Inorganic Chemistry

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C−N Bond-Forming Self-Condensation of Amide Promoted by $MoCl_5$ at Room Temperature

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S Supporting Information

ABSTRACT: The acylamidinium complex $MoOCl_4[MeC(O)N(Ph)C(Me){=}NHPh]$ (**2**) was obtained by selective self-condensation of MeC(O)NHPh promoted by $MoCl_5$. Otherwise, the stable chloroiminium salt $[MoOCl_4\{HC(O)NMe_2\}][CH(Cl){=}NMe_2]$ (**3**) was isolated from $HC(O)NMe_2/MoCl_5$.

Early-transition-metal halides in high oxidation states are feasible materials for a huge number of metal-directed reactions.[1] In this context, the relevant oxophilicity of $MoCl_5$ (**1**) has been exploited for performing several transformations involving oxygen compounds, including the oxidative coupling of alkoxyarenes,[2] chlorination of alcohols, aldehydes, and epoxides,[3] N-acylation of sulfonamides,[4] acylative cleavage of ethers,[5] and C−C coupling.[6]

In spite of the interesting catalytic performances, the reactivity of **1** with limited amounts of oxygen species has not been exhaustively explored heretofore.[7] Actually, the good elucidation of this chemistry is complicated by the high moisture sensitivity of **1** and by the fact that organic substrates may be readily activated by coordination to **1** even at room temperature.[8,9] Somehow amazingly, the list of crystallographically characterized compounds, obtained by a simple Lewis base addition to **1**, is restrained to $MoCl_5(OPCl_3)$.[8c]

An improved knowledge of the direct interaction of **1** with oxygen donors may help the understanding and advancement of related catalytic processes. Moreover, some information about the mechanistic aspects of the long-time-known $MoCl_5$-catalyzed polymerizations of olefins or acetylenes may be achieved. Indeed, these processes were often reported to be associated with the presence of "oxygen promoters" (e.g., amides, ethers).[10] On the other hand, there is current interest for the metal-catalyzed activation of amides by transition-metal derivatives;[11] indeed, such organic species are the least reactive among a series of carbonylic compounds, and, for instance, the Lewis acidic $TiCl_4$[12] and MX_5 (M = Nb, Ta; X = F, Cl)[13] were reported to interact with amides, giving stable coordination adducts. In view of the above considerations, we decided to study the reactivity of **1** with small amounts of simple amides. Thus, molybdenum pentachloride reacted with a 2-fold excess of MeC(O)NHPh, in strictly anhydrous dichloromethane, affording an emerald-green solution after a few hours. The product of the reaction was identified as the paramagnetic [$\mu_{eff}(293\ K) = 1.60\ \mu_B$] molybdenum(V) adduct $MoOCl_4[MeC(O)N(Ph)C(Me){=}NHPh]$ (**2**).[14] The molecular structure of **2** is drawn in Figure 1.

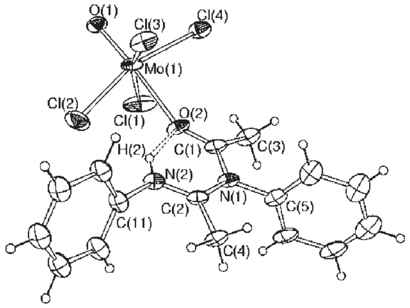


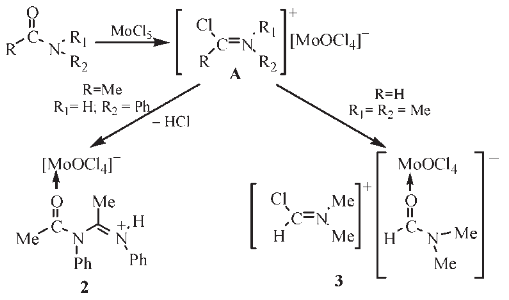
Figure 1. Molecular structure of **2**. Displacement ellipsoids are at the 30% probability level. Selected bond lengths (Å) and angles (deg): Mo(1)−O(1) 1.647(6), Mo(1)−O(2) 2.386(5), C(1)−O(2) 1.222(10), C(1)−N(1) 1.409(9), N(1)−C(2) 1.379(9), C(2)−N(2) 1.292(11); O(1)−Mo(1)−O(2) 174.8(3), O(2)−C(1)−N(1) 119.3(7), C(1)−N(1)−C(2) 123.2(7), N(1)−C(2)−N(2) 122.1(7).

The zwitterionic complex **2** consists of a cationic acylamidinium ligand $[MeC(O)N(Ph)C(Me){=}NHPh]^+$ coordinated to the $[MoOCl_4]^-$ anion. The molybdenum center displays a distorted octahedral geometry with the two O ligands in mutual trans positions [O(1)−Mo(1)−O(2) 174.8(3)°], analogous to that previously seen in the structurally characterized anion $[MoOCl_4(DMF)]^-$ (DMF = *N*,*N*-dimethylformamide).[15] The Mo(1)−O(1) [1.647(6) Å] and Mo(1)−O(2) [2.386(5) Å] interactions are considerably different: the former has double-bond character, whereas the latter is a single-coordination bond. The $[MeC(O)N(Ph)C(Me){=}NHPh]^+$ ligand displays bonding parameters similar to those found in the previously described acylamidinium salts $[HC(O)NHCH{=}NH_2][SbCl_6]$[16] and $[{}^tBuC(O)NHC({}^tBu){=}NH_2]_2[S_2O_7]$.[17] In particular, both C(1)−O(2) [1.222(10) Å] and C(2)−N(2) [1.292(11) Å] interactions are almost pure double bonds, while the O(2)−C(1)−N(1)−C(2)−N(2) core is nearly planar [mean deviation from the least-squares plane 0.0202 Å]. Interestingly, an intramolecular hydrogen bond is present between N(2)−H(2) and the molybdenum-bound O(2) [N(2)−H(2) 0.858(10) Å; H(2)···O(2) 1.83(5) Å; N(2)···O(2) 2.558(7) Å; N(2)−H(2)···O(2) 141(8)°].

The IR spectrum of **2** (solid state) reflects the X-ray features: a broad envelope absorption centered at 1618 cm^{-1} has been attributed to the stretching vibrations of the C=O[18] and C=N

Received: January 19, 2011
Published: March 31, 2011

Scheme 1. $MoCl_5$-Assisted Activation of Amides



bonds, whereas the band related to the Mo═O stretching falls at 986 cm^{-1}. In addition, a weak absorption at 3181 cm^{-1} may account for the N−H···O interaction. The UV−vis spectrum (CH_2Cl_2 solution) is in accordance with that available in the literature for molybdenum(V) oxochloro compounds.[8b,e,19]

The synthesis of **2** appears to be basically the result of a multistep process. Hence, chlorine−oxygen exchange between the molybdenum center and one MeC(O)NHPh molecule may take place first, affording the chloroiminium salt [C(Me)(Cl)═NHPh][$MoOCl_4$] (see compound **A** in Scheme 1).[20] Then, the chloroiminium cation would undergo nucleophilic attack by a second amide, possibly favored by preliminary coordination of the same amide to $[MoOCl_4]^-$. It is remarkable that mediation of the molybdenum species makes possible a coupling reaction that was never observed in the past, despite the fact that the chemistry of chloroiminium compounds with amides has been extensively explored.[21] The formation of the C−N bond to give **2** requires the release of HCl as a consequence of concerted cleavage of N−H and C−Cl bonds.

In order to collect evidence for formation of the supposed intermediate **A** (see Scheme 1), we treated **1** in CH_2Cl_2 with 1 equiv of MeC(O)NHPh. Thus, a dark-red solid was obtained upon removal of the solvent and analyzed by IR spectroscopy. The presence of intense absorption bands at 1674 cm^{-1} (C═N)[22] and 996 cm^{-1} (Mo═O)[9] agrees with the formation of **A**.[23] The absence of further absorptions in the carbonyl region indicates that activation of the amide C═O moiety has occurred to a complete degree. Coherent with the pathway depicted in Scheme 1, treatment of the dichloromethane mixture obtained from a 1:1 molar reaction of **1** with MeC(O)NHPh, with a second 1 equiv of amide, does yield a green solution of **2**.

The overall reaction leading to **2** is an unprecedented example of metal-assisted self-condensation of amide, giving an acylamidinium cation via activation of the C═O and N−H bonds. Four points deserve to be outlined: (a) couplings of amide fragments generally take place with C−C bond generation;[24] (b) to the best of our knowledge, the preparation of acylamidinium species by amide self-condensation was never reported before;[25] (c) in general, the amide C═O bond is hardly activated by transition-metal derivatives; (d) oxygen abstraction by $MoCl_5$ from carbonylic compounds was previously conjectured, but no unambiguous X-ray evidence has been provided until now.[8b]

In accordance with the pathway proposed for the 1:2 molar ratio reaction of **1** with acetanilide, the analogous reaction with N-disubstituted amide should stop at the stage of the chloroiminium salt. In fact, the absence of N-bound hydrogen atoms disfavors the C−N bond formation because of the impossibility to eliminate HCl. In order to investigate the point, we have studied the reactivity of **1** with DMF. The 1:2 molar reaction, performed in dichloromethane, afforded a green solution of [$MoOCl_4${HC(O)NMe_2}][CH(Cl)═NMe_2] (**3**).[14]

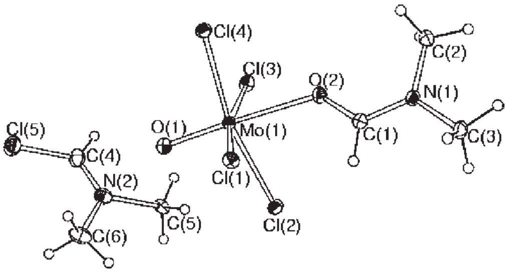


Figure 2. Structure of **3**. Displacement ellipsoids are at the 30% probability level. Selected bond lengths (Å) and angles (deg): Mo(1)−O(1) 1.662(3), Mo(1)−O(2) 2.234(3), O(2)−C(1) 1.246(5), C(1)−N(1) 1.317(5), N(1)−C(2) 1.455(5), N(1)−C(3) 1.467(5), Cl(5)−C(4) 1.673(5), C(4)−N(2) 1.259(6), N(2)−C(5) 1.536(6), N(2)−C(6) 1.472(6); O(1)−Mo(1)−O(2) 177.43(12), O(2)−C(1)−N(1) 123.5(4), C(1)−N(1)−C(2) 122.2(3), C(1)−N(1)−C(3) 120.9(3), C(2)−N(1)−C(3) 116.6(3), Cl(5)−C(4)−N(2) 122.8(4), C(4)−N(2)−C(5) 122.3(4), C(4)−N(2)−C(6) 123.5(4), C(5)−N(2)−C(6) 114.2(4).

The X-ray structure of the paramagnetic [μ_{eff}(293 K) = 1.62 μ_B] **3** is drawn in Figure 2.[14] It consists of $[MoOCl_4\{HC(O)NMe_2\}]^-$ anions[15] and chlorodimethyliminium $[CH(Cl){=}NMe_2]^+$ cations. The cation displays a distorted octahedral geometry, with HC(O)NMe_2 in the trans position with respect to Mo═O. The Mo(1)−O(1) [1.647(6) Å] and Mo(1)−O(2) [2.386(5) Å] interactions are in agreement with a double bond and a single bond, respectively.

The chlorodimethyliminium cation $[CH(Cl){=}NMe_2]^+$ (the Vilsmeier reagent) was formerly described[26,27] and has found vast application in synthetic chemistry.[21,28] The X-ray characterization is reported here for the first time; however, some related compounds have been structurally determined, e.g., [C(Me)(Cl)NH_2]Cl,[29] [C(Me)(Br)═NH_2]Br,[30] [C(Me)(Cl)═NH_2](15-crown-5)-[$TaCl_6$],[31] and [C(Ph)(Cl)═NC(Ph)(C_7H_{10})(Cl)][$SbCl_6$].[32] The C(4)−N(2) length [1.259(6) Å] is as expected for a double bond; otherwise, C(4)−Cl(5) [1.673(5) Å] is shorter than a single C(sp^2)−Cl bond,[33] thus indicating some π interaction.

The IR spectrum of **3** shows absorptions ascribable to the iminium moiety (1658 cm^{-1}), the coordinated amide (1634 vs 1679 cm^{-1} typical of uncoordinated HC(O)NMe_2[34]), and the Mo═O unit (971 cm^{-1}).

The 1:1 molar reaction of **1** with DMF in dichloromethane yielded, after workup, a dark-red solid showing strong IR absorptions at 1653 cm^{-1} (C═N)[22] and 998 cm^{-1} (Mo═O).[9] This evidence suggests the presumable formation of the salt [CH(Cl)═NMe_2][$MoOCl_4$] (see compound **A** in Scheme 1). The addition of a further 1 equiv of HC(O)NMe_2 results in the simple coordination of the amide to the metal, giving **3**. The lack of proton on the nitrogen atom of the HC(O)NMe_2 ligand in **3** prevents coupling with the iminium, at variance with that observed when MeC(O)NHPh was employed.

■ ASSOCIATED CONTENT

S Supporting Information. X-ray crystallographic data in CIF format, experimental procedures for the synthesis, and crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org. The supplementary crystallographic data for **2** (CCDC 794357) and **3** (CCDC 794358) can also be obtained free of charge, upon request, from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

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ACKNOWLEDGMENT

The authors thank the Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR, Roma), Programma di Ricerca Scientifica di Notevole Interesse Nazionale 2007−2008, for financial support.

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