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# Carbonylmolybdenum complexes with di(imino)pyridine and related ligands: Reduction of a di(imino)pyridine to an aminoiminopyridine system under mild conditions

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## Abstract

The reactions of  $[Mo(CO)_6]$  towards a 2,6-di(imino)pyridine  $L^1$  and related ligands were studied. The reaction with  $L^1$  afforded two new complexes,  $[Mo(CO)_4L^1]$  (1) and  $[Mo(CO)_4L^2]$  (2), where  $L^2$  is the 2-amino-6-iminopyridine ligand arising from the hydrogenation of one imine function of  $L^1$ ; similar reaction with a 2-acetyl-6-iminopyridine ligand  $L^3$  afforded  $[Mo(CO)_4L^3]$  (3). Compounds 1, 2 and 3 have been fully characterised by IR, <sup>1</sup>H NMR and X-ray crystallography; they present a metal ion in a pseudo-octahedral environment, the three organic ligands acting with bidentate N<sub>2</sub> coordination modes. One of the imine functions in 1, the amine function in 2, and the ketone function in 3 are uncoordinated.

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Keywords: Carbonyl complexes; Molybdenum complexes; NNN ligands; Crystal structures

# 1. Introduction

It has long been known that 2,6-di(imino)pyridine derivatives form a large variety of molecular architectures when they are coordinated to metals [1]. In the last few years, this family of ligands has found a renewal of attention since some of their complexes act as active catalysts for olefin polymerisation [2]. In these coordination compounds, subtle variations on the ligand result in deep modification of catalytical activities. In this context, attempts to slightly modify the 2,6-di(imino)pyridine ligands were done and two convenient methods were described for 2-amino-6-iminopyridines either by exploiting attack by nucleophilic reagents at the imine carbon atoms [3] or complexation to trimethylaluminium and hydrolysis [4,5]. In the course of a general study related to the reactivity of a 2,6-di(imino)pyridine ligand (see L<sup>1</sup> Scheme 1) towards metal derivatives which could be precursors of magnetic compounds [6], we were interested in molybdenum carbonyl complexes. We report here the syntheses, crystal structures and NMR data of three new compounds resulting in UVirradiation or thermal reaction of  $[Mo(CO)_6]$  with di(imino) pyridine (L<sup>1</sup>) or acetyliminopyridine (L<sup>2</sup>) ligands. An alternative synthetic route for a 2-amino-6-iminopyridine ligand (L<sup>2</sup>) (without nucleophilic attack or complexation to trimethylaluminium) in complex **2** is presented (Scheme 1).

# 2. Experimental

## 2.1. General procedures

 $L^1$  was prepared according to the literature [7]; a slightly modified method was followed for  $L^3$  preparation. The  $L^1$ 

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Scheme 1.  $L^1$  and/or  $L^3$  ligands and syntheses of complexes 1 [Mo(CO)<sub>4</sub> $L^1$ ], 2 [Mo(CO)<sub>4</sub> $L^2$ ] and 3 [Mo(CO)<sub>4</sub> $L^3$ ]. R is the 2,6-diisopropylphenyl group; [Mo] = Mo(CO)<sub>4</sub>.

purity was carefully checked by <sup>1</sup>H NMR and no trace of L<sup>2</sup> was detected. All complexes were synthesised using standard Schlenck techniques under purified nitrogen; the solvents were freshly distilled and degassed just before use. For irradiation experiments, the UV lamp used was a Philips HPK 125-W mercury vapor lamp. Elemental analyses were performed by the "Service Central d'Analyses du CNRS", Gif-sur-Yvette, France. Infrared spectra were recorded on a Nicolet Nexus FT-IR instrument (KBr pellets). NMR spectra were recorded on a Bruker AMX 400 MHz.

# 2.2. Syntheses

## 2.2.1. Thermal syntheses of complexes 1 and 2

A stoichiometric mixture of  $[Mo(CO)_6]$  (548 mg; 2.08 mmol) and  $L^1$  (1.00 g; 2.08 mmol) was introduced in a Schlenck round-flask. THF (120 mL) was poured via cannulation and the mixture was refluxed for 48 h. THF was removed under reduced pressure, then the resulting crude red solid was dissolved into a minimum amount of diethylether. Chromatography on a column of silica gel with diethylether/hexane 2:1 as eluent gave, after evaporation, 2 as a bright red powder (270 mg; 0.39 mmol; yield: 19%). Complex 1 was eluted later as a second red band with the same eluent (140 mg; 0.20 mmol; yield: 10%). Some secondary products were not eluted. Compound 1: Anal. Calc. for  $C_{37}H_{43}MoN_3O_4 \cdot (CH_2Cl_2)_{0.25}$ : C, 62.9; H, 6.2; N, 5.9. Found: C, 62.9; H, 6.2; N, 6.1%. IR (KBr, cm<sup>-1</sup>): 2967 m, 2927 m and 2869 w ( $v_{CH}$ ); 2014 s, 1903 vs, 1883 vs and 1838 vs ( $v_{CO}$ ); 1648 m ( $v_{C=N}$ imine). Compound 2: Anal. Calc. for C37H45Mo-N<sub>3</sub>O<sub>4</sub> · H<sub>2</sub>O: C, 62.6; H, 6.7; N, 5.9. Found: C, 62.9; H, 6.7; N, 5.9%. IR (KBr, cm<sup>-1</sup>): 3367 m ( $v_{NH}$ ); 2965 s, 2926 m and 2867 w (v<sub>CH</sub>); 2010 s, 1898 vs, 1870 s and 1834 vs ( $v_{CO}$ ); 1608 m and 1587 m ( $v_{C=N}$  imine). For <sup>1</sup>H NMR data, see Table 1.

## 2.2.2. Exclusive synthesis of complex 1

*Method A:* A mixture of  $L^1$  (500 mg; 1.04 mmol) and [Mo(CO)<sub>6</sub>] (275 mg; 1.04 mmol) was stirred in THF (100 mL) under vacuum and left under UV-irradiation for 48 h. The THF was then removed by evaporation and the resulting solid treated as described above to give **1** as a pink crystalline powder (yield: 40%).

Method B:  $[Mo(CO)_6]$  (137 mg; 0.52 mmol) was heated for 48 h at 130–140 °C in acetonitrile (120 mL) to displace some carbonyl groups. After removal of the solvent, the crude product was suspended in THF (100 mL) and was then added by small fractions to a hot solution of L<sup>1</sup> (250 mg; 0.52 mmol) in THF (80 mL). The mixture was refluxed for 18 h, then the solvent was evaporated and the solid treated by chromatography as described above (yield: 70%).

## 2.2.3. Synthesis of complex 3

L<sup>3</sup> (575 mg; 1.78 mmol) and [Mo(CO)<sub>6</sub>] (472 mg; 1.79 mmol) were poured in a Schlenck round-flask. THF (80 mL) was added and the solution, which turned to purple after 15 mn, was refluxed at 80 °C for 48 h. The solvent was then removed under reduced pressure to give a crude red product which was dissolved into a minimum amount of dichloromethane. Chromatography on a column of silica gel with dichloromethane/hexane 4:1 as eluent gave, after evaporation, **3** as a red powder (450 mg; 0.85 mmol; yield: 48%). *Anal.* Calc. for C<sub>25</sub>H<sub>26</sub>MoN<sub>2</sub>O<sub>5</sub>: C, 56.6; H, 4.9; N, 5.3. Found: C, 56.1; H, 5.0; N, 5.0%. IR (KBr, cm<sup>-1</sup>): 2968 w, 2927 w and 2867 w ( $v_{CH}$ ); 2012 s, 1909 vs, 1881 vs and 1819 vs ( $v_{C=O}$ ); 1708 m ( $v_{C=O}$ ).

#### 2.3. X-ray structure analyses

Suitable crystals for X-ray studies were obtained from acetone  $(1 \cdot 2(CH_3)_2CO)$ , pentane for 2 and diethylether/

<sup>1</sup> H NMR data for complexes 1, 2 and 3 in CDCl <sub>3</sub>							
	$ \begin{array}{c} d \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $	$ \begin{array}{c} d \\ N \\ N \\ H_{e} \\ H_{e} \\ h_{b} \\ h_$	$ \begin{array}{c} & & \\ & & \\ & & \\ & a \\ & & \\ & b \\ & a \end{array} \begin{pmatrix} c \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\$				
	Ligand $L^1: C_{33}H_{43}N_3$	Ligand L <sup>2</sup> : C <sub>33</sub> H <sub>45</sub> N <sub>3</sub>	Ligand L <sup>3</sup> : C <sub>21</sub> H <sub>26</sub> N <sub>2</sub> O				
	$[Mo(CO)_4L^1](1)$	$[Mo(CO)_4L^2]$ (2)	$[Mo(CO)_4L^3]$ (3)				
$\delta_{a}$ and $\delta_{b}$ $\delta_{c}$	7.30–7.15 m (6H) 8.10 t (1H; ${}^{3}J_{\rm HH} = 8.6$ Hz)	7.30–7.13 m (6H) 8.05 t (1H; ${}^{3}J_{\rm HH} = 8.4$ Hz)	7.48–7.27 m (3H) 8.09 t (1H; ${}^{3}J_{HH} = 8.0$ Hz)				
$\delta_{\rm d}$ and $\delta_{\rm d'}$	7.90 d (2H; ${}^{3}J_{\rm HH} = 8.6$ Hz)	8.35 d (1H; ${}^{3}J_{HH} = 8.4$ Hz); 7.88 d (1H; ${}^{3}J_{HH} = 8.4$ Hz)	8.01 d (1H; ${}^{3}J_{HH} = 8.0$ Hz) 7.47 d (1H; ${}^{3}J_{HH} = 8.0$ Hz)				
$\delta CH(CH_3)_2$	3.00 h (4H; ${}^{3}J_{\rm HH} = 9.0$ Hz)	3.42 h (2H; ${}^{3}J_{HH} = 9.0$ Hz) 2.88 h (2H; ${}^{3}J_{HH} = 9.1$ Hz)	2.83 h (2H; ${}^{3}J_{\rm HH} = 8.0$ Hz)				
$\delta \operatorname{CH}(\operatorname{C}H_3)_2$	1.30 d (24H; ${}^{3}J_{\rm HH} = 9.0$ Hz)	1.20 d (imine) (12H; ${}^{3}J_{HH} = 9.1$ Hz) 1.36 d (3H; ${}^{3}J_{HH} = 9.0$ Hz) 1.33 d (3H; ${}^{3}J_{HH} = 9.0$ Hz) 1.14 d (3H; ${}^{3}J_{HH} = 9.0$ Hz) 1.06 d (3H; ${}^{3}J_{HH} = 9.0$ Hz)	1.36 d (6H; ${}^{3}J_{HH} = 8.0$ Hz) 1.09 d (6H; ${}^{3}J_{HH} = 8.0$ Hz)				
$\delta$ NCC $H_3$	2.40 s (6H)	1.65 d (3H; ${}^{3}J_{HH} = 8.9$ Hz) 2.29 s (3H)	2.32 s (36H)				
Others protons	_	H <sub>e</sub> 3.26 large (1H) H <sub>f</sub> 5.14 q (1H; ${}^{3}J_{HH} = 8.9$ Hz)	CH <sub>3</sub> C=O 2.87 s (3H)				

Chemical shifts ( $\delta$ ) quoted relative to TMS as an internal standard.

s: singlet; d: doublet; t: triplet; q: quadruplet; h: heptuplet; m: multiplet.

hexane 2/1 for 3. X-ray measurements have been carried out on an Oxford CCD (for 1 and 3) and on a Nonius Kappa CCD (for 2) diffractometer with Mo  $K_{\alpha}$  radiation (Table 2).

The measured intensities were reduced with CrysAlis RED [8] (for 1 and 3) and with DENZO [9] (for 2) programs. The structures were solved by direct methods with SIR92 [10] for 1 and 3 and SHELXS97 [11] for 2; refinements with full-matrix least-squares with SHELXL97 [11] based on  $F^2$ . All non-hydrogen atoms were refined with anisotropic thermal parameters. Both hydrogen atoms responsible for imine bond reduction in 2 were found on difference Fourier map and isotropically refined. Other not chemically significant hydrogens were placed in calculated positions and included in final refinements in a riding model. Crystallographic data and final discrepancy factors are gathered in Table 1. Molecular graphics were obtained from ORTEP-3 [12].

## 3. Results and discussion

# 3.1. Syntheses

Table 1

The stoichiometric reaction of hexacarbonylmolybdenum with  $L^1$  in refluxed THF afforded, after chromatography, two new compounds **1** and **2**. Both IR spectra display absorption bands of carbonyl ligands and coordinated iminopyridine ligand. For **2**, a supplementary absorption was pointed out at 3367 cm<sup>-1</sup>. It was assigned to a  $v_{\rm NH}$  vibration in agreement with the <sup>1</sup>H NMR spectrum which exhibited a large signal at  $\delta = 3.26$  ppm (Table 1); associated with the presence on the NMR spectrum of a signal at  $\delta = 5.14$  ppm (Table 1), these features indicate that one imine function of the di(imino)pyridine  $L^1$  ligand is hydrogenated to a secondary amine group generating a modified ligand  $L^2$  (Scheme 1). On the contrary, the IR and <sup>1</sup>H NMR data for 1 (Table 1) are consistent with the presence of the starting di(imino)pyridine  $L^1$  ligand with a bidentate coordination mode. In agreement with the elemental analyses, 2 was formulated as the tetracarbonyl complex  $[Mo(CO)_4L^2]$  and 1 as the unreduced complex  $[Mo(CO)_4L^1]$ ; these formulations were corroborated by the crystal structure determinations. It is worthy to note that derivative 1 was exclusively produced using either the thermal or the photochemical procedures described in the experimental part.

With the asymmetric acetyliminopyridine ligand  $L^3$  (Scheme 1), reaction towards [Mo(CO)<sub>6</sub>] afforded the new compound **3** for which <sup>1</sup>H NMR data (Table 1) clearly showed the presence of the starting ligand and not the corresponding acetylaminopyridine one. The spectroscopic data and the elemental analyses agreed with

Table 2
Crystal data and structure refinement for compounds $1 \cdot 2(CH_3)_2CO$ , 2 and 3

	$1 \cdot 2(CH_3)_2CO$	2	3
Empirical formula	C <sub>43</sub> H <sub>55</sub> MoN <sub>3</sub> O <sub>6</sub>	C37H45MoN3O4	C <sub>25</sub> H <sub>26</sub> MoN <sub>2</sub> O <sub>5</sub>
$M(\mathbf{g} \cdot \mathbf{mol}^{-1})$	805.84	691.70	530.42
Temperature (K)	170(2)	120(2)	170(2)
Crystal system, space group	monoclinic, $P2_1/c$ (14)	monoclinic, $P2_1/c$ (14)	monoclinic, $P2_1/c$ (14)
a (Å)	14.321(5)	11.1880(2)	12.089(5)
b (Å)	10.645(5)	16.5765(3)	14.140(5)
c (Å)	28.393(5)	18.8410(4)	15.859(5)
β (°)	98.002(5)	95.592(1)	115.427(5)
$V(Å^3)$	4286(3)	3477.6(2)	2448(2)
Z	4	4	4
$D_{\rm calc} ({\rm Mg}{\rm m}^{-3})$	1.249	1.321	1.439
Absorption coefficient $(mm^{-1})$	0.353	0.419	0.573
F(000)	1696	1448	1088
Crystal size $(mm^{-3})$	$0.78 \times 0.39 \times 0.10$	$0.18 \times 0.13 \times 0.08$	$0.24 \times 0.05 \times 0.05$
$\theta$ Range (°) for collection	3.36-29.18	1.018-30.508	3.19-23.25
hkl Ranges	-18 + 18, -13 + 9, -37 + 36	-15 + 15, -20 + 23, -25 + 25	-13 + 13, -15 + 15, -13 + 17
Reflections collected/unique $(R_{int})$	27070/8804 (0.0326)	14656/9056 (0.0411)	13662/3504 (0.058)
Data/restraints/parameters	8804/0/492	9056/0/414	3504/0/298
Final <i>R</i> indices $[I > 2\sigma(I)]^{a,b}$	$R_1 = 0.0358, wR_2 = 0.0756$	$R_1 = 0.0518, wR_2 = 0.1034$	$R_1 = 0.0378, wR_2 = 0.0586$
Goodness-of-fit on $F^2$	0.939	1.042	0.925
Largest difference peak, hole (e $Å^{-3}$ )	1.002, -0.268	0.613, -1.175	0.427, -0.326

 ${}^{w} R(F) = \Sigma ||F_{o}| - |F_{c}|/\Sigma |F_{o}|, Rw(F^{2}) = |\Sigma w(F_{o}^{2} - F_{c}^{2})^{2} / \Sigma |w(F_{o}^{2})^{2}|$  ${}^{b} w = 1/[\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP] \text{ with } P = (F_{o}^{2} + 2F_{c}^{2})/3.$ 

the formulation of **3** as the tetracarbonyl complex  $[Mo(CO)_4L^3]$ .

# 3.2. Crystal structures

Compounds 1, 2 and 3 crystallise in the monoclinic space group  $P2_1/c$  (Table 2). In the three cases, the asymmetric unit contains one molybdenum atom, four carbonyl groups and one organic ligand located on general positions; that of 1 also contains two molecules of acetone in

general positions. ORTEP drawing and selected bond lengths and angles are displayed in Figs. 1–3 and Table 3.

In compounds 1–3, the molybdenum cores exhibit pseudo-octahedral environments, the organic ligand acting with a bidentate N<sub>2</sub> coordination mode. Distortions of the octahedral environment mainly arise from (i) the usual *trans* influence induced by the donor nitrogen atoms of the L ligand (the MoC bond lengths in *trans* of L are *ca* 0.05-0.10 Å shorter than those in *trans* of a CO ligand)[13] and (ii) the usual bite of this ligand (N<sub>pyridine</sub>MoN<sub>imine</sub>



Fig. 1. Perspective drawing of the compound  $[Mo(CO)_4L^1]$  (1) showing the atom numbering. Thermal ellipsoids are drawn at the 40% probability level. Carbonyl bond lengths (Å): Mo–C(34) 2.058(3); C(34)–O(1) 1.138(3); Mo–C(35) 1.961(2); C(35)–O(2) 1.165(3); Mo–C(36) 2.012(3); C(36)–O(3) 1.154(3); Mo–C(37) 1.958(3); C(37)–O(5) 1.163(3).



Fig. 2. ORTEP representation of the asymmetric unit for compound  $[Mo(CO)_4L^2]$  (2). Thermal ellipsoids are drawn at the 30% probability level. Carbonyl bond lengths (Å): Mo–C(34) 2.018(3); C(34)–O(1) 1.157(4); Mo–C(35) 1.969(3); C(35)–O(2) 1.161(4); Mo–C(36) 2.057(3); C(36)–O(3) 1.141(4); Mo–C(37) 1.950(3); C(37)–O(4) 1.164(4).



Fig. 3. ORTEP representation of the asymmetric unit for compound  $[Mo(CO)_4L^3]$  (3). Thermal ellipsoids are drawn at the 40% probability level. Carbonyl bond lengths (Å): Mo-C(22) 2.027(5); C(22)-O(1) 1.142(4); Mo-C(23) 1.948(5); C(23)-O(2) 1.158(5); Mo-C(24) 1.933(5); C(24)-O(3) 1.164(4); Mo-C(25) 2.027(5); C(25)-O(4) 1.144(4).

Table 3 Selected bond lengths (Å) and bond angles (°) in  $1\cdot 2(CH_3)_2CO,\,2$  and 3

1 · 2(CH <sub>3</sub> ) <sub>2</sub> CO		2	2		3	
Mo-N(1)	2.304(2)	Mo-N(1)	2.314(2)	Mo-N(1)	2.279(3)	
Mo-N(2)	2.234(2)	Mo-N(2)	2.232(2)	Mo-N(2)	2.239(3)	
C(6) - N(2)	1.291(3)	C(6) - N(2)	1.289(4)	C(6) - N(2)	1.292(4)	
C(20)–N(3)	1.273(3)	C(20)–N(3)	1.465(4)	C(8)–O(5)	1.188(4)	
C(34)–Mo–N(1)	94.26(8)	C(34)-Mo-N(1)	91.5(1)	C(22)-Mo-N(1)	93.9(2)	
C(35)-Mo-N(1)	107.23(8)	C(35)-Mo-N(1)	109.6(1)	C(23)–Mo–N(1)	168.2(2)	
C(36)-Mo-N(1)	92.15(7)	C(36)-Mo-N(1)	92.9(1)	C(24)-Mo-N(1)	103.8(2)	
C(37)–Mo–N(1)	166.30(8)	C(37)–Mo–N(1)	164.7(1)	C(25)-Mo-N(1)	91.8(2)	
N(2)-Mo-N(1)	72.02(6)	N(2)–Mo–N(1)	71.58(8)	N(2)–Mo–N(1)	71.8(2)	

angles ca 72°) [6]. The Mo–N<sub>pyridine</sub> bond lengths are slightly longer (0.03–0.08 Å) than the Mo–N<sub>imine</sub> ones. In compounds **1–3**, the coordinated imine groups present essentially similar CN bond lengths (from 1.289(4) to 1.292(4) Å); it is worthy to note that coordination of the imine nitrogen atom does not deeply affect the CN<sub>imine</sub> bond length (1.273(3) Å for the uncoordinated imine function in **1**). On the contrary, structural data for **2** clearly show a strong difference between the CN<sub>imine</sub> (C(6)–N(2) 1.289(4) Å) and the C(20)–N(3) (1.465(4) Å) bond lengths. The later, which is in good agreement with those usually observed for Csp<sup>3</sup>–Nsp<sup>3</sup> bonds [14], indicates the change of the imine function into an amine function; examination of bond angles around C(20) (from 108 to 112°) corroborates this result.

In the three compounds, the system containing the pyridine ring and the coordinated imine group is essentially planar; the distance from the molybdenum atom to the mean plane is significantly greater in compounds 2 and 3 (0.50 and 0.43 Å, respectively) than in 1 (0.14 Å). In contrast to the essentially in-plane conformation of the coordinated iminopyridine systems, there is a marked deviation of the no co-ordinated groups from co-planarity with the pyridyl ring (the N1–C5–C20–N3 torsion angles are, respectively, 113.4 and 136.4° for 1 and 2) [5].

These features indicate that in complex 2 the bidentate  $L^2$  ligand possesses a *transoid* relationship between the imine and the amine groups similar to that observed in the free  $L^2$  unit [5] and therefore very different from the *cisoid* conformation associated with the tridentate coordination mode [15]; in compound 1, the  $L^1$  is also in such conformation relationship.

## 3.3. Discussion

Formation of compound **1** is in agreement with previous studies, which indicated that di(imino)pyridine reacts with hexacarbonylmolybdenum to afford tetracarbonyl complexes in which the organic ligand presents a bidentate coordination mode through the pyridine and one of the two imino nitrogen donor atoms [16,17]. The unexpected formation of compound 2, which includes an aminoiminopyridine ligand, is of interest because of the small number of examples of imine hydrogenation without CN bond cleavage. It corroborates the possibility of reduction of such ligand in mild conditions and it is likely that the solvent is the source of hydrogen. Such situation was clearly demonstrated in the cases of rhodium (I) complexes for which reduction of the two imine functions occurred when the reaction was carried out in acetonitrile/ethanol mixtures but was not observed in pure acetonitrile [18].

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## Appendix A. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 299799–299801. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax +44 1223 336 003; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2006.06.005.

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