

Nitrogen atom exchange between molybdenum, tungsten and carbon. A convenient method for N-15 labeling†

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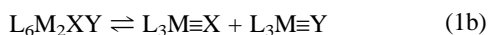
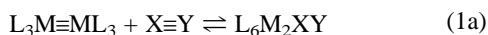
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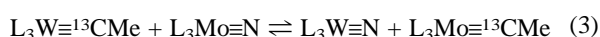
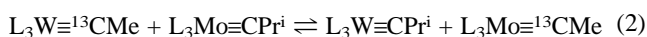
The compound (Bu^tO)₃W≡N serves to exchange the nitrogen atoms between nitriles (MeC≡N and PhC≡N), itself and (Bu^tO)₃Mo≡N in solution at room temperature.

Modern computational methods aid in identifying new modes of reactivity based upon their predictions of thermodynamic preference and reaction pathways. We are currently examining the reactions shown in eqn. (1) by experimental procedures and

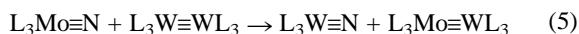


computational methods based on model compounds (M = Mo or W; L = alkoxide, thiolate, amide, alkyl; X = Y = N or CR, X = N, Y = CR).^{1–5}

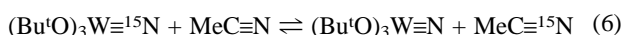
The reaction **1b** involves the reversible formation and rupture of X–Y and M–M bonds and was the subject of a recent communication in this journal dealing with the coupling of benzylidene ligands when M = W and L = 2-MeC₆H₄S.⁵ During this work we noted that the calculated barrier to X–Y and M–M bond formation was higher than that for X, Y group transfer via L₃M(μ-X)(μ-Y)ML₃ intermediates. This prompted us to probe for the existence of such reactions. We describe herein the isotopically labeled reactions shown in eqn. (2), (3) and (4), where L = OBU^t that confirm the predictions based on the computations.⁶



Evidence for X, Y group exchange in reactions (2)–(4) was seen by NMR spectroscopy⁶ (¹H, ¹³C or ¹⁵N) and by mass spectrometry. The calculations based on model compounds L = OH or CH₃, X = Y = N or CH predict that the thermodynamic products involving the reactants present in eqn. (4) are N≡N and L₃Mo≡WL₃ but these are not observed. However, L₃Mo≡WL₃ (where L = OBU^t) is seen in reaction (5) although the L₃Mo≡WL₃ compound reacts further with L₃Mo≡N⁷ to give Mo₂L₆ and L₃W≡N.^{6,8}



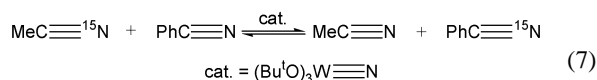
The facility of nitrogen atom exchange in reactions (3)–(5) led us to examine the potential for nitrogen atom exchange between molybdenum, tungsten and carbon.⁹ The compound (Bu^tO)₃W≡N⁸ was shown to exchange its nitrogen atom with that of acetonitrile, eqn. (6) and furthermore catalyze ¹⁵N



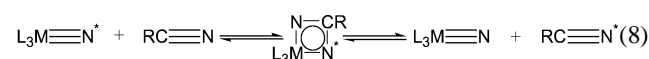
scrambling with benzonitrile, eqn. (7). See Fig. 1.

The ¹⁵N/¹⁴N scrambling in reactions (6) and (7) has been monitored by ¹⁵N NMR spectroscopy and mass spectrometry.⁹ Rather interestingly the closely related compound (Bu^tO)₃Mo≡N⁷ does not exhibit similar nitrogen atom exchange with MeC≡¹⁵N or catalyze scrambling with PhC≡N, at room temperature in d₈-THF. However, upon addition of a trace amount of (Bu^tO)₃W≡N, scrambling of nitrogen atoms occurs leading to formation of PhC≡¹⁵N and (Bu^tO)₃Mo≡¹⁵N.

In order to establish that the ¹⁵N labeling exchange observed in reaction **7** occurs exclusively as a result of nitrogen atom exchange and not cyano group exchange, we followed the reaction between PhC≡N, Me¹³C≡N and MeC≡¹⁵N in d₈-THF in the presence of (Bu^tO)₃W≡N. By NMR spectroscopy the appearance of Me¹³C≡¹⁵N and PhC≡¹⁵N could be detected but no ¹³C enrichment of the benzonitrile cyano group carbon was detected. See Fig. 2.



The seemingly most plausible pathway leading to nitrogen atom exchange involves the formation of a 2 + 2 cycloaddition reactive intermediate as represented schematically by eqn. (8).



This bears analogy to the reaction pathway of alkyne metathesis by (Bu^tO)₃W≡CR complexes.^{10–12} Calculations employing density functional theory¹³ on the model reactants (HO)₃W≡N and MeC≡N predict that formation of the five-coordinate intermediate shown in Fig. 3 to be enthalpically higher in energy than the starting materials by 18 kcal mol⁻¹. In contrast, formation of the related molybdenum 2 + 2 cycloaddition product is enthalpically disfavored by an additional 10 kcal mol⁻¹.

Based on these preliminary results we believe that these and related nitrogen atom exchange reactions hold considerable promise for ¹⁵N isotope labeling studies in a wide variety of chemical systems. Furthermore, it should be possible to link nitrogen atom exchange reactions to dinitrogen cleavage via a reactive mononuclear L₃M fragment of the type pioneered by Cummins.^{14–16}

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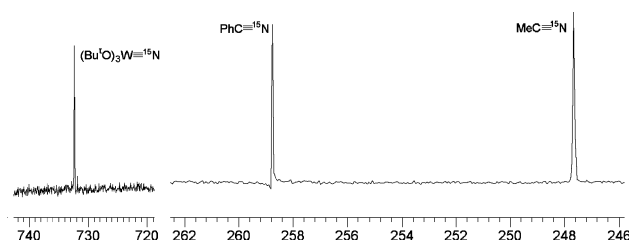


Fig. 1 ¹⁵N NMR spectrum of the reaction between labelled MeC≡¹⁵N and PhC≡N (natural abundance) in the presence of (Bu^tO)₃W≡N recorded in d₈-THF at 298 K, 50.6 MHz, showing the ¹⁵N for ¹⁴N atom exchange.

† Dedicated to Professor Dr. G. Huttner on the occasion of his 65th birthday.

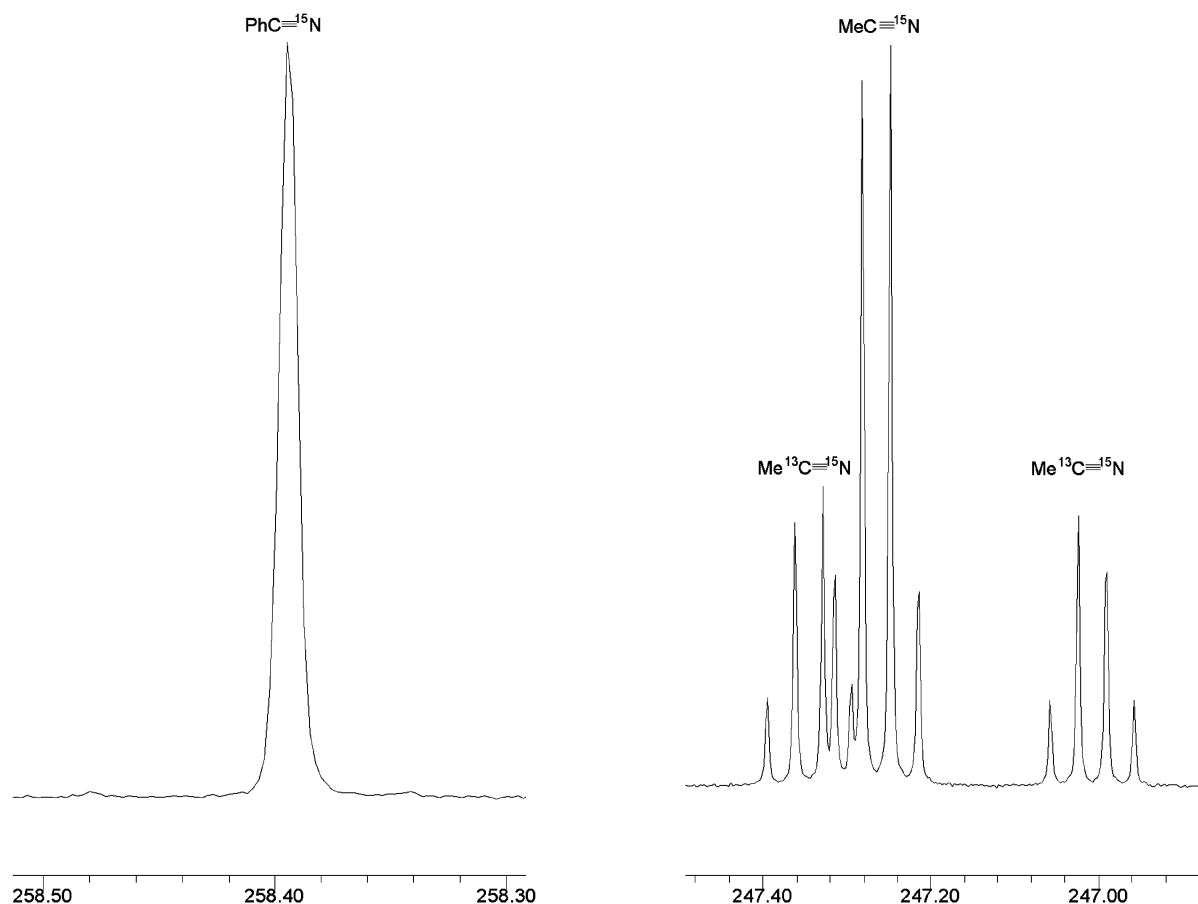


Fig. 2 ^{15}N NMR spectrum of the reaction mixture between $\text{Me}^{13}\text{C}\equiv\text{N}$, $\text{MeC}\equiv^{15}\text{N}$ and $\text{PhC}\equiv\text{N}$ in the presence of a trace of $(\text{Bu}^t\text{O})_3\text{W}\equiv\text{N}$ recorded in d_8 -THF at 298 K, 50.6 MHz. The $\text{PhC}\equiv^{15}\text{N}$ signal shows enhancement due to ^{15}N atom exchange and appears as a singlet due to lack of coupling to ^1H or ^{13}C whereas the $\text{MeC}\equiv\text{N}$ ^{15}N signal shows coupling to ^1H , $^3J(^1\text{H}-^{15}\text{N}) = 1.7$ Hz and for $\text{Me}^{13}\text{C}\equiv^{15}\text{N}$ coupling to ^{13}C , $^1J(^{13}\text{C}-^{15}\text{N}) = 17$ Hz. The signal thus appears as a central 1:3:3:1 quartet flanked by ^{13}C satellites. The unsymmetrical nature of the ^{13}C satellites arises from $^{12}\text{C}/^{13}\text{C}$ isotopic chemical shift perturbation.

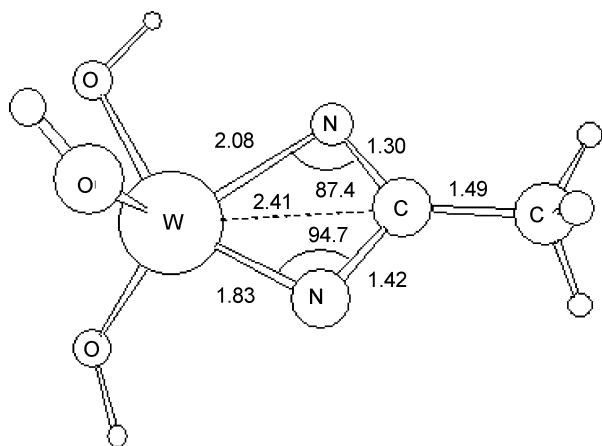


Fig. 3 A drawing of the calculated geometry for the minimum energy of a hypothetical reactive intermediate $(\text{HO})_3\text{W}(\eta^2\text{-N}_2\text{CMe})$ showing the asymmetric nature of the metallacycle.

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- These reactions were followed by ^1H , $^{13}\text{C}\{^1\text{H}\}$ and ^{15}N NMR spectroscopy and the labeled compounds $\text{L}_3\text{W}\equiv^{13}\text{CMe}$ and $\text{L}_3\text{W}\equiv^{15}\text{N}$ were prepared by the 'chop-chop' reaction¹ between $\text{L}_3\text{W}\equiv\text{WL}_3$ and $\text{Me}^{13}\text{C}\equiv\text{N}$ and $\text{MeC}\equiv^{15}\text{N}$ respectively ($\text{L} = \text{OBU}^t$). All spectra were acquired at room temperature over a 12–16 h period after which time a statistical isotopic distribution of ^{15}N was observed. Selected ^{13}C NMR data (d_6 -benzene, 125.8 MHz): $^{13}\text{C}\{^1\text{H}\}$: $\text{L}_3\text{W}\equiv^{13}\text{CMe}$, δ 254.1, $J(^{183}\text{W}-^{13}\text{C})$ 306.5 Hz; $\text{L}_3\text{Mo}\equiv^{13}\text{CMe}$, δ 279.6; $\text{L}_3\text{W}\equiv^{13}\text{CPr}^i$, δ 268.3; $\text{L}_3\text{Mo}\equiv^{13}\text{CPr}^i$, δ 292.7. ^{15}N NMR data (d_8 -THF, 50.6 MHz): $\text{L}_3\text{W}\equiv^{15}\text{N}$, δ 731.8, $J(^{183}\text{W}-^{15}\text{N})$ 54; $\text{L}_3\text{Mo}\equiv^{15}\text{N}$, δ 828.8 (relative to NH_3). The compound $\text{L}_3\text{W}\equiv\text{MoL}_3$ shows two singlets in the ^1H NMR spectrum (d_6 -benzene, 298 K, 400 MHz), δ 1.58 and 1.60 and a molecular ion with the anticipated isotope pattern for MoWL_6^+ in the mass spectrum.
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