Unexpected Coupling of Cp and Two RNC Ligands at a $\{Mo_2(\mu\text{-}SMe)_3\}$ Nucleus

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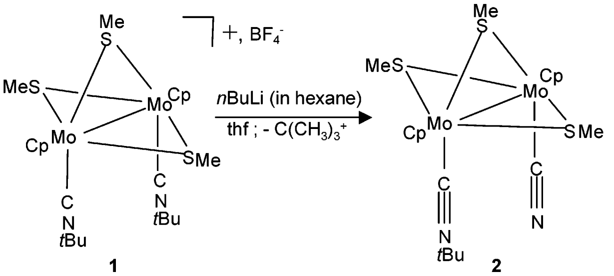
Received June 10, 2003

Summary: Reaction of the bis-isonitrile complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(t\text{-}BuNC)_2](BF_4)$ *(**1**) with n-BuLi (in hexane) produced the dealkylated derivative* $[Mo_2Cp_2(\mu\text{-}SMe)_3(t\text{-}BuNC)(CN)]$ *(**2**) in quantitative yield. However, upon treatment with either NaOH (suspension) or* $(Me_4N)OH$ *(in MeOH), **1** was converted into a mixture of **2** and the μ-alkylidyne species* $[Mo_2Cp(\mu\text{-}SMe)_3\{\mu\text{-}(\eta^5\text{-}C_5H_4)(t\text{-}BuN)CN(t\text{-}Bu)C\}]$ *(**3**), in which a deprotonated Cp and both isonitrile ligands of **1** are now linked by new carbon−carbon and carbon−nitrogen bonds.*

Metal-assisted coupling of isocyanides has provided a useful synthetic route to a wide variety of new nitrogen-containing organic ligands or compounds.[1] This reaction can proceed either through metal-mediated reductive coupling of the isocyanides[2] or by consecutive insertions of isocyanides into metal−carbon bonds to give N-chelated cyclic compounds. These insertion reactions can be initiated in various ways: by oxidative addition of alkyl halides to $[M](RNC)_n$ complexes,[3] by addition of an excess of isocyanide to metal complexes,[1b,4] or by thermolysis.[5] Most coupling reactions between isocyanides involve formation of carbon−carbon bonds,[3−5] while only a few give rise to new carbon−nitrogen bonds.[6] It has been shown that many different alkyl or aryl groups can migrate onto an isocyanide carbon atom.[7] In contrast, comparable examples involving the migratory insertion of cyclopentadienyl, despite its ubiquity as a ligand, are extremely rare.[8] This has prompted us to investigate the reactivity of the readily accessible bis-isonitrile derivative $[Mo_2Cp_2(\mu\text{-}SMe)_3(t\text{-}BuNC)_2](BF_4)$ (**1**)[9] to see if the close proximity of two isonitrile and two cyclopentadienyl ligands in this complex induces multiple coupling reactions. Accordingly, we are currently studying reactions of **1** with various bases. We describe here our preliminary results concerning the synthesis of a μ-alkylidyne derivative $[Mo_2Cp(\mu\text{-}SMe)_3\{\mu\text{-}(\eta^5\text{-}C_5H_4)(t\text{-}BuN)CN(t\text{-}Bu)C\}]$ (**3**) through the formation of new carbon−carbon and carbon−nitrogen bonds. We also note that the reaction of **1** with bases may yield the dealkylated product $[Mo_2Cp_2(CN)(t\text{-}BuNC)(\mu\text{-}SMe)_3]$ (**2**) rather than the coupling derivative **3**, depending on the base.

A mixture of $[Mo_2Cp_2(\mu\text{-}SMe)_3(t\text{-}BuNC)_2](BF_4)$ (**1**) and *n*-BuLi (excess) in tetrahydrofuran was heated under reflux for 14 h. The reaction was then deemed complete, and ^1H NMR showed that a single diamagnetic organometallic species **2** had been formed in approximately 95% yield (eq 1). Further spectroscopic study of the isolated material confirmed that the cationic compound **1** had undergone dealkylation at one of its two isocyanide ligands.[9] The formulation of **2** as a cyano complex was confirmed by X-ray analysis of a single crystal of the monohydrate of **2**, obtained from a cooled CH_2Cl_2−pentane solution (Figure 1).[10] The Mo−



1 **2** (1)

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(9) Full details of the synthesis and characterization of compounds **1**−**3** are provided as Supporting Information.

10.1021/om030447r CCC: $25.00
Publication on Web 09/11/2003

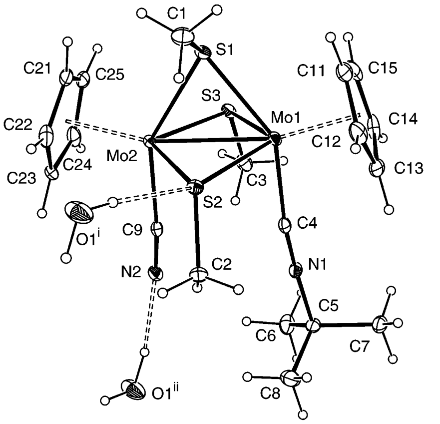
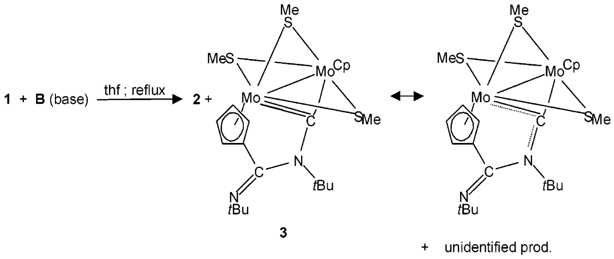


Figure 1. View of the structure of $[Mo_2Cp_2(\mu\text{-}SMe)_3(t\text{-}BuNC)(NC)]\cdot H_2O$, $(\mathbf{2})\cdot H_2O$. Selected distances (Å) and angles (deg): Mo1−Mo2 2.804(1), Mo1−C4 2.093(4), C4−N 1.150(5), N1−C5 1.461(5), Mo2−C9 2.145(4), C9−N 1.151(5), Mo1−C4−N1 173.5(3), Mo2−C9−N2 173.9(3), C4−N1−C5 176.1(4), S2···O1^i 3.415(5), S2···H−O1^i 170(6), N2···O1^{ii} 2.868(5), N2···H−O1^{ii} 170(6). Here and in Figure 2 broken lines indicate hydrogen bonds or Mo−Cp(centroid) vectors, 20% probability ellipsoids are shown, and hydrogen atoms are drawn as spheres of arbitrary radius. Symmetry code: (i) x, $1 + y$, z; (ii) $1 - x$, $1 - y$, $-z$.

C(isocyanide) bond [2.093(4) Å] in **2** is slightly shorter than the Mo−C(cyano) bond [2.145(4) Å], possibly reflecting electron release from the *t*-Bu group. Both are a little longer than comparable Mo−C bond lengths [2.02(2)−2.09(3) Å] in the binuclear compound $[(bpy)(t\text{-}BuNC)_4Mo(\mu\text{-}CN)Mo(t\text{-}BuNC)_4(bpy)](PF_6)_3$.[11] Slight departures from linear coordination at the isonitrile C4 and N1 and cyano C9 atoms of **2** [Mo1−C4−N1 = 173.5(3)°, C4−N1−C5 = 176.1(4)°, Mo2−C9−N2 173.9(3)°] probably arise as much from intramolecular overcrowding as from differential back-bonding into the π^*(NC) orbitals.[12] C−N bond distances in **2** [1.155(5) and 1.153(5) Å] are close to the values expected for a C≡N triple bond.[13]

Dealkylation involves ejection of a *t*-Bu group, most probably as the radical Me_3C^+, whose the stability is well known.[14] No attempt was made to determine the fate of the leaving *t*-Bu group. Indeed, cleavage of the N−C *single* bond of an isocyanide has previously been accomplished either by straightforward thermal decomposition of a cationic transition metal compound[11,15] or by thermolysis of ML_n complexes in the presence of excess isocyanide under both harsh[16] and mild[12,17] conditions. Although, the fate of the *tert*-butyl group has not been systematically determined in these previous works, the formation of either *tert*-butyl alcohol or isobutylene has been proposed. The dealkylation reaction in **1** is unusual in that it requires the presence of a base: R−NC cleavage did not occur when **1** was heated in neat THF.

Reaction of **1** with the base $(Me_4N)OH$ (in MeOH) or NaOH (suspension) again afforded compound **2**; however, an additional product **3** (eq 2) was also obtained.



(2)

B	2	3
$(Me_4N)OH$ (in MeOH)	73%	25%
NaOH (suspension)	53%	15%

The yields of **2** were markedly lowered (from 95% to 73−53%) when tetramethylammonium or sodium hydroxide was used in place of *n*-butyllithium. The formation of **3** may be related to the availability of molecules with the potential to act as ligands: thus, a potential donor, respectively MeOH or H_2O, is present when the base employed is $(Me_4N)OH$ or NaOH, whereas only nondonating hexane is present with *n*-BuLi. This conclusion is substantiated by the observation that the yield of **3** is noticeably increased when the reaction of **1** with base is conducted in the presence of a large excess of donating ligands (e.g., *t*-BuNC),[9] as shown in eq 3.

$$1 + \mathbf{B}\ (\text{base}) \xrightarrow[\text{thf ; reflux}]{t\text{BuNC (10 equiv.)}} 2 + 3 + \text{unidentified prod.} \qquad (3)$$

B	2	3
n-BuLi	47%	33%
$(Me_4N)OH$	41%	54%
NaOH	30%	69%

Complex **3** formally results from consecutive couplings of the terminal carbon atom of one isonitrile group with an η^5-cyclopentadienyl ligand and with the nitrogen atom of the second isocyanide ligand, all three reacting ligands being initially attached to one or another of the metal atoms of the Mo_2 core of **1**. The resulting formation of a μ-alkylidyne ligand through such a three-ligand condensation process is without precedent. It appears that the presence of excess donor molecules (MeOH, H_2O, RNC) differentially accelerates the **1** → **3** coupling reaction at the expense of the **1** → **2** dealkylation process (see eqs 2 and 3).

Complex **3** was characterized from spectroscopic[9] and X-ray diffraction studies.[18] The molecular structure (see Figure 2) demonstrates that a C5, originally the donor

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(10) Full details of crystallographic data of **2** are provided as Supporting Information.

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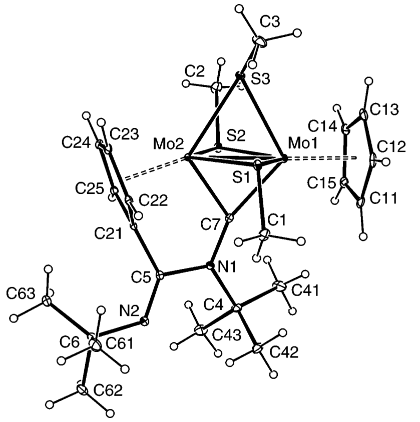
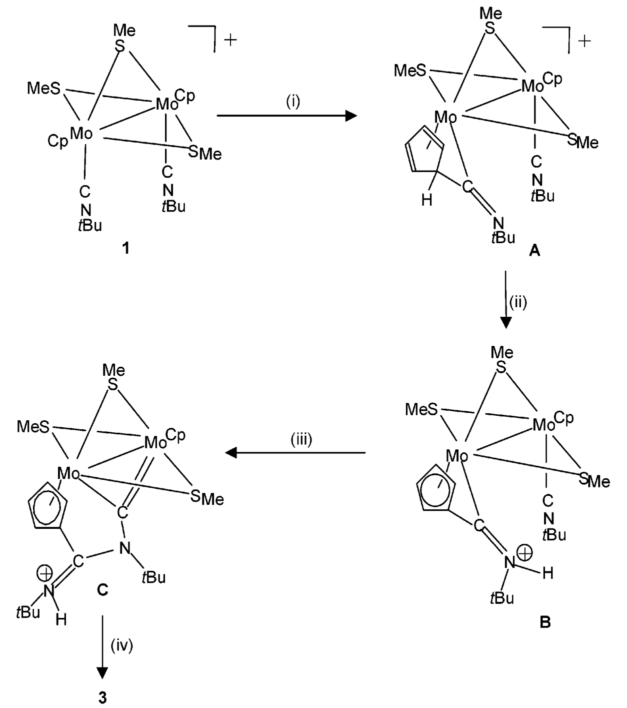


Figure 2. View of a molecule of [$Mo_2Cp(\mu\text{-}SMe)_3\{\mu\text{-}(\eta^5\text{-}C_5H_4)(t\text{-}BuN)CN(t\text{-}Bu)C\}$] (**3**). Selected bond lengths (Å) and angles (deg): Mo1−Mo2 2.584(1), Mo1−C7 2.117(2), Mo2−C7 2.006(2), C7−N1 1.361(2), N1−C4 1.516(2), N1−C5 1.448(2), N2−C5 1.263(2), N2−C6 1.479(2), Mo1−C7−N1 158.3(1), Mo2−C7−N1 124.2(1), Mo1−C7−Mo2 77.6(1).

atom of an isontrile, has detached from Mo and is now bonded through C21 to a cyclopentadienyl ring and through N1 to the second isonitrile ligand. The resulting μ-alkylidyne $\mu\text{-}(\eta^5\text{-}C_5H_4)(t\text{-}BuN)CN(t\text{-}Bu)C$ ligand uses C7 to bridge the two molybdenum atoms but also engages in a conventional η^5-cyclopentadienyl interaction with Mo2. The unsymmetrical relationship of the new ligand to the two Mo atoms leads to C7 being closer to Mo2 than to Mo1 [Mo−C7 2.117(2) and 2.006(2) Å]; the Mo2−C7 bond length agrees well with values of 1.994(2) and 1.996(2) Å in the symmetrical μ-alkylidyne complex [$Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}CCH_2\text{-}n\text{-}Pr)$] thought to contain Mo−C bonds on the order of 1.5 Å.[19] The quasi-chelating linkage of the μ-alkylidyne ligand to Mo2 also causes a narrowing of the Mo2−C7−N1 angle [124.2(1)°] at the expense of Mo1−C7−N1 [158.3(1)°]. The chain C6−N2−C5−N1−C7 shows pronounced bond length alternation [1.48, 1.26, 1.45, 1.36 Å], with respective torsion angles across N2−C5 and C5−N1 of 179° and 161°. The length of the Mo−Mo single bond in **3** [2.584(1) Å] is typical of values for other [$Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}X)$] complexes.[20] ^1H and $^{13}C\{^1H\}$ NMR data[9] for **3** are in accord with the formulation proposed by the X-ray study. In particular, the Mo-bound ^{13}C atom of the μ-alkylidyne moiety appeared at low field (δ 366.9), and a signal which could be assigned to an imine-like carbone (C=N−R) was detected at 149.1 ppm.

The novel reaction that gives rise to **3** may proceed through either an intramolecular or intermolecular path. The latter possibility is less likely since **3** was obtained by the action of base on **1** in the absence of excess of *t*-BuNC (eq 2). However, formation of **3** seems to be facilitated by donor ligands, since the presence of excess *t*-BuNC (see eq 3) led to significantly increased yields. Indeed, the reaction of **1** with BuLi in the presence of an excess of *t*-BuNC afforded **3** in 33% yields. As no intermediate has been detected, the mechanism of the reaction can only be a matter of speculation at present. However, there are precedents for several steps in the mechanism depicted in Scheme 1. The first step, after coordination of donating ligand L, involves stepwise 1,1-migration of a Cp carbon atom to the carbon of a RNC ligand to give the η^4-cyclopentadiene intermediate **A** and has analogies with the known migration of an η^1-Cp′ group (Cp′ = C_5H_5, C_5H_4Me, C_5Me_5) to a coordinated RNC ligand.[8,21] It is followed by a rapid 1,3-cyclopentadiene proton shift which yields iminium intermediate **B**. Further 1,2-migration of the new alkyl ligand to the second coordinated isocyanide group forms the μ-alkylidyne intermediate **C**; related isonitrile dimerization occurring via C,N-coupling reactions has been previously described.[6] Elimination of the iminium proton by reaction of **C** with a base finally gives **3**. This mechanism is consistent with the observations that base must be present in order to form **3** and that free donor is needed to initiate the process. The order of steps (with the exception of the first) cannot be assigned without further investigation. Finally, we emphasize that, although there are precedents for each of the two separate steps required for the insertion of two *t*-BuNC moieties into a Mo−C(Cp) bond, the combined coupling reaction is unprecedented and gives rise to a novel nitrogen-containing μ-alkylidyne ligand.

Scheme 1[a]



[a] L = *t*-BuNC, MeOH, H_2O; B = base (OH^-, *n*-Bu^-). (i) +L, 1,1-migration; (ii) 1,3-H migration, −L; (iii) 1,2-migration; (iv) +B, −BH.

Supporting Information Available: Synthetic, spectroscopic, and analytical data for **1**, **2**, and **3** and additionally for **2** and **3** tables giving details of the structure determinations, atomic parameters, and bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Full details of crystallographic data of **3** are provided as Supporting Information.

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