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**Preliminary communication**

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# Unprecedented formation of a dihydropyridine dimer from carbon monoxide and pyridine mediated by a dioxodimesitylmolybdenum(VI) complex

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## Abstract

Pyridine solutions of $Mo(O)_2(mesityl)_2$ under a few atmospheres pressure of carbon monoxide at room temperature yield dimesityl ketone **1** (5%) and 1,1′-bis(mesitoyl)-1,1′,4,4′-tetrahydro-4,4′-bipyridine (**2**) (25%). These experiments show a rare example of a carbonylation reaction involving a dioxo molybdenum(VI) complex as well as an unprecedented *N*-acylation of a pyridine by CO mediated by a transition metal complex.

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Although there has been much studies of stoichiometric and catalytic carbonylation reactions of nitrogen compounds mediated by transition metal complexes, direct acylation of the nitrogen atom of a pyridine has not previously been reported. Moreover, most carbonylation reactions described up to now have involved low-valent complexes [1].

In continuation of our investigations of carbonylation of the new dioxo-alkylidene and -phosphonium-ylide-molybdenum(VI) complexes [2], we have studied the behaviour of dioxodimesitylmolybdenum(VI) (mesityl = $2,4,6\text{-}Me_3C_6H_2$). We report here our initial findings on the first example of a tetrahydro-4,4′-dipyridyl formation in a system involving $Mo(O)_2(mesityl)_2$, pyridine, and carbon monoxide.

When a pyridine solution (10 ml) of $Mo(O)_2(mesityl)_2$ (1 g, 2.7 mmol) is stirred for 48 h at room temperature under CO (3 atm), the initial yellow colour turns slowly to red. Removal of pyridine under vacuum yields an oily red residue which is stable in pyridine or dichloromethane but readily decomposes in less polar solvents such as toluene or n-pentane. Chromatography under nitrogen of either the red residue or of the toluene or n-pentane extracts on a silica gel column with an n-hexane/ether mixture as eluant, affords two major products (Scheme 1), while trace amounts of bimesityl are also formed.

The dimesityl ketone (**1**) (5% yield), was identified from its IR and $^{13}C$ NMR spectra by comparison with an authentic sample. For **2** (25% yield), the 200 MHz

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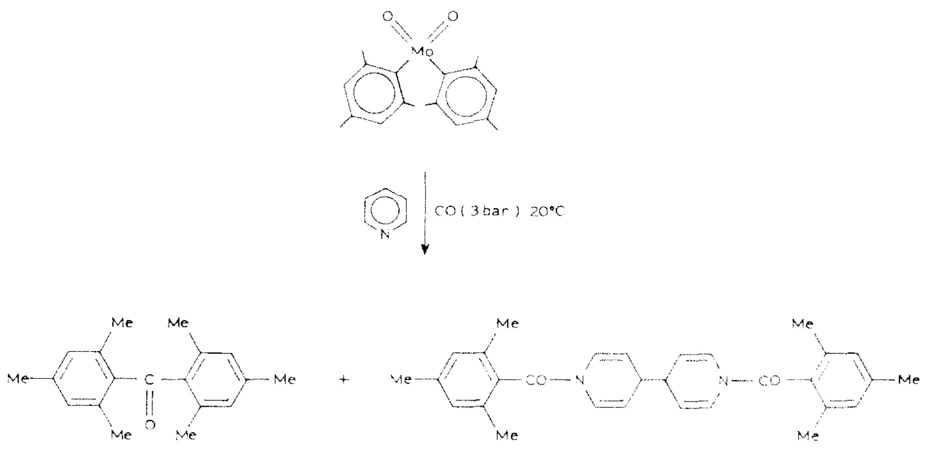


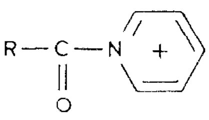
(1) (2)

Scheme 1

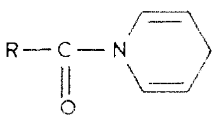
$^1$H NMR spectral data (including double resonance experiments) together with the 50.31 MHz $^{13}$C NMR spectral data (including two dimensional heteronuclear chemical shift correlation) showed it to be 1,1′-bis(mesitoyl)-1,1′,4,4′-tetrahydro-4,4′-bipyridine [3 *], a dihydropyridine dimer [7 *].

The formation of **1** is rather remarkable in itself, since carbonylation reactions involving $d^0$ complexes are less common than those involving low valent ones; it can be accounted for in terms of a reductive elimination after coordination and migratory insertion of carbon monoxide. The formation of **2** under the conditions used represents an unprecedented reaction. It can be seen to be the result of a reductive carbon monoxide pyridine acylation mediated by an arylmolybdenum(VI) complex. Although a detailed mechanism of such a reaction is still a matter of speculation, we believe that the overall process can be tentatively rationalized as follows.

The first step must be the coordination of carbon monoxide to a dioxodimesitylmolybdenum(VI) molecule, followed by a migratory insertion of CO into the metal–mesityl bond. In the absence of any possibility of oxidatively promoted or Lewis acid assisted migrations [9], it is conceivable that one effect of the Mo$^{VI}$ electron-demanding species might be to enhance the mesityl migration step since the CO group cannot π-bond strongly to the metal, and, another to promote the nucleophilic attack of the mesitoyl carbonyl by a pyridine molecule, giving rise, upon reductive elimination, to an acylpyridinium species (**3**) [10 *].



R = mesityl



(**3**) (**4**)

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* This and other references marked with asterisks indicate notes occurring in the list of references.

In the absence of an external nucleophile, a one-electron transfer to the sufficiently electrophilic acylpyridinium [11], from any reduced molybdenum species formed in the various reductive elimination steps occurring during the reaction, could account for the formation of an oxidized Mo species [12 *] and a pyridinyl radical (**4**). The dimerization of the latter would then generate **2** [13]. The high regioselectivity observed for **2** can be attributed to the bulk of the mesitoyl group attached at the nitrogen atom and to the greater thermodynamic stability of the 1,4-dihydropyridine structure [14].

These results are of interest on several grounds. In the first place this is the first account of a molybdenum(VI)-mediated *N*-acylation of pyridine with carbon monoxide. Furthermore, this reaction shows how critically the fate of the acyl function can depend on both the structure and the oxidation state of the metal [9], and it represents a novel type of CO activation since carbonylations involving $d^0$ metal complexes are rare except with the oxophilic early transition elements [15].

**Acknowledgement.** We thank Professor C. Roussel and Dr. L. Stella for helpful discussions.

## References and notes

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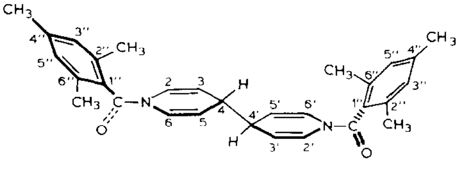
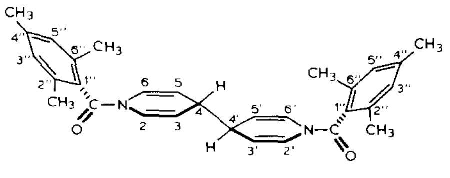
3 Isolated as yellow-orange solid, IR (KBr mull): $\nu$(CO) 1678 $cm^{-1}$, $\nu$(C=C) 1618 $cm^{-1}$; UV (95% ethanol): $\lambda_{max}$ 260 m$\mu$; m.p. 142° C (decomp.) **2** can be crystallized as white crystals from a toluene solution after n-pentane addition, as noted before for dimers of this kind [4]. Anal. Found: C, 79.2; H, 72; N, 5.9; O, 7.7. $C_{30}H_{32}N_2O_2$ calcd.: C, 79.6; H, 7.1; N, 6.2; O, 7.1%.
NMR numbering scheme:


*trans*-form


*cis*-form

$^1$H NMR ($CDCl_3$): $\delta$ (ppm) 7.44, 7.42 (dd, 2H, *J* 8.4, 2.1 Hz, H-2(2′)), 6.86, 6.84 (s, 4H, H-3″(5″)), 6.12, 6.11 (dd, 2H, *J* 8.4, 2.1 Hz, H-6(6′)), 5.09, 5.04 (ddd, 2H, *J* 8.4, 3.4, 2.4 Hz, H-3(3′)), 4.71, 4.65 (ddd, 2H, *J* 8.4, 3.3, 2.4 Hz, H-5(5′)), 3.07 (m, 2H, H-4(4′)), 2.30, 2.26, 2.16, 2.13, 2.04 (s, $CH_3$).
$^{13}$C $^1$H NMR ($CDCl_3$): $\delta$ (ppm) 167.23 (CO), 138.92, 138.74 (C-4″), 134.30, 134.23, 134.18, 134.10 (C-2″, C-6″), 131.63 (C-1″), 128.20, 128.26, 128.31 (C-3″, C-5″), 125.26, 125.19 (C-6, C-6′), 122.83, 122.88 (C-2, C-2′), 109.98 (C-3, C-3′), 108.07, 107.93 (C-5, C-5′), 40.26, 40.22 (C-4, C-4′) 21.02, 20.90 ($CH_3$-4″), 18.81 ($CH_3$-2″, $CH_3$-6″).
Hindered rotation about the amide bond in **2** can give rise to two diastereoisomers possibly in unequal amounts. For the $^1$H NMR spectrum this results in a large splitting of the adjacent ring protons, and, for most resonances, a fine structure is observed in resolution-enhanced $^1$H and $^{13}$C

NMR spectra obtained by the Gaussian Multiplication Technique [5]. Restricted rotation about the mesityl–carbonyl bond is also evident from the $^1$H NMR spectrum of the methyl group resonances. However, neither coalescence nor line broadening was observed in variable-temperature NMR experiments in pyridine-$d_5$ up to 110 °C, indicating a very high energetic barrier to rotation [6].

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10 When the reaction was run in pyridine-$d_5$, the $^{13}$C NMR spectrum of the solution analyzed immediately shows, besides of the mesityl groups and of the pyridine ring, a singlet at 177 ppm which can be tentatively assigned to a deshielded CO of an acylpyridinium ion (the same spectrum is obtained from a $CDCl_3$ solution of the red residue before workup).

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12 The exact nature and molecularity of the molybdenum complex present at the end of the reaction is unknown. Isolated as a red-brick solid insoluble in most solvents, gives a $^{13}$C NMR spectrum DMSO-$d_6$ which shows the presence of pyridine as the sole ligand. In view of its poor solubility and the strong absorptions at 955 and 735 cm$^{-1}$ in the IR spectrum, we think it may be a polymeric species with terminal and $\mu$-oxo bonds.

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