Unsaturated dinickel–molybdenum clusters with N-heterocyclic carbene ligands†

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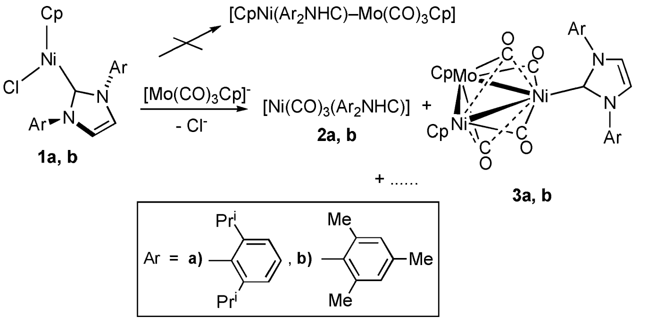
The first examples of mixed metal trinuclear clusters carrying N-heterocyclic carbene (NHC) ligands were isolated from reactions of the complexes [Ni(NHC)ClCp] [NHC = bis-(2,6-diisopropylphenyl)- or bis-(2,4,6-trimethylphenyl)-imidazol-2-ylidene] with $[Mo(CO)_3Cp]^-$; the unsaturated 46-electron clusters have triangular $MoNi_2$ cores and the reaction pathway activates usually inert Ni–Cp and Ni–NHC bonds.

N-Heterocyclic carbenes (NHCs) are an important manifold of ligands that are increasingly being used in synthesis and catalysis. NHC complexes are often more air and thermally stable than their isoelectronic trialkylphosphine analogues.[1] Nevertheless, only a handful of clusters which incorporate these ligands are known, and heterobimetallic (htb) species as well as tri- or higher nuclearity mixed metal clusters are almost unknown.[2,3]

Many htb complexes activate small molecules in a unique manner.[4] Our group has long been interested in the chemistry and reactions of such species.[5] We have reported the synthesis of μ-methylene complexes in which the ligand spans nickel–molybdenum or –tungsten bonds[6] and have observed a variety of coupling reactions between CH_2 groups spanning these metal–metal bonds and other ligands. Similar couplings have also been observed with other htb systems.[7] Despite the high stability of NHC ligands and the significant electronic and steric differences that exist between methylene and NHC groups, we believed that if htb complexes with NHC ligands anchored onto the bimetallic framework were available, coupling reactions between NHC groups and other ligands, hitherto quite rare, might be promoted by the htb centers.[8]

We have reported that the reaction of $[W(CO)_3Cp]^-$ with $[Ni(PMe_3)ICp^*]$‡ afforded the tungsten-bound phosphine complex $[NiW(CO)_3(PMe_3)Cp^*Cp]$ (Ni–W), in a phosphine migration reaction.[6c] We attempted the synthesis of $[NiMo(CO)_3(NHC)Cp_2]$ species in similar fashion, by reacting $[Ni((Pr_2Ar)_2NHC)ClCp]$[9a] **1a** in a 1 : 1 molar ratio with the molybdenum anion $[Mo(CO)_3Cp]^-$.§ However the expected $[NiMo(CO)_3((Pr_2Ar)_2NHC)Cp_2]$ (Ni–Mo) was not obtained. Instead, **2a** and **3a** (see below) were harvested from this reaction, together with some unreacted **1a** and traces of $[Mo_2(CO)_6Cp_2]$ (Mo–Mo). The mixture was separated by column chromatography, and pure **2a** and **3a** were isolated.

Elemental analysis, NMR spectroscopy and a single crystal X-ray diffraction study established **2a** as the previously reported and structurally characterized species $[Ni(CO)_3((Pr_2Ar)_2NHC)]$.[10] While **3a** displays a ^1H NMR spectrum in agreement with that expected for the compound $[NiMo(CO)_3((Pr_2Ar)_2NHC)Cp_2]$, its IR spectrum exhibits a suspiciously low energy ν(CO) stretching frequency at 1747 cm^{-1} (other absorptions at 1892 and 1813 cm^{-1} were also seen).¶ The low frequency absorption, inconsistent with terminal or even μ_2-CO ligands, suggests the presence of a μ_3-CO group spanning a trinuclear cluster. Scheme 1 gives the reaction and structures of **2a** and **3a**.



Scheme 1 Reactions of [Ni(NHC)ClCp] with $[Mo(CO)_3Cp]^-$.

The structure of **3a** was established unambiguously by a single crystal X-ray diffraction study.* Fig. 1 shows the molecular structure of **3a**, $[MoNi_2(CO)_4((Pr_2Ar)_2NHC)Cp_2]$ and establishes its nature as a trinuclear $MoNi_2$ 46-electron unsaturated cluster. One nickel atom (Ni1) has been stripped of its Cp group and bears a $(Pr_2Ar)_2NHC$ group as its only terminal ligand. The observed Ni1–C1 distance of 1.907(1) Å is slightly longer than the corresponding 1.875(1) Å distance noted in $[Ni((Pr_2Ar)_2NHC)ClCp]$.[9a] The other nickel atom, Ni2, is still bonded to a Cp group but has no NHC ligand linked to it. The metallic triangular core is asymmetric, with Ni–Mo distances of 2.5300(6) (Ni1–Mo) and 2.7108(7) Å (Ni2–Mo). The Ni1–Mo bond distance is the shortest such value known and the relatively close proximity of the two bonded metals probably reflects the partial multiple bond character of this bond. No Ni=Mo bond distances have been reported, but Ni–Mo bonds in clusters normally lie in the range 2.62–2.72 Å.[11] A molecule with a formal Ni=W bond has a nickel–tungsten distance of 2.46 Å.[12]

All four CO groups in the cluster are interacting with more than one metal. The normal Ni1–Ni2 bond of 2.4264(7) Å is spanned by an asymmetrically μ_2-bridging CO ligand while one of the three CO groups on the Mo atom interacts in a μ_2-*semi*bridging fashion with Ni1. The other two Mo-bound CO groups interact (weakly in one case, and more significantly in the other) with both nickel atoms, so that they are perhaps best regarded as semi-triply bridging CO ligands.

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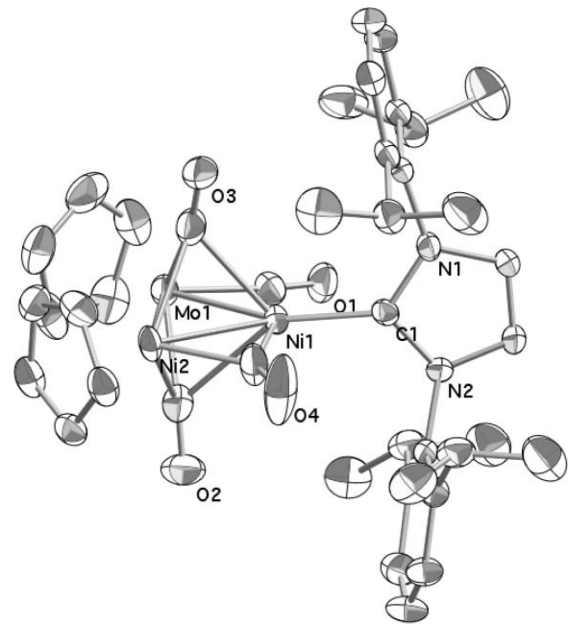

Fig. 1 Molecular structure of **3a** showing all non-H atoms. Ellipsoids are shown at the 50% probability level and key atoms are labelled. Pertinent bond lengths (Å) and angles (°): Ni1–Ni2 = 2.4264(7), Ni1–Mo = 2.5300(6), Ni2–Mo = 2.7108(7), Ni–C1 = 1.907(4); Ni1–Ni2–Mo = 58.97(2), Ni2–Ni1–Mo = 66.27(2) and Ni1–Mo1–Ni2 = 55.029(17).

While it is not easy to rationalise the formal electron count in **3a**, it is clear that Ni1, which carries the $(Pr_2Ar)_2NHC$ ligand, is unsaturated. It is this nickel atom which forms the short bond to molybdenum. The nickel atom is electronically stabilized by the strong electron-donating properties of the NHC ligand and, in addition, is shielded from its environment by the enormous bis-2,6-diisopropylphenyl pendant groups of this ligand, as shown by space filling models. These steric and electronic effects stabilize and protect the unsaturated metal. The centroids of the two Cp ligands essentially lie in the $MoNi_2$ plane, maximizing their distance from the massive NHC ligand.

The reaction of $[Mo(CO)_3Cp]^-$ with $[Ni(Mes_2NHC)ClCp]$[9b] **1b** under similar reaction conditions analogously afforded a mixture of complexes **2b**[10] and **3b** (Scheme 1), together with some unreacted **1b** and traces of $[Mo_2(CO)_6Cp_2]$ (Mo–Mo). Structural data are not available for the bis-mesityl analogue $[MoNi_2(CO)_4(Mes_2NHC)Cp_2]$ **3b**. However, solid-state IR and solution NMR spectroscopic data¶ of this species parallel those of **3a** and suggest that the two complexes have similar structures. The isolated yields of **3b** were lower than for **3a**.§ The lower yield of **3b** may reflect the smaller steric footprint of the $(Mes)_2NHC$ ligand which thus offers less steric protection to the cluster.

Excess **1** does not increase the yield of clusters **3** as even at 1 : 1 (Ni : Mo) stoichiometry, unreacted **1** is recovered. We have also demonstrated that room temperature benzene-d_6 solutions of **3b** decompose slowly to yield **2b** as a reductive elimination product. This decomposition route may indeed be the mechanistic pathway to complexes **2** in this reaction. Note that the nickel atom bearing the NHC ligand [Ni1 in the X-ray study of **3a**] is already interacting with three CO ligands (and weakly with a fourth).

The reaction pathway leading to the formation of clusters **3** is highly unusual as it gives rise to molecules (**2** and **3**) in which cleavage of normally robust Ni–Cp bonds has occurred in diamagnetic nickel complexes. Formation of **3** also entails the rupture of the metal–NHC bonds originally present in complexes **1**. We have previously noted that Ni–Cp* bonds are not inert and hence, Ni–Cp* cleavage and subsequent Cp* ligand transfer is not unusual in NiCp* chemistry.[13] However the rupture of Ni–Cp bonds under relatively mild conditions is very unusual for diamagnetic 18-electron nickel complexes. Metal–NHC bond cleavage is also a relatively rare phenomenon.[8a–d,14]

Further investigations into reactions leading to complexes **3** and related reactions are in progress.

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Notes and references

‡ Throughout this manuscript, Cp = η^5-C_5H_5, Cp' = η^5-C_5H_4Me, Cp* = η^5-C_5Me_5, $(Pr_2Ar)_2NHC$ = bis-(2,6-diisopropylphenyl)imidazol-2-ylidene, Mes_2NHC = bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene.

§ **3a** was prepared by reacting $Na[Mo(CO)_3Cp]\cdot 2DME$ (275 mg, 0.61 mmol) with $[Ni((Pr_2Ar)_2NHC)ClCp]$, **1a** (336 mg, 0.61 mmol) in THF at 45 °C for 8.5 h. Silica gel chromatography of the concentrated mixture using toluene as an eluting solvent separated unreacted **1a** from traces of $[Mo_2(CO)_6Cp_2]$ (Mo–Mo), pale pink **2a** and dark green **3a**. Green needles of **3a** (173 mg, 0.205 mmol, 34% based on Mo) were obtained from toluene–pentane solutions at −20 °C. **3b** was prepared similarly from $[Ni(Mes_2NHC)ClCp]$, **1b** (17% based on Mo).

¶ Selected physical data for **3a** and **3b**: **3a**; ^1H NMR (C_6D_6, 300 MHz, δ/ppm, J/Hz): 1.05 (d, 12H, J = 8.8, CH*Me*$_2$); 1.52 (d, 12 H, J = 8.8, 12H, CH*Me*$_2$); 3.13 (m, 4H, C*H*Me$_2$); 4.99 and 5.00 (2 × 5H, 2*Cp*); 6.69 (2H, NC*H*); 7.26 (m, 4H, *m*-H); 7.29 (m, 2H, *p*-H). ^{13}C NMR (C_6D_6, 75 MHz, δ/ppm): 194.6 (N–*C*–N); 146.6, 136.1, 130.3 and 125.0 (C_{Ar}), 124.3 (N*C*H=N*C*H); 94.1 and 91.9 (2 *Cp*), 28.4 (*C*HMe$_2$), 26.7 and 22.9 (CH*Me*$_2$). IR [ATR, ν(CO)/cm^{-1}]: 1892 (m), 1813 (s, br), 1747 (s, br). **3b**; ^1H NMR (C_6D_6, 300 MHz, δ/ppm, J/Hz): 2.12 (6H, *p*-Me); 2.30 (12H, *o*-Me); 4.96 and 5.03 (2 × 5H, 2 *Cp*); 6.29 (2H, NC*H*); 6.90 (4H, *m*-H). ^{13}C NMR (C_6D_6, 75 MHz, δ/ppm): 192.0 (N–*C*–N), 138.9 (*ipso*-C_{Ar}), 136.2 (*p*-C_{Ar}), 135.7 (*o*-C_{Ar}), 129.8 (*m*-C_{Ar}), 123.4 (N*C*H=N*C*H), 94.0 and 92.1 (2*Cp*), 21.1 (*p*-Me), 18.9 (*o*-Me). IR [ATR, ν(CO)/cm^{-1}]: 1882 (m), 1797 (s, vbr), 1747 (s, br).

* Crystal data for **3a**, $C_{41}H_{46}MoN_2Ni_2O_4$, $Z = 4$, M 844.16, $D_c = 1.466$ g cm^{-3}, $\lambda = 0.71069$ Å (Mo-K$_\alpha$), monoclinic, space group $P2_1/c$, $a = 11.9951(7)$ Å, $b = 17.6958(8)$ Å, $c = 20.1788(10)$ Å, $\beta = 116.754(3)°$, $V = 3824.7(3)$ Å^3, $T = 172(2)$ K, $\mu = 1.34$ mm^{-1}, 23780 measured reflections, 8702 independent, 5001 with $I > 2\sigma(I)$. $R = 0.0542$, gof = 0.975.

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