Mo(OBu^t)_3\text{'}} \qquad (7)$$

$$2\ \underset{\textbf{20}}{\text{'}Mo(OBu^t)_3\text{'}} \longrightarrow \underset{\textbf{19}}{(Bu^tO)_3Mo{\equiv}Mo(OBu^t)_3} \qquad (8)$$

stantiated,[30] and the –N(R)Ar-substituted complex demonstrated a greater affinity for the nitrogen atom than the alkoxide-substituted complex. The reaction is interesting in that it provides precedent for synthesis of a metal–metal multiple bond from a metal nitride, and also in that the observation of a blue intermediate [eqn. (6)] suggested that more might be learned about the mechanism of this type of N-atom transfer.[30]

An interesting spin on the N-atom transfer reaction occurred when **4** was treated with alkoxynitride **17** under an atmosphere of N_2 (benzene, 25 °C).[30] Under these conditions, formation of the dimer **19** was nearly shut down, while formation of nitride **5** proceeded smoothly. The very slow reaction of **4** directly with N_2,[9] assessed in control experiments to occur to an extent of $\leqslant$5% per day under these conditions,[30] cannot account for the smooth conversion of **4** to **5** in the presence of **17**, suggesting that **17** catalyzes the splitting of N_2 by **4** [eqn. (9)].[30] This

$$\underset{\mathbf{20}}{\text{'Mo(OBu}^t)_3\text{'}} + \underset{\mathbf{4}}{\text{Mo[N(R)Ar]}_3} \xrightarrow{N_2} \underset{\mathbf{5}}{\text{N}\equiv\text{Mo[N(R)Ar]}_3} + \underset{\mathbf{17}}{\text{N}\equiv\text{Mo(OBu}^t)_3} \quad (9)$$

supposition was substantiated by experiments involving reaction of **4** with **17** under an atmosphere of $^{15}N_2$, which resulted in label incorporation into both the alkoxynitride **17** and **5** isolated after the reaction.[30] A mechanistic scenario accommodating the data involves (i) N-atom transfer to generate **5**, (ii) concomitant formation of some form of ‘$Mo(OBu^t)_3$’, **20**, and N_2 splitting either by **20** alone or *via* a heterodinuclear species such as putative $(Bu^tO)_3Mo(\mu\text{-}N_2)Mo[N(R)Ar]_3$ **21**. Combining the latter three steps provides a plausible mechanism for the observed result, namely that the splitting of N_2 by **4** is accelerated in the presence of alkoxynitride **17**.[30]

In pursuit of more information regarding the putative N-atom bridged complexes in intermetal nitrogen atom transfer reactions, it was elected to treat **4** and analogues with another nitridomolybdenum amide complex, namely $NMo(NMe_2)_3$ **22**.[10] This particular choice was prompted by speculation that an N-atom bridged species might possess greater thermal stability if the two molybdenum fragments involved possess electronically similar ligand sets. Dimethylamide ligands, in addition, were regarded as small enough to permit N-atom transfer. The latter consideration is important in that control experiments[10] showed that no reaction occurs between **4** and $NMo[N(Bu^t)Ph]_3$ **8**, or between **5** and $Mo[N(Bu^t)Ph]_3$ **23**.

A striking teal color was generated upon mixing the three-coordinate complex $Mo[N(R)Ar_{4F}]_3$ (**24**, Ar_{4F} = 4-C_6H_4F) with **22** in toluene or ether [eqn. (10)].[10] The nitride-bridged

$$\underset{\mathbf{24}}{\text{Mo[N(R)Ar}_{4F}]_3} + \underset{\mathbf{22}}{\text{N}\equiv\text{Mo(NMe}_2)_3} \longrightarrow \underset{\mathbf{25}}{(\text{Me}_2\text{N})_3\text{Mo}{=}\text{N}{=}\text{Mo[N(R)Ar}_{4F}]_3} \quad (10)$$

complex $(Me_2N)_3Mo(\mu\text{-}N)Mo[N(R)Ar_{4F}]_3$ **25** was isolated in good yield and characterized by a variety of techniques including X-ray diffraction (Fig. 3).[10] Although the structure was of marginal quality due to dimethylamide disorder, the nitride nitrogen appeared to be situated equidistant from the two dissimilarly ligated Mo centers.

Although this particular μ-nitride species (**25**) seemed relatively robust, a more fragile analog was generated by treatment of **22** with the ‘parent’ complex **23** [eqn. (11)].[10] Thus

$$\underset{\mathbf{23}}{\text{Mo[N(Bu}^t)\text{Ph]}_3} + \underset{\mathbf{22}}{\text{N}\equiv\text{Mo(NMe}_2)_3} \longrightarrow \underset{\mathbf{27}}{(\text{Me}_2\text{N})_3\text{Mo}{=}\text{N}{=}\text{Mo[N(Bu}^t)\text{Ph]}_3} \quad (11)$$

was derived a suitable synthesis of the symmetrical μ-nitride complex $(\mu\text{-}N)[Mo(NMe_2)_3]_2$ **26**, by treatment of **23** with 2 equiv. of **22**. The notion is that the unsymmetrical ligated μ-nitride complex $(Me_2N)_3Mo(\mu\text{-}N)Mo[N(Bu^t)Ph]_3$ **27** is thermally unstable, and serves as a source of ‘$Mo(NMe_2)_3$’ **28** under the reaction conditions [eqn. (12)]. Trapping of **28** by the second

$$\underset{\mathbf{27}}{(\text{Me}_2\text{N})_3\text{Mo}{=}\text{N}{=}\text{Mo[N(Bu}^t)\text{Ph]}_3} \rightleftharpoons \underset{\mathbf{28}}{\text{'Mo(NMe}_2)_3\text{'}} + \underset{\mathbf{22}}{\text{N}\equiv\text{Mo[N(Bu}^t)\text{Ph]}_3} \quad (12)$$

equiv. of **22** provides the symmetrically substituted nitride derivative, nitridodimolybdenum–hexadimethylamide [**26**, eqn. (13)]. Using this procedure, thermally sensitive **26** could be

$$\underset{\mathbf{28}}{\text{'Mo(NMe}_2)_3\text{'}} + \underset{\mathbf{22}}{\text{N}\equiv\text{Mo(NMe}_2)_3} \rightleftharpoons \underset{\mathbf{26}}{(\text{Me}_2\text{N})_3\text{Mo}{=}\text{N}{=}\text{Mo(NMe}_2)_3} \quad (13)$$

isolated in pure form by fractional crystallization, and was characterized by X-ray crystallography (Fig. 4). The μ-N atom in **26** resides at a crystallographic center of inversion, with a Mo–N distance of 1.7990(8) Å. This distance is consistent with an Mo–N double bond,[10] the Mo≡N distance in **8** being 1.658(5) Å.[9] A molecular-orbital description of **26** also suggests a bond order of two between both molybdenum atoms and the bridging nitride ligand, the highest-lying three electrons being in a π-symmetry molecular orbital that possesses a node at the bridging nitrogen atom. A compound fascinating in its simplicity, **26** is related to the well known dimer $Mo_2(NMe_2)_6$ **29**[11] by formal insertion of a neutral nitrogen atom into the metal–metal triple bond. Indeed, thermal decomposition of **26** gives rise to a mixture of **22** and **29**.[10]

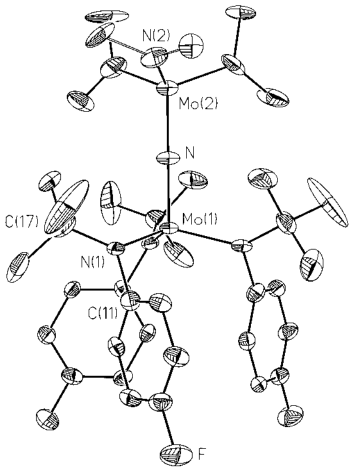

Fig. 3 Thermal ellipsoid representation of $(Me_2N)_3Mo(\mu\text{-}N)Mo[N(R)Ar_{4F}]_3$ **25**, from an X-ray study.[10] The Mo–N–Mo axis resides on a crystallographic threefold axis; the resulting NMe_2 disorder is not shown. Ellipsoids are at the 35% probability level. The Mo(1)=N bond length is 1.82(4) Å, while the Mo(2)=N bond length is 1.83(4) Å.

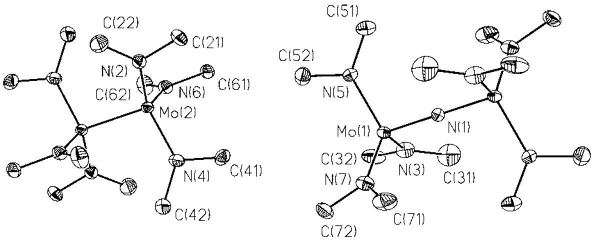

Fig. 4 Thermal ellipsoid representation of $(\mu\text{-}N)[Mo(NMe_2)_3]_2$ **26** and $Mo_2(NMe_2)_6$ **29**, from an X-ray study in which the two occurred together in a 1:1 cocrystal.[10] Ellipsoids are at the 35% probability level. The Mo(1)=N(1) bond length is 1.7990(8) Å, while the Mo(1)–N(5) bond length is 1.953(8) Å.

The molybdenum systems described in this section do much to augment our knowledge of intermetal N-atom transfer reactions. Importantly, as earlier surmised[29] it is now established[10] that N-atom bridged species play an important role as intermediates in the transfer process. Some of the mixed-valence N-atom bridged species have been isolated, such that much can be expected to be gained from a study of their physical properties, decomposition kinetics, and other reaction chemistry. An intriguing aspect of the chemistry is that sources of the reactive, sterically-unhindered fragments ‘$Mo(OBu^t)_3$’ **20**[30] and ‘$Mo(NMe_2)_3$’ **28**[10] are available *via* N-atom transfer chemistry. Now that N-atom abstractors such as **4** are readily prepared, it is likely that other synthetic applications of N-atom transfer chemistry will result.

Molybdenum–phosphorus chemistry: establishment of the terminal phosphide ($M\equiv P$) functionality

The chemistry in this section stemmed from a desire to explore in broad terms the reactivity of **4** and related three-coordinate molybdenum compounds. Having learned about the pronounced stability of the $Mo\equiv N$ triple bond in **5**,[9] it was of interest to see if the analogy could be pushed to phosphorus, an endeavor which if successful would lead to an unknown functional group: the terminal phosphide, $M\equiv P$.[32] As described below, it is indeed possible to draw several analogies between the molybdenum–nitrogen and the molybdenum–phosphorus chemistries.

Activation of white phosphorus

White phosphorus, consisting of tetrahedral P_4 molecules, is the most abundant form of elemental phosphorus.[33] The majority of its transition-metal mediated reactions involve metal carbonyl fragments and cluster chemistry.[34] The closest precedent for the reaction of a three-coordinate molybdenum compound with white phosphorus comes, as so many good things do, from the labs of Malcolm Chisholm. Thus, the dimethylamine adduct of the tungsten dimer $W_2(OCH_2Bu^t)_6$ **30** was treated with P_4 in an attempt to prepare the $W\equiv P$ functional group.[35] What was obtained instead is the interesting complex, $(\eta^3\text{-}P_3)W(OCH_2Bu^t)_3(HNM_2)$, **31**.[35] The latter can be understood as a P_4 molecule with one vertex replaced by the isolobal tungsten tris-alkoxide fragment.[36]

In contrast to Chisholm's tungsten chemistry, three-coordinate **4** reacts smoothly with P_4 in toluene at 25 °C to afford the desired terminal phosphide derivative $P\equiv Mo[N(R)Ar]_3$ **32**, [eqn. (14)].[37] The analog stemming from reaction of 'parent'

$$\underset{\mathbf{4}}{Mo[N(R)Ar]_3} \xrightarrow{P_4} \underset{\mathbf{32}}{P\equiv Mo[N(R)Ar]_3} \qquad (14)$$

$Mo[N(Bu^t)Ph]_3$ **23** with P_4, namely $PMo[N(Bu^t)Ph]_3$ **33**, was prepared similarly,[10] and both have been characterized by X-ray diffraction. Compounds **32** and **33** are diamagnetic yellow–gold crystalline solids that dissolve readily in standard organic solvents. They, like their three-coordinate precursors, are readily prepared on 5–10 g scales.

A most intriguing feature of the NMR spectra of the terminal phosphide compounds is that their ^{31}P signal appears downfield of 1200 ppm! The latter phenomenon has been studied in detail by solid-state NMR techniques, and by computational methods.[38] The enormous downfield isotropic signal is interpreted[38] as arising from an unusually large chemical shift anisotropy in the system, consonant with field-induced mixing of the ground state with a paramagnetic excited state. The excited state in question is thought to involve promotion of electron density from an M–P σ bonding orbital into an orbital that is M–P π^* in character.[38]

Structurally, phosphide compounds **32** and **33** are similar to nitride **8**, and the respective $Mo\equiv P$ bond distances 2.119(4) and 2.111(2) Å are of interest (Fig. 5). Triple-bond covalent radii can be estimated for both Mo and P using the reference compounds P_2 and $Mo_2(NMe_2)_6$, giving the prediction of 2.055 Å for an $Mo\equiv P$ triple bond.[37] Agreement with the experimental values is seen to be quite close.

Triamidoamine-supported[39] molybdenum and tungsten phosphide complexes $PMo(Me_3SiNCH_2CH_2)_3N$ **34** and $PW(Me_3SiNCH_2CH_2)_3N$ **35** were reported close on the heels[40] of **32**; **35** exhibited a $W\equiv P$ distance of 2.162(4) Å, with an interesting added twist that the tungsten–phosphorus coupling constant had an unanticipated low value of 138 Hz. Organophosphide and phosphinidene complexes of tungsten exhibit much larger values of J_{WP}.[40] The data may be taken as an indication that the phosphorus 3s orbital participates little in the tungsten–phosphorus bonding, but rather accommodates a rather low-lying lone pair of electrons. Interestingly, compounds **35** and **34** were prepared not *via* a reaction with elemental phosphorus, but rather through treatment of precursor chloro complexes with Li[P(H)Ph] in what must involve a complex sequence of steps.[40] Such methodology was later successful for the preparation of the corresponding terminal arsenide complexes, $As\equiv M(Me_3SiNCH_2CH_2)_3N$ (M = Mo **36**, W **37**), which have been the subject of a force-constant study.[41]

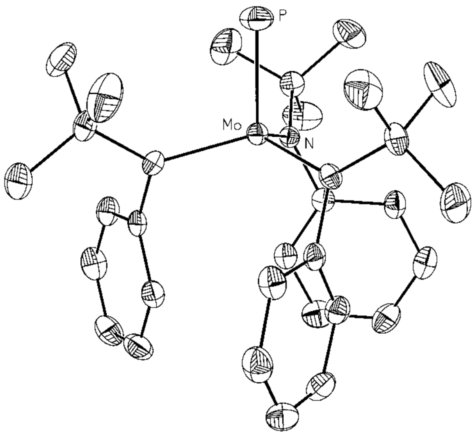

Fig. 5 Thermal ellipsoid representation of $P\equiv Mo[N(Bu^t)Ph]_3$ **33**, from an X-ray study.[10] The P–Mo bond is coincident with a crystallographic threefold axis. Ellipsoids are at the 35% probability level. The $Mo\equiv P$ bond length is 2.111(2) Å, while the Mo–N bond length is 1.973(2) Å.

Reactions of terminal phosphide complexes with oxo, sulfur atom, and nitrene donors

First off it should be stated that like nitride **5**, phosphide **32** is not an exceptionally reactive compound. In part, the low reactivity of **32** toward certain reagents (including benzonitrile, benzaldehyde and methyl iodide) can be ascribed to the substantial steric shielding of the $M\equiv P$ triple bond by *tert*-butyl groups. However, phosphide **32** does undergo some reactions involving addition of a terminal substituent to the phosphorus atom, especially in cases where a cumulene-like moiety Mo=P=X (X = O,[42] S[37] or NMes[37]) with a delocalized π system can arise.

Sulfur atom transfer to the terminal phosphide

The so-called PS complex, $S{=}P{=}Mo[N(R)Ar]_3$ **38** was prepared either in 62% yield in a slow reaction of **32** with elemental sulfur [43 h, OEt_2, 25 °C, eqn. (15)], or in 50% yield in a rapid reaction with ethylene sulfide [1.5 h, OEt_2, 25 °C, eqn. (16)].[37]

$$\underset{\mathbf{32}}{P\equiv Mo[N(R)Ar]_3} \xrightarrow{1/8\ S_8} \underset{\mathbf{38}}{S{=}P{=}Mo[N(R)Ar]_3} \qquad (15)$$

$$\underset{\mathbf{32}}{P\equiv Mo[N(R)Ar]_3} \xrightarrow{SC_2H_4} \underset{\mathbf{38}}{S{=}P{=}Mo[N(R)Ar]_3} \qquad (16)$$

The purple–red compound exhibits a ^{31}P NMR signal at δ 383, a dramatic upfield shift relative to phosphide **32**. That **38** exists as discrete monomeric units in the solid state was verified by X-ray crystallography (Fig. 6).[42] The Mo–P and P–S bond lengths are respectively 2.100(2) and 1.921(3) Å, and the angle at P is linear. It is a striking observation that the Mo–P distance is not significantly different than in the terminal phosphide species. Since the P–S distance is similar to what has been found for phosphine sulfides, perhaps the best valence-bond description of the 'PS' complex is, in fact, $S\text{–}P\equiv Mo[N(R)Ar]_3$, with appropriate formal charges: positive on P and negative on S. An important point to take into consideration in any analysis of the bonding in the PS complex **38** relative to phosphide **32** is that in the former the phosphorus 3s orbital is necessarily utilized in the σ framework, while in the latter all indications[38] are that it does not participate in the bonding.

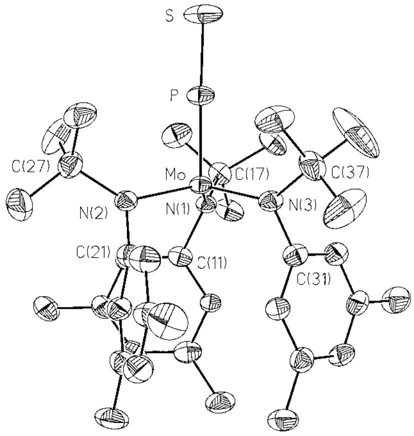

Fig. 6 Thermal ellipsoid representation of SPMo[N(R)Ar]$_3$ **38**, from an X-ray study,[42] Ellipsoids are at the 35% probability level. The P=S bond length is 1.921(3) Å, while the Mo=P bond length is 2.100(2) Å.

Although the importance of the S=P=Mo[N(R)Ar]$_3$ resonance structure for **38** has not yet been substantiated chemically, the S–P$\equiv$Mo[(R)Ar]$_3$ structure being favored by crystallographic data,[42] some support for the former structure comes from reactivity studies on the corresponding oxo derivative.[42] Before leaving the PS complex, however, it should be noted that formation of **38** by sequential addition of the elements phosphorus and sulfur to three-coordinate **4** represents an exceedingly satisfying and simple synthesis of a previously unknown type of cumulene.

Oxo transfer to the terminal phosphide

Underscoring the relatively unreactive nature of **32**, early attempts to synthesize the 'PO' complex, O=P=Mo[N(R)Ar]$_3$ **39** resulted in no reaction. Reagents employed unsuccessfully include pyridine- and trimethylamine-*N*-oxides and dry oxygen. The harsh and hydrocarbon-insoluble oxidant iodosylbenzene was also treated with **32**, but the reaction resulted in extensive decomposition. Dimethyldioxirane (Me_2CO_2) is a powerful, thermally unstable, hydrocarbon-soluble oxidant that is typically used as 5% solutions in acetone.[43] Treatment of phosphide **32** with the Me_2CO_2 ultimately proved a successful route to the PO complex **39**.[42]

Accordingly, treatment of a gold dichloromethane solution of **32** at -78 °C with the stoichiometric amount of Me_2CO_2 gave rise to an intense purple color [eqn. (17)].[42] It proved necessary to precipitate PO **39** from the reaction mixture by addition of cold acetonitrile. Once pure, the purple, diamagnetic [$\delta(^{31}P)$ 269.8] **39** can be manipulated at 25 °C with minimal decomposition. The most common problem encountered in handling **39** is that, under a variety of conditions, phosphide **32** is regenerated from it.

$$\underset{\mathbf{32}}{P{\equiv}Mo[N(R)Ar]_3} + O_2CMe_2 \longrightarrow \underset{\mathbf{39}}{O{=}P{=}Mo[N(R)Ar]_3} + OCMe_2 \qquad (17)$$

X-Ray crystallography showed PO **39** to possess an essentially linear angle at P [177.6(8)°], and Mo–P and P–O distances of 2.079(5) and 1.49(2) Å, respectively.[42] Thus, like the phosphorus monosulfide complex **38**, PO **39** exhibits a shorter Mo$\equiv$P distance than phosphide **32**! This can indeed be taken as evidence that the O–P$\equiv$[N(R)Ar]$_3$ resonance structure is an important contributor, with appropriate formal charges. The P–O distance is essentially the same as for free phosphorus monoxide,[44] tricyclohexylphosphine oxide[45] and some μ_3-PO complexes in clusters.[46]

Some evidence lending credence to the O=P=Mo[N(R)Ar]$_3$ resonance structure for **39** is available in the form of reaction chemistry.[42] This resonance structure is reminiscent of the resonance structure, O=C=ML$_n$, invoked for metal carbonyls in describing the classic Fischer carbene synthesis.[47] Thus can be seen the analogy to organic carbonyls, and the fact that nucleophiles add to the complexed CO carbon understood. Likewise, the zirconocene reagent Cp_2ZrMe_2, which possesses nucleophilic methyl groups in conjunction with an oxophilic metal center, reacts with PO **39** with formation of a phosphorus–carbon and a zirconium–oxygen bond.[42] The product, **40**, is the result of insertion of the PO moiety into the Zr–Me bond. Compound **40** is orange–brown and diamagnetic, and structurally can be deemed analogous to Mo(NMe$_2$)$_4$[48] or Mo[P(Cyclohexyl)$_2$]$_4$.[49] The Mo–P and P–O bonds in **40** are 2.169(2) and 1.613(5) Å, such that multiple bonding between molybdenum and the trigonal-planar phosphorus center can be invoked.[42] Also, an analogy can be extended to relate compound **40**, with its Zr–O–P–Mo moiety, to 'zirconoxy carbenes' prepared by reaction of zirconocene derivatives with metal carbonyl complexes.[50]

Thus was the first complex containing a terminal PO, or phosphorus monoxide, ligand prepared and characterized.[42] Previous examples of complexes containing PO ligands have involved oxidation of bridging phosphide ligands in multimetallic clusters.[46] The PO molecule has garnered attention as a free species, due to its presence in interstellar space, and as a heavy analog of nitric oxide.[51] It will certainly be of interest to determine the extent of the chemistry of PO as a ligand in coordination chemistry, especially given the analogy with NO. Although information concerning the P–O bond strength in **39** is not yet available, preliminary results show that the complex is readily deoxygenated by triethylphosphine.

Reaction of **32** *with an aryl azide*

In some respects, the reactivity patterns of phosphide **32** are reminiscent of an electron-poor triogranophosphine. One reaction characteristic of triorganophosphines is that with organoazides to produce phosphinimines, a reaction known as the Staudinger reaction.[52] Seeking to push the analogy between **32** and PR$_3$ compounds, **32** was treated in ether with mesityl azide at 25 °C over a period of *ca.* 22 h [eqn. (18)].[37] The reaction afforded a diamagnetic blue–green product, which turned out to be (MesNP)Mo[N(R)Ar]$_3$ **41**, the product of a Staudinger-like addition of mesitylazide to **32** with loss of dinitrogen. The compound displays a single –N(R)Ar ligand environment according to room-temperature proton and carbon NMR spectroscopies.[37]

$$\underset{\mathbf{32}}{P{\equiv}Mo[N(R)Ar]_3} + N_3Mes \xrightarrow{-N_2} \underset{\mathbf{41}}{MesN{=}P{=}Mo[N(R)Ar]_3} \qquad (18)$$

X-Ray crystallography showed **41** to possess an essentially linear Mo–P–N angle,[37] and confirmed the molecular connectivity. Interestingly, **41** is a unique phosphorus-monosubstituted aryldiazonium complex; the related 'iminophosphenium' cation [PNAr*]$^+$ (Ar* = 2,4,6-$C_6H_2Bu^t_3$) is known as a discrete species, having been isolated and characterized as its tetrachloroaluminate salt.[53]

Thus was the reactivity of phosphide **32** confirmed to be related, at least to a degree, to that characteristic of triorganophosphines. It is interesting that, to date, the reactivity of terminal phosphide complexes M$\equiv$P is restricted to the addition of groups to the P terminus. No reactions have yet been identified in which the M$\equiv$P triple bond engages in cycloaddition reactions, despite the fact that such reactions are prevalent for closely related high-valent terminal phosphinidene complexes.[54] Further developments can be expected for phosphide complexes in this regard, especially if they can be generated in conjunction with a less sterically demanding ancillary ligand coordination sphere.

One-coordinate carbon multiply-bonded to molybdenum: the terminal carbide functionality

Having found that the $\mathrm{Mo[N(R)Ar]_3}$ fragment is well suited as a platform for the construction of molybdenum–element multiple bonds, it was only natural to turn attention to some questions in the organometallic genre. A specific question of interest had to do with whether a carbide complex anion, *e.g.* $^{-}\mathrm{[C{\equiv}Mo\{N(R)Ar\}_3]}$ **42**, isoelectronic to nitride **5**, could be accessed. Indeed, one-coordinate carbon was known previously only in, for example, carbon monoxide, isocyanides and cyanide ion. The functional group constituted by one-coordinate carbon bonded only to a single metal center was unknown.

To follow the chemistry it was deemed worthwhile to utilize a ^{13}C label for the carbon in question. This was made feasible by the observation that $\mathrm{Mo[N(R)Ar]_3}$ **4** readily binds carbon monoxide in an irreversible fashion.[55] Thus, carbonyl $\mathrm{(O^{13}C)Mo[N(R)Ar]_3}$ **43** was obtained in 88% yield as a brown paramagnetic species [eqn. (19)].[55] Magnetic susceptibility measurements were consistent with assignment of carbonyl **43** as a low-spin complex of molybdenum(III), an IR band at 1797 cm^{-1} was attributed to ν_{CO} for complex **43**, and the ^{2}H NMR spectrum of **43** revealed a single –N(R)Ar ligand environment.[55]

$$\underset{\mathbf{4}}{\mathrm{Mo[N(R)Ar]_3}} \xrightarrow{\mathrm{CO}} \underset{\mathbf{43}}{\mathrm{OCMo[N(R)Ar]_3}} \qquad (19)$$

Now the problem remained of turning the carbonyl oxygen into a leaving group. A strategy was adopted whereby complex **43** would be (i) reduced to its corresponding anion and (ii) treated with a suitable electrophile. In practice it was observed that treatment of **43** with an excess of sodium amalgam in THF provided the desired anion [**44**, eqn. (20)] which is diamagnetic and can be written with a molybdenum–carbon triple bond as in $^{-}\mathrm{[O{-}C{\equiv}Mo\{N(R)Ar\}_3]}$. The hope was that anion **44** would behave as a nucleophile in a manner analogous to an alkoxide ion. Although **44** could be isolated as its sodium salt, it was simply generated *in situ* for treatment with electrophiles. Pivalyl chloride was identifed as a suitable electrophile and, accordingly, the neutral diamagnetic 'carbido pivalate' complex $\mathrm{Bu^tC(O)O{-}^{13}C{\equiv}Mo[N(R)Ar]_3}$ **45**, was obtained in 82% yield as a beige solid, and was fully characterized [eqn. (21)].[55]

$$\underset{\mathbf{43}}{\mathrm{OCMo[N(R)Ar]_3}} \xrightarrow{\mathrm{Na/Hg}} \underset{\mathrm{Na}[\mathbf{44}]}{\mathrm{Na^+[^-O{-}C{\equiv}Mo\{N(R)Ar\}_3]}} \qquad (20)$$

$$\underset{\mathrm{Na}[\mathbf{44}]}{\mathrm{Na^+[^-O{-}C{\equiv}Mo\{N(R)Ar\}_3]}} + \mathrm{Bu^tC(O)Cl} \xrightarrow{-\mathrm{NaCl}} \underset{\mathbf{45}}{\mathrm{Bu^tC(O)O{-}C{\equiv}Mo[N(R)Ar]_3}} \qquad (21)$$

But for the great stability of the $\mathrm{{-}C{\equiv}Mo[N(R)Ar]_3}$ core under reductive conditions, the synthesis might have reached a dead end with compound **45**. It was hoped that the pivalate moiety would be removed under reductive conditions, with the desired carbide anion $^{-}\mathrm{[C{\equiv}Mo\{N(R)Ar\}_3]}$ **42** perhaps to be obtained directly. Although the situation did not prove to be so simple, it was indeed the case that reductive conditions resulted in removal of the $\mathrm{{-}O_2CBu^t}$ group, albeit less than quantitatively. Subjection of **45** to an excess of solid sodium mirror in THF led [eqn. (22)], according to ^{13}C NMR monitoring, to production of a mixture containing the desired 'sodium carbide' (Na[**42**], identified tentatively as several peaks in the vicinity of δ 500), methylidyne $\mathrm{HC{\equiv}Mo[N(R)Ar]_3}$ **46**, and the carbonyl anion **44**.

$$\underset{\mathbf{45}}{\mathrm{Bu^tC(O)O{-}C{\equiv}Mo[N(R)Ar]_3}} \xrightarrow{\mathrm{i\ Na^0,\ ii\ MeCN}} \underset{\mathbf{46}}{\mathrm{HC{\equiv}Mo[N(R)Ar]_3}} \qquad (22)$$

Given the complexity of the mixture, it was opted to attempt protonation of **42** to methylidyne **46**, and to attempt separation of the latter from the salt of **44**. Fortunately, addition of the crude mixture to acetonitrile was found to effect the desired transformation. Being relatively insoluble in acetonitrile, methylidyne **46** was easily separated from the soluble salt of **44**. The isolated yield of **46** was 53%, based on the neutral carbonyl precursor **43**.[55] Methylidyne **46** has a characteristic ^{13}C NMR peak at δ 287, accompanied by a J_{CH} of 157 Hz. A recent single-crystal X-ray diffraction study shows **46** to be a pseudo-threefold symmetric species with an Mo≡C triple bond distance of 1.699(5) Å.

Now the task at hand was to deprotonate **46** and to isolate **42** as a salt with a large cation, this in order to sequester a version of **42** having one-coordinate carbon. Given the interpretation that the preceding chemistry had relied upon deprotonation of acetonitrile by **42**, it was evident that a strong base would be required for deprotonation of methylidyne **46**. Benzylpotassium[56] was chosen, as it can conveniently be weighed out as a solid and because potassium, being a heavier alkali metal, should exhibit a decreased tendency to coordinate to a carbanion (compared with Li or Na), especially if complexed with a suitable crown ether or cryptand complement. Reaction in THF of methylidyne **46** with K(benzyl) led, as desired [eqn. (23)], to production of the potassium salt of carbide **42**, isolated in 69% yield as a solvent-free dimer (X-ray, Fig. 7). In $\mathrm{C_6D_6}$, where K[**42**] presumably retains its dimeric structure, a single sharp ^{13}C signal is observed for the carbide carbon at δ 494.5. A closer look (X-ray) at the structure of dimeric K[**42**] reveals a central $\mathrm{K_2C_2}$ square, with the coordination at K complemented by π complexation of two –N(R)Ar aryl groups per potassium. The structure thus incorporates encapsulation of the potassium cations by lipophilic residues, accounting for the observed good solubility of the compound in $\mathrm{C_6D_6}$, and also for the lack of retention of THF.

$$\underset{\mathbf{46}}{\mathrm{HC{\equiv}Mo[N(R)Ar]_3}} + \mathrm{K(benzyl)} \xrightarrow{-\mathrm{toluene}} \underset{\mathrm{K}[\mathbf{42}]}{\mathrm{K^+[^-C{\equiv}Mo\{N(R)Ar\}_3]}} \qquad (23)$$

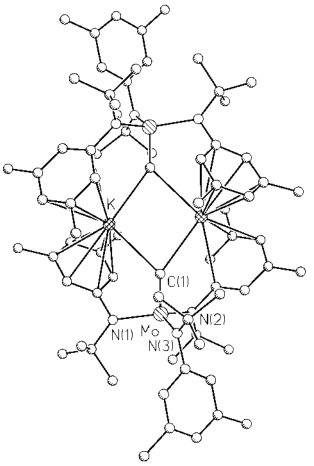

Fig. 7 Ball and stick representation of dimeric potassium carbide $\mathrm{K_2[42]_2}$, from an X-ray study.[55] A crystallographic center of inversion is located at the center of the dimer. The C(1)≡Mo distance is 1.68(3) Å, while the K···C distance is 2.94(2) Å.

Encapsulation of the potassium was achieved in two ways;[55] addition of cryptofix-2,2,2 to a solution of K[**42**] gave [K(2,2,2-crypt)][**42**] [eqn. (24)], whereas when K[**42**] was treated with 2 equiv. of benzo-15-crown-5, the salt [K(benzo-15-crown-5)$_2$][**42**] was produced [eqn. (25)]. Both salts exhi-

$$\underset{\mathrm{K}[\mathbf{42}]}{\mathrm{K^+[^-C{\equiv}Mo\{N(R)Ar\}_3]}} \xrightarrow{\text{2,2,2-crypt}} \underset{[\mathrm{K(2,2,2\text{-}crypt)}][\mathbf{42}]}{\mathrm{[K(2,2,2\text{-}crypt)^+][^-C{\equiv}Mo\{N(R)Ar\}_3]}} \qquad (24)$$

$$\underset{\mathbf{K[42]}}{\mathrm{K^+[^-C{\equiv}Mo\{N(R)Ar\}_3]}} \xrightarrow{\text{benzo-15-crown-5}} \underset{\mathbf{[K(benzo\text{-}15\text{-}crown\text{-}5)_2][42]}}{\mathrm{[K(benzo\text{-}15\text{-}crown\text{-}5)_2{}^+][^-C{\equiv}Mo\{N(R)Ar\}_3]}} \quad (25)$$

bited low benzene solubility, in contrast to the dimeric precursor K[**42**], suggesting that the new salts consisted of discrete anions and cations. Remarked upon initially as a curious observation was the fact that the carbide ^{13}C signal (THF) for the new salts was rather broad.[55] Thanks in part to a suggestion from Professor Klaus H. Theopold, it has been determined that proton exchange between methylidyne **46** and its conjugate base takes place on the NMR timescale, with rate parameters such that a small percentage of **46** is sufficient to broaden substantially the carbide ^{13}C signal. For [K(2,2,2-crypt)][**42**], the ^{13}C signal in question was reported as δ 482.8, but this parameter is sensitive, of course, to the presence of small quantities of **46**. It is now known that addition of K(benzyl) to a THF solution of [K(2,2,2-crypt)][**42**] results in dramatic sharpening of the carbide ^{13}C signal, presumably due to removal of trace quantities of methylidyne **46**.

X-Ray crystallographic confirmation of the presence of Mo-bound one-coordinate carbon was obtained with the structure of [K(benzo-15-c-5)$_2$][**42**], which exhibits discrete and separate cations and anions (Fig. 8).[55] An interesting metrical parameter is the Mo≡C distance to the carbido carbon, 1.713(9) Å, which is not significantly different from the corresponding value found for methylidyne **46**. Also noteworthy is the fact that anion **42** displays conformational features very similar to those (described above) for the isoelectronic nitride **5**.[9]

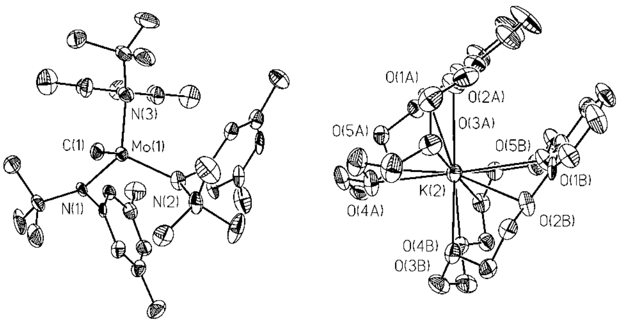

Fig. 8 Thermal ellipsoid representation of carbide salt [K(benzo-15-crown-5)$_2$][**42**], from an X-ray study.[55] The Mo≡C distance is 1.713(9) Å.

Thus was established one-coordinate carbon as a viable functional group in organometallic chemistry.[55] It is interesting to reflect on the circuitous nature of the compound's synthesis, the carbide carbon arising from carbon monoxide.[57] Much remains to be elucidated with regard to terminal carbide reactivity, and with respect to the issue of synthesis of neutral or even cationic variants. In the present case, anion **42** displays a marked downfield shift for its carbido carbon nucleus, a circumstance likely arising from a large ^{13}C chemical shift anisotropy.[38] More detailed studies should shed light on this interesting finding, in conjunction with information on the M≡C bonding in this unusual species.

Terminal oxo, sulfide, selenide and telluride complexes

In the preceding sections we have seen that Mo[N(R)Ar]$_3$ **4** offers ready synthetic inroads to triple bonds involving Mo and C,[55] N[9] or P.[37] Also, several complexes of the sort Y=X=Mo[N(R)Ar]$_3$ were described (*e.g.* YX = OP **39**,[42] SP **38**,[42] MesNP **41**[37] and ON **11**[8]) which all are linear cylindrically symmetric 8π systems analogous to CO$_2$ or N$_2$O, and thus anticipated to be rather stable. Thus, the triple bonds and the 8π systems can be regarded as the 'sinks' in the chemistry of Mo[N(R)Ar]$_3$ **4**. Especially intriguing in this regard is the observation that the reaction of **4** with N$_2$O led to exclusive N–N bond cleavage, rather than to formation of the putative oxo species, O=Mo[N(R)Ar]$_3$ **12**.[8] The latter result runs completely counter to the known chemistry of nitrous oxide, a molecule that prefers to act as an oxo source with liberation of N$_2$.[18] Our interest piqued by these observations, we set out to prepare oxo **12** by an alternate route. When this endeavor was successful, a further course of action was undertaken involving synthesis of the heavier congeners of **12**, namely E=Mo[N(R)Ar]$_3$ (E = S **47**, Se **48** and Te **49**).[58]

The synthesis of the paramagnetic, chocolate-brown oxomolybdenum(v) complex **12** proved to be straightforward, involving addition of pyridine-*N*-oxide to an ethereal solution of **4**.[20] Such a procedure [eqn. (26)] led to isolation of **12** in 72% yield. Characterization of **12** included EPR spectroscopy, magnetic susceptibility measurements, ^{2}H NMR spectroscopy, and X-ray crystallography.[20]

$$\underset{\mathbf{4}}{\mathrm{Mo[N(R)Ar]_3}} + \mathrm{O{\leftarrow}NC_5H_5} \xrightarrow{-\text{pyridine}} \underset{\mathbf{12}}{\mathrm{O{=}Mo[N(R)Ar]_3}} \quad (26)$$

The structure of monomeric **12** is significant in being of low symmetry relative to its threefold symmetric relatives, of which nitride **5** is representative.[9] The low symmetry of **12** arises from three disparate O–Mo–N–C$_{tert}$ dihedral angles: 40, 3 and 62°;[20] a typical value for threefold symmetric analogues being 35°. Electronic structure arguments indicate that the low symmetry of **12** (and its heavier congeners, described below) is a consequence of the d^1 electron configuration. The unpaired electron resides, according to calculations, in an orbital that has π^* character with respect to the Mo=O multiple bond. Since there are two such orbitals, but only one electron to populate them, the complex is subject to a Jahn–Teller distortion involving the disposition of the –N(R)Ar ligands. The latter adopt an orientation that minimizes repulsive interactions between the unpaired electron and the Mo–N π bonds. The heavier chalcogenide complexes **47**, **48** and **49**, which have less ionic character to their Mo=E bonds than in the case of oxo complex **12**, likewise exhibit low-symmetry structures, but these are C_s as opposed to the case for **12**, which in the solid state has C_1 symmetry. Despite the low symmetry of all the E=Mo[N(R)Ar]$_3$ complexes, in solution they are fluxional as judged by their ^{2}H NMR spectra, which show but a single signal at 25 °C.[20]

Whereas the oxo compound **12** was not amenable to preparation by the direct reaction of Mo[N(R)Ar]$_3$ **4** with dioxygen, the heavier chalcogenide derivatives all could be prepared by interaction of **4** with the respective elemental chalcogen.[20] Thus, S=Mo[N(R)Ar]$_3$ **47** was obtained in 63% yield subsequent to treatment of **4** with S$_8$ [eqn. (27)]. Reaction of **4** with elemental selenium gave Se=Mo[N(R)Ar]$_3$ **48** in 80% yield after 11 h in ether at 25 °C. Elemental tellurium reacted only sluggishly with **4**, such that catalytic PEt$_3$ was employed, to catalyze the reaction *via* the phosphine telluride. The result was the isolation in 73% yield of Te=Mo[N(R)Ar]$_3$ **49**, as a dark brown solid. Characterization of the molybdenum(v) chalogenide complexes by EPR spectroscopy provided increasingly well resolved rhombic spectra on going from E = O to E = Te. Density functional calculations indicated that the covalent character of the Mo=E bond increased as O ≪ S < Se < Te. The Mo=E bond lengths, as determined by X-ray crystallography are E = O, 1.706(2); S, 2.1677(12); Se, 2.3115(6) and Te, 2.5353(6) Å (see Fig. 9 for a representative drawing of telluride **49**).[20]

$$\underset{\mathbf{4}}{\mathrm{Mo[N(R)Ar]_3}} + \underset{\mathrm{E\,=\,S,\ Se\ or\ Te/PEt_3}}{1/n\,\mathrm{E}_n} \longrightarrow \underset{\mathrm{E\,=\,S}\ \mathbf{47},\ \mathrm{Se}\ \mathbf{48},\ \mathrm{Te}\ \mathbf{49}}{\mathrm{E{=}Mo[N(R)Ar]_3}} \quad (27)$$

A very telling set of experiments involved thermochemical measurements made on reactions that lead to oxo **12** and sulfide **47**.[20] For instance, the heat of reaction of **4** with pyridine-*N*-oxide was measured, permitting estimation of the bond dissociation enthalpy *D*(MoO) as 155.6 ± 1.6 kcal mol^{-1}. This

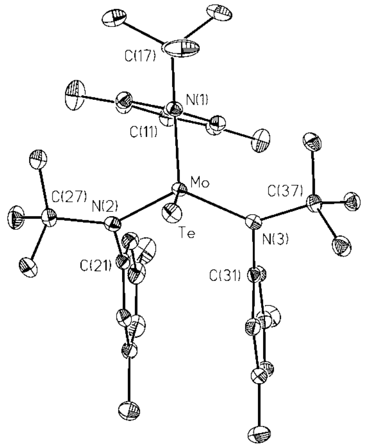

Fig. 9 35% probability level thermal ellipsoid representation of terminal telluride **49**, from an X-ray study.[20] The Te=Mo bond length is 2.5353(6) Å. Reproduced with permission from *J. Am. Chem. Soc.*

measurement indicates that **12** possesses one of the strongest metal–oxo bonds known,[59] and carries the corollary that the result of N_2O reaction with **4** is not a consequence of any thermodynamic bias.[19] Although there is a paucity of data for terminal metal–sulfur bond strengths in the literature, a *D*(MoS) of 104.4 ± 1.2 kcal mol^{-1} was obtained for **47** from measurement of the heat of reaction of ethylene sulfide with **4**.[20] The latter is an alternative method for preparing **47**, an example of thiirane desulfurization.[60] Although experimental data are not available for the selenide– and telluride–molybdenum bond dissociation enthalpies, density functional theoretical methods predict values of 91 and 71 kcal mol^{-1}, respectively, for **48** and **49**.[20]

Molecular orbital calculations performed for sulfide **47**, as for the other chalcogenide complexes, indicate the SOMO (singly occupied molecular orbital) to be largely Mo–E π^* in character. The SOMO is high-lying relative to the highest-lying doubly occupied level, additionally, such that the complexes should be regarded as one-electron reductants.[20] This behavior is manifested both in terms of intermolecular and intramolecular redox chemistry. An example of the former is the ferrocenium triflate or iodine oxidation of **12** to provide salts of the $[O{\equiv}Mo\{N(R)Ar\}_3]^+$ cation. Chalcogenide complexes **12**, **47**, **48** and **49** are all thermally sensitive, with Bu^t radical elimination from the –N(R)Ar ligands occurring at elevated temperatures. Thermolysis (60–80 °C, 5–25 h) of the Mo=E complexes accordingly led to first-order decay, with the products being a new series of diamagnetic molybdenum(VI) chalcogenide complexes, E=Mo(=NAr)$[N(R)Ar]_2$ (E = O **50**, S **51**, Se **52**, Te **53**). The thermal instability of **12** and its heavier molybdenum(V) congeners contrasts sharply with the thermally robust nature of nitride **5**[9] and phosphide **32**.[37] such that although the chalcogenide complexes[20] are isolable and could be characterized, they do not represent 'sinks' in the chemistry of $Mo[N(R)Ar]_3$ **4**.

Concluding remarks

The isolation and characterization of three-coordinate molybdenum(III) complexes has been facilitated by the use of bulky *N-tert*-butylanilide ancillary ligands. The remarkable new complexes, embodied by $Mo[N(R)Ar]_3$ **4**, display a wealth of dramatic new reaction chemistries, and thereby have opened up new areas of inquiry in transition metal chemistry. Accordingly, dinitrogen cleavage to molecular molybdenum nitride **5** has been realized under mild and mechanistically well defined conditions.[9] The same nitride forms in equimolar amounts with nitrosyl **11**, in a highly unusual example of nitrous oxide N–N bond cleavage by **4**.[8] New vistas have opened for intermetal N-atom transfer reactivity; N-atom bridged intermediates have been characterized,[10] and the atom transfer reaction has been coupled with N_2 cleavage and metal–metal bond formation.[30] White phosphorus, with its tetrahedral P_4 molecules, has been harnessed to provide examples of terminal phosphide species,[37] the phosphorus analog of nitride **5**.[9] The sinks in the system have been identified as featuring Mo–element triple bonds or three-membered 8π-electron cumulenes, with $Mo[(R)Ar]_3$ comprising a terminus. These observations have permitted the chemistry to be extended to encompass the terminal carbide functionality (one-coordinate carbon bonded to a single metal),[55] and a molybdenum complex of phosphorus monoxide.[42]

As the reactivity patterns for **4** become more well established, it will be of interest to probe the detailed effects of ligand-induced steric requirements in the system, and to search for routes to related three-coordinate compounds based on other metals, including tungsten. Because $Mo[N(R)Ar]_3$ **4** can be prepared in multigram quantities, and can be prepared inexpensively for synthetic applications without deuterium-enrichment in the –N(R)Ar ligand,[61] it may be expected that the compound will find manifold applications in synthetic chemistry. At the very least, the reaction pathways uncovered in the context of studying **4** and related compounds can serve as a starting point for the mechanism-based design of new reagents or catalyst systems.

Finally, the characterization of $Mo[N(R)Ar]_3$ **4**[8] and the initial elucidation[23] and documentation[9] of its reaction chemistry[37] serve as a striking reminder of the riches that surely do remain to be mined within the realm of exploratory synthetic inorganic chemistry.

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