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Aggregation of Nitrido–Metal Complexes: The Example of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Mo}(\text{N})\text{Cl}_2]$

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Whereas the chemistry of high-oxidation state cyclopentadienyl transition metal oxides has been the subject of intensive study,^[1] the corresponding nitrido complexes have only

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received little attention; the only examples are $[\{\text{Cp}^*\text{Ta}(\text{N})\text{Cl}\}_n]$ ($n = 3, 4$) $[\{\text{Cp}^*\text{V}(\text{N})\text{Cl}\}_2]$, $[\text{CpOs}(\text{N})(\text{CH}_2\text{SiMe}_3)_2]$ and $\text{Li}[\text{Cp}^*\text{W}(\text{N})\text{Me}_3]$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$).^[2a-c] The tantalum and vanadium compounds can be thought of as aggregates of varying nuclearity of the hypothetical mononuclear fragments $\{\text{Cp}^*\text{M}(\text{N})\text{Cl}\}$ ($\text{M} = \text{V}, \text{Ta}$). Here we report on the aggregation of a $\{\text{Cp}^*\text{Mo}(\text{N})\text{Cl}_2\}$ transient to form the first examples of $\text{Cp}^*\text{Mo}^{\text{VI}}$ nitrido complexes, which illustrate the electronic and steric effects of the Cp^* ligand in the chemistry of nitrido complexes. The general interest is related to the search for stable models^[3] of poorly understood metathesis catalysts obtained by in situ alkylation of nitridomolybdenum(vi) complexes.^[4] Another point of interest is the reactivity of the nitrido ligand^[5] and how this is influenced by the presence of the cyclopentadienyl ring.

The standard synthetic strategy (Scheme 1)^[5] introduces the nitrido ligand and two oxidizing equivalents from an azide. Our

Scheme 1.

starting material is the recently reported **1**.^[6] When NaN_3 in acetonitrile was employed as the azide source, gas evolution ensues and a purple solution is obtained, from which purple crystals of $2 \cdot 0.25 \text{CH}_2\text{Cl}_2$ (see Scheme 2) are collected in 39% yield after crystallization from dichloromethane/ether/pentane. Elemental analyses and NMR spectra indicate that the compound has incorporated one CH_3CN molecule per two $\{\text{Cp}^*\text{Mo}(\text{N})\text{Cl}_2\}$ units (see Scheme 2). Reaction of **1** with $(\text{CH}_3)_3\text{SiN}_3$ in CH_2Cl_2 also proceeds with gas evolution, but a emerald-green solution is now obtained. Crystals of paramagnetic (EPR) **3** (see Scheme 2) were isolated in 43% yield by diffusion of *n*-hexane; **3** crystallizes with two molecules of CH_2Cl_2 . The structures of both compounds were elucidated by X-ray crystallography.

The structure analysis of **2** (Fig. 1)^[7] shows that acetonitrile forms part of a symmetric six-membered $\text{Mo}_2\text{N}_3\text{C}$ ring, which is the first known example of a dimetallatriazene. The molecule can also be described as a dinuclear molybdenum complex with nitrido and acetamidinato(3-) bridging ligands. The planes defined by C1, C2, N2, N3 and Mo1, N1, Mo2 are twisted by an angle of 16.7° along the virtual twofold axis N1-C1-C2. Although the ring is hence not quite planar, the π -electron density is evidently delocalized: the Mo-N1 distances of $1.790(7) \text{ \AA}$ (Mo1-N1) and $1.851(7) \text{ \AA}$ (Mo2-N1) are intermediate between those for the typical $\text{Mo}\equiv\text{N}$ bond ($1.64 \text{ \AA}$)^[8] and a Mo-N dative bond [e.g., $2.16(1) \text{ \AA}$ in $[\{\text{MoNCl}_3(\text{OPCl}_2)_3\}_4]$,^[9] $2.18(3) \text{ \AA}$ in $[\{\text{MoNMe}_2(\text{OtBu})_3\}_4]$ ($t\text{BuC}_5\text{H}_4\text{N}_2$)^[3a]] and slightly shorter than those for the $\text{Mo}=\text{N}$ double bonds, as for instance

Fig. 1. PLATON diagram of the molecular structure of **2**. Relevant distances [$\text{\AA}$] and angles [$^\circ$]: Mo1-N1 $1.790(7)$, Mo2-N1 $1.851(7)$, Mo1-N2 $2.089(8)$, Mo2-N3 $2.082(7)$, N2-C1 $1.34(1)$, N3-C1 $1.33(1)$, Mo-Cl (average for Mo1 and Mo2) $2.432(2)$, Mo1-N1-Mo2 $161.4(4)$, Mo1-N2-C1 $132.8(6)$, Mo2-N3-C1 $131.9(6)$, N2-C1-N3 $123.6(7)$.

in $[\{\text{MoN}[\text{S}_2\text{P}(\text{OCH}_3)_2]_2\}_4]$ (av $1.868(12) \text{ \AA}$).^[10] The open Mo1-N1-Mo2 angle of $161.4(4)^\circ$ indicates strong participation of the π electrons to the Mo-N1 bonding. The other two Mo-N bond lengths (Mo1-N2 and Mo2-N3) are considerably longer (av $2.086(8) \text{ \AA}$) and the Mo-N-C angles more closed (av $132.4(6)^\circ$), consistent with less multiple bond character for the bonds between the Mo centers and the $(\text{CH}_3\text{CN}_2)^{3-}$ nitrogen donors. The C-N bonds (av $1.34(1) \text{ \AA}$) are typical of partial double bond character, as found for instance in aromatic N-heterocycles (in the $1.32\text{--}1.35 \text{ \AA}$ range).^[11] The coordination geometry around the Mo atoms can be described as a four-legged piano stool with two *cis*-chloro ligands, the bridging nitrido ligand, and one of the CH_3CN_2 nitrogen atoms occupying the four basal positions. The two four-legged piano stools share a common vertex identified by the nitrido ligand in such a way that the two Cp^* ligands are *anti* with respect to each other.

The structure of the pentanuclear mixed-valence complex **3**^[12] (Fig. 2) is unusual and shows that the molecule can be

Fig. 2. ORTEP diagram of the molecular structure of **3**. Relevant distances [$\text{\AA}$] and angles [$^\circ$]: Mo1-N1 $2.14(2)$, Mo1-N3 $1.70(2)$, Mo2-N1 $1.73(2)$, Mo2-N2 $2.12(2)$, Mo3-N2 $1.68(2)$, Mo3-N3 $2.09(2)$, Mo3-N4 $2.13(2)$, Mo4-N4 $1.69(2)$, Mo4-N5 $2.21(2)$, Mo5-N5 $1.69(2)$, Mo-Cl (average for Mo1, Mo2 and Mo4) $2.407(10)$, Mo-Cl (average for Mo3) $2.378(6)$, Mo-Cl (average for Mo5) $2.284(7)$, N1-Mo1-N3 $80.9(7)$, N1-Mo2-N2 $81.8(7)$, N2-Mo3-N3 $85.3(8)$, N2-Mo3-N4 $107.7(8)$, N3-Mo3-N4 $166.4(7)$, Cl31-Mo3-Cl32 $155.0(2)$, N4-Mo4-N5 $130.7(7)$, Mo1-N1-Mo2 $158.5(9)$, Mo2-N2-Mo3 $154.4(11)$, Mo1-N3-Mo3 $157.2(11)$, Mo3-N4-Mo4 $167.0(12)$, Mo4-N5-Mo5 $175.3(11)$.

described as an aggregate of four $\text{Cp}^*\text{Mo}(\text{N})\text{Cl}_2$ moieties and a central $\text{Mo}(\text{N})\text{Cl}_2$ unit. One $\text{Cp}^*\text{Mo}(\text{N})\text{Cl}_2$ dimer forms a trimetallatriazene together with the nitridomolybdenum(v) center, whereas the other dinuclear unit is coordinated in a chain-like fashion to the central Mo atom. The assignment of the oxidation state v to Mo3 is in agreement with the geometry and structural parameters of comparable compounds such as $[\text{Mo}(\text{N})\text{X}_2\text{L}_2]$ ($\text{X}^- = \text{L} = \text{Cl}^-$; $\text{X} = \text{N}_3^-$, $\text{L} = \text{N}\equiv\text{Mo}(\text{N}_3)-(\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2)_2$).^[13]

The Mo_3N_3 cycle in **3** is almost planar (the largest distances from the least-squares plane are 0.098 Å for N2, and -0.051 Å for N3) and contains localized, alternating $\text{Mo}\equiv\text{N}$ triple (av 1.70(3) Å) and $\text{N}\rightarrow\text{Mo}$ dative bonds (av 2.12(3) Å). Theoretical work predicts particular stability for compounds containing a cyclic M_3N_3 moiety,^[14] regardless of whether the Mo-N multiple bonds are delocalized or not. Compound **3** is the first example of a cyclic M_3N_3 unit with localized bonds. This localization is probably the result of the single d electron on Mo3, which encourages square-pyramidal coordination geometry for Mo3 and the presence of only one multiple bond in the apical position at this metal center. The Mo-N bonds are also localized in the lateral chain, as illustrated in the drawing of **3** in Scheme 2. There are four different coordination geometries in **3**: *cis*-

$\text{Cp}^*\text{MoN}_2\text{Cl}_2$ for the Mo1 and Mo2 centers (analogous to the Mo centers in **2**), square-pyramidal (MoN_3Cl_2) for Mo3, *trans*- $\text{Cp}^*\text{MoN}_2\text{Cl}_2$ for Mo4, and an unprecedented three-legged piano stool ($\text{Cp}^*\text{MoNCl}_2$) for Mo5. The existence of the latter geometry in **3** suggests that the mononuclear species $[\text{Cp}^*\text{MoNCl}_2]$ **1** is more nucleophilic at the nitrido ligand than it is electrophilic at the metal.

As in the structure of **2**, the six-membered ring in **3** has the two Cp^* rings on opposite sides of the Mo_3N_3 plane. A molecular model where the two Cp^* ligands are placed on the same side of the ring reveals an unbearable steric situation. This is because the four-legged piano stool geometry forces the Mo-Cp* vectors to lie almost perpendicular to the Mo_3N_3 plane. Based on this observation, we suggest that a trinuclear ($\text{Cp}^*\text{MoCl}_2\text{N}$)₃ compound, in which two Cp^* rings would be forced to reside on the same side of the three-membered ring, cannot exist. In the related trimer of tantalum reported by Roesky et al.,^[2a] a greater distance between the Cp^* rings is allowed by the three-legged piano stool geometry around the metals.

A possible route for the formation of compounds **2** and **3** follows from Scheme 2. The hypothetical $\text{Cp}^*\text{Mo}(\text{N})\text{Cl}_2$ intermediate **I** oligomerizes to **II** and **III** because of the pronounced basicity of the nitrido ligand. In acetonitrile, these intermediates are likely to be coordinated by a solvent molecule at the unsaturated metal center. Subsequent addition of **II** could lead to a $[\text{Cp}^*\text{MoCl}_2\text{N}]_x$ polymer (a polymeric Cp^* metal nitride, e.g. $[\text{Cp}^*\text{Ta}(\text{N})\text{Cl}]_n$, has been observed^[2b]) but other alternatives are available to intermediates **II** and **III**. A CH_3CN adduct of **II** can cyclize to afford **2** directly through attack of the nucleophilic nitrido ligand at the C atom of the ligand. In CH_2Cl_2 , **III** can cyclize but, in doing so, a strong steric interaction is established between two Cp^* rings (e.g. see **IV**). Therefore, one Cp^* ring is likely to be lost at this stage to give **V**. The reaction is completed by coordination of **II** to the unsaturated Mo^{V} center.

The EPR spectrum of **3** in CH_2Cl_2 shows a resonance at $g = 1.965$ ($a_{\text{Mo}} = 46.0$ G), similar to those reported for other pentacoordinated Mo^{V} nitrido complexes.^[13,15] Compound **3** reacts with THF to form a yellow solution with a new EPR resonance at $g = 1.957$ ($a_{\text{Mo}} = 48.5$ G), which we assign to $[\text{MoNCl}_2(\text{thf})_2]$. On the other hand, acetonitrile reacts with **3** to form a purple solution containing **2** as shown by NMR spectroscopy and exhibiting an EPR spectrum ($g = 1.957$, $a_{\text{Mo}} = 48.9$ G) which we assign to $[\text{MoNCl}_2(\text{CH}_3\text{CN})_2]$.

Our results indicate that the less encumbering Cp ligand should be capable of stabilizing a trimeric $[\{\text{CpMoNCl}_2\}_3]$ structure, while Cp^* is not. With regard to the possible existence of a dinuclear $[\{\text{Cp}^*\text{Mo}(\mu\text{-N})\text{Cl}_2\}_2]$ structure analogous to that of Doherty's vanadium compound,^[2c] no evidence of such a structure exists and the observation of an open-chain dinuclear unit in the structure of **3** suggests that it is unstable. Important factors may be the greater tendency of Mo (with respect to V) to reach an electronically saturated configuration, and the ability of all bridging N atoms to act as eight-electron donors in **3**, whereas in a (hypothetical) $[\{\text{Cp}^*\text{Mo}(\mu\text{-N})\text{Cl}_2\}_2]$ structure with a Mo-N-Mo angle smaller than 120° the N atoms could at best provide six electrons to the metal centers.

In conclusion, the electron-donating character of Cp^* and the availability of lone pairs for π bonding on the chloro ligands enhance the nitrido nucleophilicity and suppress electrophilicity at the electronically unsaturated metal center. Based on these principles, compounds of type $[\text{Cp}^*\text{Mo}(\equiv\text{N}\rightarrow\text{A})\text{Cl}_2]$ ($\text{A} = \text{Lewis acid}$) appear to be reasonable synthetic targets

Scheme 2.

Experimental Procedure

2: A suspension of $[\text{Cp}^*\text{Mo}(\text{CO})_2\text{Cl}_3]$ (207 mg, 0.53 mmol) in CH_3CN (30 mL) was kept at 60 °C for 30 min. NaN_3 (34 mg, 0.52 mmol) was added to the resulting burgundy solution and the mixture was stirred at 25 °C for 30 min (gas evolution and color change to purple). The mixture was evaporated to dryness and the residue was extracted with CH_2Cl_2 . After filtration, the solution was layered with a mixture of Et_2O (15 mL) and pentane (15 mL) and cooled slowly to –35 °C. Purple crystals of $2 \cdot 0.25 \text{ CH}_2\text{Cl}_2$ (67 mg, 39%) were isolated by decanting off the mother liquor and drying the solid under vacuum. $^1\text{H NMR}$ (CD_2Cl_2 , 25 °C): δ = 2.52 (s, 3H, N_2CCH_3), 1.99 (s, 30H, Cp^*). Analysis for $\text{C}_{22.25}\text{H}_{33.5}\text{Cl}_{4.25}\text{Mo}_2\text{N}_3$ ($= 2 \cdot 0.25 \text{ CH}_2\text{Cl}_2$). Calc.: C, 38.48; H, 4.86; N, 6.05, Cl 22.97. Found: C, 38.18; H, 4.96; N, 5.88, Cl 22.49. A crystal suitable for X-ray analysis was chosen under mother liquor.

3: A suspension of $[\text{Cp}^*\text{Mo}(\text{CO})_2\text{Cl}_3]$ (351 mg, 0.892 mmol) in CH_2Cl_2 (30 mL) was heated under reflux for 2 h. To the resulting solution of $[\{\text{Cp}^*\text{MoCl}_3\}_2]$ [6], $(\text{CH}_3)_3\text{SiN}_3$ (125 μL , 108 mg, 0.94 mmol) was added and the mixture was stirred at 25 °C for 30 min (gas evolution and color change to emerald green). Diffusion of a 50 mL *n*-hexane layer gave black crystals of $3 \cdot 2 \text{ CH}_2\text{Cl}_2$ (124 mg, 43%). EPR (CH_2Cl_2 , 25 °C): g = 1.965, a_{Mo} = 46.0 G. Analysis for $\text{C}_{42}\text{H}_{64}\text{Cl}_{14}\text{Mo}_3\text{N}_3$ ($= 3 \cdot 2 \text{ CH}_2\text{Cl}_2$). Calc.: C, 31.24; H, 3.99; N, 4.34. Found: C, 31.17; H, 4.29; N, 4.34.

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