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Bimetallic μ-cyanoimide complexes prepared by NCN group transfer†

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A cyanoimide [NCN] transfer reagent has been developed and applied to the synthesis of the μ-NCN systems ($\mu^2;\eta^1,\eta^1$-NCN) {M[N(R)Ar]$_3$}$_2$ (Ar = $C_6H_3Me_2$-3,5; M = V or U, R = Bu^t; M = Mo, R = Pr^i).

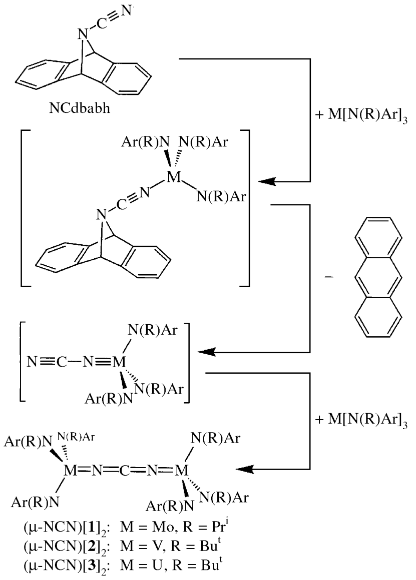
Small molecules or ions comprised of combinations of the elements C, N and O hold inherent fascination due to their simplicity and their importance with respect to the global cycles that involve them. Studies in which reactive metal complexes are employed for small molecule activation can shed light on manifolds of processes that permit such substrates to be manipulated. Recent reports involving dinitrogen, nitrous oxide, carbon monoxide, and cyanate ion serve to exemplify this approach. The present work is concerned with cyanoimide ion, [NCN]$^{2-}$, the attributes of which as a ligand in coordination chemistry currently are not well understood. To this end has been developed a new reagent for the synthesis of cyanoimide complexes, a reagent based on the bicyclic amine 2,3:5,6-dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene (Hdbabh). For references relating to this work see ESI.†

As reported by Carpino *et al.*, the synthesis of Hbdabh proceeds *via* an *N*-bromo derivative, Brdbabh or alternatively from the hydrobromide salt BrH$_2$dbabh.[1,2] Treatment of Brdbabh with trimethylsilyl cyanide in DMF has been found to provide the desired *N*-cyano derivative NCdbabh in essentially quantitative yield as colorless leaflets subsequent to recrystallization from diethyl ether.[3] Cyano-dbabh thus prepared constitutes a reagent for transfer of the neutral [NCN] fragment to reducing metal complexes under mild conditions, the reactions being two-electron redox events that occur with concomitant release of anthracene.[4] Methodology based on the ability of the dbabh skeleton to effect group transfer coupled with anthracene formation has been documented previously in the case of [N]$^-$ transfer to form chromium(VI) nitrido complexes.[5]

Several metal complexes have been found to effect smooth [NCN] abstraction from cyano-dbabh. Treatment of a molybdenum metallaziridine–hydride complex known to serve as a source of the relatively unhindered three-coordinate molybdenum(III) fragment Mo[N(Pr^i)Ar]$_3$ **1** (Ar = $C_6H_3Me_2$-3,5),[6] with 0.5 equiv. of NCdbabh in diethyl ether at 25 °C led to rapid and essentially quantitative formation of the diamagnetic dinuclear μ-cyanamide derivative (μ-NCN)[**1**]$_2$. Anthracene removal was effected by filtration of the reaction mixture through activated charcoal, and orange crystals of (μ-NCN)[**1**]$_2$ were obtained in 63% yield by storing a concentrated Et_2O solution at −35 °C (Scheme 1). Prepared analogously using the ^{13}C-labeled reagent N^{13}Cdbabh[3] was the isotopomer (μ-N^{13}CN)[**1**]$_2$, an isotopomer of interest due to its ^{13}C NMR quintet ($^1J_{CN}$ 24 Hz) at 176 ppm and its strong IR ν_{NCN} stretch appearing at 2061 cm^{-1}, this value being red-shifted by 61 cm^{-1} relative to that for its unlabeled counterpart.[3] A low energy band at 475 nm in the visible spectrum of (μ-NCN)[**1**]$_2$ is assigned tentatively to a fully allowed transition from the molecule's e_u HOMO to its e_g LUMO, assuming idealized D_{3d} symmetry for the complex. Calculation of the HOMO–LUMO gap for a model system, using NH$_2$ in place of N(Pr^i)Ar ligands, gave a value (1.38 eV) well in accord with the experimentally observed quantity.[3,7]

Based on the orbital scheme developed for diamagnetic (μ-NCN)[**1**]$_2$, an analogous divanadium complex was expected to exist as a ground-state triplet. Such a complex was obtained upon reaction of V[N(R)Ar]$_3$ **2**[8,9] (R = Bu^t) with 0.5 equiv. of NCdbabh (Scheme 1). The purple–black microcrystalline solid thus obtained analyzed correctly for (μ-NCN)[**2**]$_2$, exhibited the expected strong ν_{NCN} at 2037 cm^{-1} {(μ-N^{13}CN)[**2**]$_2$ had an IR stretch at 1982 cm^{-1}}, and was found to possess a μ_{eff} of 3.01 μ_B in solution at 25 °C.[3] Purification of (μ-NCN)[**2**]$_2$ was accomplished as for the molybdenum derivative, the isolated yield being 91%. The divanadium complex (μ-NCN)[**2**]$_2$ shows an interesting electrochemistry. Two reversible reduction processes can be observed at −1.61 and −2.42 V (*vs.* [FeCp$_2$]$^{0/+}$). An oxidation event at −0.68 V was found to be in a range convenient for chemical oxidation. Oxidation of (μ-NCN)[**2**]$_2$ thus was accomplished using silver triflate, a regimen providing paramagnetic {(μ-NCN)[**2**]$_2$}[O$_3$SCF$_3$] in 56% yield. Oxidized (μ-NCN)[**2**]$_2$ was characterized fully, including its magnetochemistry and X-band EPR spectrum in solution.[3]

That complex (μ-NCN)[**1**]$_2$ contains a linear 5-atom MoNCNMo chain was confirmed by single-crystal X-ray crystallography (Fig. 1(a)),§ the molecular structure in question being found to incorporate a crystallographic center of inversion at the cyanoimide carbon along with a Mo–N–C angle of 176.6(4)° (two crystallographically independent molecules were confined



Scheme 1 Reaction scheme for 0.5 equiv. of NCdbabh with the metal complexes M[N(R)Ar]$_3$ to form the μ-cyanoimide complexes of the type (μ-NCN)[M{N(R)Ar}$_3$]$_2$ (M = Mo, R = Pr^i; M = V or U, R = Bu^t). Intermediate complexes have not been observed.

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† Electronic supplementary information (ESI) available: introductory section with associated references as well as synthetic, spectroscopic, crystallographic and DFT calculation details for all complexes. See http://www.rsc.org/suppdata/cc/b0/b006517j/

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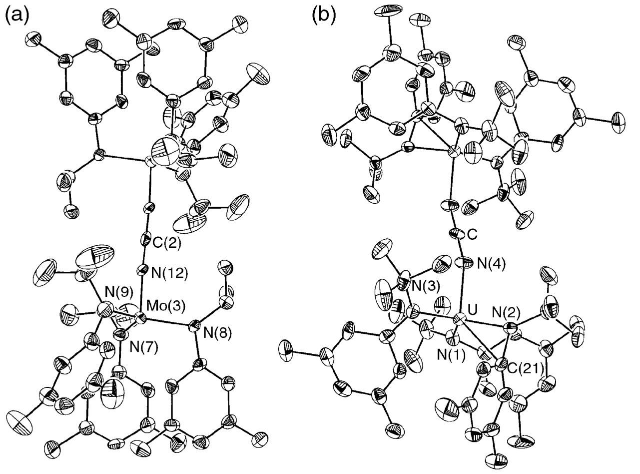

Fig. 1 (a) Structural diagram of (μ-NCN)[**1**]$_2$ with thermal ellipsoids at the 35% probability level. Selected distances (Å) and angles (°): Mo(3)–N(7) 1.947(6), Mo(3)–N(8) 1.994(6), Mo(3)–N(9) 1.960(7), Mo(3)–N(12) 1.852(7), N(12)–C(2) 1.233(7); Mo(3)–N(12)–N(2) 176.6(4). (b) Structural diagram of (μ-NCN)[**3**]$_2$ with thermal ellipsoids at the 35% probability level. Selected distances (Å) and angles (°): U–N(4) 2.226(7), U–N(1) 2.219(6), U–N(2) 2.225(6), U–N(3) 2.291(6), N(4)–C 1.189(8), U–C(21) 2.787(8); C–N(4)–U 162.6(5).

in the asymmetric unit, one of which possessed an inversion center about the cyanoimide carbon). As for the μ-nitrido dimolybdenum complex (μ-N)[**1**]$_2$ studied previously,[6] the six isopropyl substituents are directed to the molecule's interior, the six aryl residues consequently occupying polar positions. Given the properties of vanadium-containing (μ-NCN)[**2**]$_2$, its structure presumably likewise incorporates a linear 5-atom chain with metal termini.[3]

In contrast is the structure of the diuranium derivative (μ-NCN)[**3**]$_2$§ derived from the reaction of (THF)U[N(R)Ar]$_3$ **3**-THF[10,11] with 0.5 equiv. of NCdbabh (Scheme 1). X-Ray crystallography revealed in this case a *bent* geometry at the cyanoimide nitrogens [U–N–C 162.6(5)°], the molecule exhibiting again, however, inversion symmetry at the cyanoimide carbon atom (Fig. 1(b)).[12] The bent geometry adopted by the cyanoimide nitrogens in (μ-NCN)[**3**]$_2$, taken together with the observation of a congruence in the U–N$_{\text{amide}}$ and U–N$_{\text{cyanoimide}}$ distances, may be indicative of relatively little π bonding in the uranium–cyanoimide interaction. In contrast, the transition-metal derivative (μ-NCN)[**1**]$_2$ exhibits a Mo–N$_{\text{cyanoimide}}$ distance shorter by 0.115(6) Å than the Mo–N$_{\text{amide}}$ distance in the same complex. Recently it has been suggested that the high nodality of its valence 5 f orbitals renders mid-valent uranium less effective at π bonding than its transition-metal counterparts.[13,14] Using the ^{13}C-labeled reagent N^{13}Cdbabh, it was found that the isotopomer (μ-N^{13}CN)[**3**]$_2$ evinces a broad ^{13}C NMR resonance at 133 ppm.

It is believed that the ultimate step in formation of these μ-cyanoimide systems is the combination of a putative terminal cyanoimide complex with unreacted complex. Formation of the bridged-cyanoimide complexes most likely occurs *via* mononuclear reduction of NCdbabh, a process evidently being slow relative to consumption of unreacted metal complex. This work establishes NCdbabh as an efficient source of the [NCN] moiety, its implementation having led to smooth assembly of dinuclear cyanoimide-bridged complexes of vanadium, molybdenum and uranium. In addition to showing that dbabh represents a versatile platform for group transfer reactions, the present work makes available for study a new class of cyanoimide-bridged dimetal complexes. Mononuclear complexes featuring a *terminal* cyanoimide ligand remain attractive as synthetic targets.[15,16]

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Notes and references

§ *Crystallographic data*: for (μ-NCN)[**1**]$_2$: C$_{100.50}$H$_{144}$Mo$_3$N$_{12}$, triclinic, space group $P\bar{1}$, M = 1808.10, a = 15.219(2), b = 18.043(3), c = 20.510(3) Å, α = 63.998(2), β = 81.112(2), γ = 80.611(2)°, U = 4972.1(12) Å^3, Z = 2, T = 183(2) K, μ(Mo-Kα) = 0.422 mm^{-1}, 15823 reflections measured, θ range 2.41–20.75°, 10252 unique reflections, R_1 = 0.0764, wR_2 = 0.1894, GOF = 1.068, residuals based on $I > 2\sigma(I)$. The residual peak and hole electron density was 1.478 and −1.390 e Å^{-3}. Two crystallographically independent molecules were present in the asymmetric unit with one of the chemically equivalent molecules possessing an inversion center about the cyanoimide carbon.

For (μ-NCN)[**3**]$_2$: C$_{73}$H$_{108}$U$_2$N$_8$, monoclinic, space group $P2_1/n$, M = 1573.73, a = 10.9163(8), b = 19.6175(14), c = 17.4079(12) Å, β = 96.8390(10)°, U = 3701.4(5) Å^3, Z = 2, T = 183(2) K, μ(Mo-Kα) = 4.413 mm^{-1}, 12242 reflections measured, θ range 2.10–21.25°, 4091 unique reflections, R (based on F) = 0.0418, wR (based on F^2) = 0.0770, GOF = 1.159, residuals based on $I > 2\sigma(I)$.

Single red-orange crystals of (μ-NCN)[**1**]$_2$ and yellow blocks of (μ-NCN)[**3**]$_2$ were grown from a Et$_2$O at −35 °C, mounted in inert oil (paratone N oil from Exxon) and transferred to a cold stream of the diffractometer. The structures were solved using direct methods and refined by full-matrix least squares on F^2. CCDC 182/1809.

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