

# Carbonyl complexes of manganese, rhenium and molybdenum with ethynyliminopyridine ligands

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Received 21 December 2005; received in revised form 21 April 2006; accepted 21 April 2006

Available online 29 April 2006

Dedicated to Prof. Víctor Riera on the occasion of his 70th birthday.

## Abstract

[MBr(CO)<sub>5</sub>] reacts with *m*-ethynylphenylamine and pyridine-2-carboxaldehyde in refluxing tetrahydrofuran to give, *fac*-[MBr(CO)<sub>3</sub>(py-2-CH=N-C<sub>6</sub>H<sub>4</sub>-*m*-(C≡CH))] (M = Mn, **1a**; Re, **2a**). The same method affords the tetracarbonyl [Mo(CO)<sub>4</sub>{py-2-CH=N-C<sub>6</sub>H<sub>4</sub>-*m*-(C≡CH)}] (**3a**) starting from [Mo(CO)<sub>4</sub>(piperidine)<sub>2</sub>]; and the methallyl complex [MoCl(η<sup>3</sup>-C<sub>3</sub>H<sub>4</sub>Me-2)(CO)<sub>2</sub>{py-2-CH=N-C<sub>6</sub>H<sub>4</sub>-*m*-(C≡CH)}] (**4a**) from [MoCl(η<sup>3</sup>-C<sub>3</sub>H<sub>4</sub>Me-2)(CO)<sub>2</sub>(NCMe)<sub>2</sub>]. The use of *p*-ethynylphenylamine gives the corresponding derivatives (**1b**, **2b**, **3b**, and **4b**) with the ethynyl substituent in the *para*-position at the phenyl ring of the iminopyridine. All complexes have been isolated as crystalline solids and characterized by analytical and spectroscopic methods. X-ray determinations, carried out on crystals of **1a**, **1b**, **2a**, **2b**, **3a**, **4a**, and **4b**, reveals the same structural type for all compounds with small variations due mainly to the different size of the metal atoms. The reaction of complexes **1a** or **2a** with dicobalt octacarbonyl affords the tetrahedrane complexes [MBr(CO)<sub>3</sub>{py-2-CH=N-C<sub>6</sub>H<sub>4</sub>-*m*-(μ-C≡CH)Co<sub>2</sub>(CO)<sub>6</sub>}] (M = Mn, **5**; Re, **6**), the structures of which have been confirmed by an X-ray determination on a crystal of compound **5**.

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**Keywords:** Ethynyliminopyridines; Carbonyl complexes; π-acetylene

## 1. Introduction

Complexes with diimine ligands are object of current interest because of their potentially useful electrochemical, spectroscopic or photochemical properties [1]. Among these, iminopyridines derived from the condensation of pyridine-2-carboxaldehyde with a primary amine are attractive because of their electronic properties which are intermediate between those of the more classic, ubiquitous bipyridine or phenanthroline [2], and the more flexible diazabutadienes [3]. Imino pyridines have been employed recently as multidentate ligands [4], and to prepare polynuclear complexes [5]. There is also interest in the use of imi-

nopyridine ligands having additional functions such as ester [6] or hydroxo [7], capable to anchor them to polymers [8] or biological molecules [9]. On the other hand, more classic complexes of Mn(II), Ni (II) and Fe(II) and other cations with functionalized iminopyridines have been reported to exhibit very interesting properties such as spin crossover [10], second order non-linear optical properties [11], luminescence [12], or mesogenic behavior [13]. Complexes of ions having d<sup>6</sup> configuration such as Mn(I), Re(I) or Mo(0); or d<sup>4</sup>, such as Mo(II) containing chelate N-donors such as bipy or phen have proved to undergo interesting reactivity in insertion of unsaturated molecules into metal alkoxy and metal-amido bonds [14]. We considered interesting to explore the chemistry of these metals with iminopyridines, and we have reported recently the preparation of molybdenum complexes with chelating iminopyridines bearing an additional carboxylate function

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capable to establish supramolecular interactions in the solid state [15]. The availability of commercial *meta*- and *para*-ethynylanilines prompted us to explore its use to introduce an additional ethynyl function. We report here the preparation of Mn, Re, and Mo complexes containing iminopyridine ligands functionalized with an additional ethynyl group, and their reactivity towards dicobalt octacarbonyl.

## 2. Results and discussion

Manganese and rhenium complexes containing *meta*-ethynyl-phenyliminopyridine ligands were obtained by one-pot reactions by heating  $[M(CO)_5Br]$  ( $M = Mn, Re$ ) with equimolar quantities of pyridine-2-carboxaldehyde and *m*-ethynylphenylamine in THF at reflux temperature (Scheme 1).

After workup, complexes *fac*- $[M(CO)_3\{py-2-CH=NC_6H_4-m-(C\equiv CH)\}]$  ( $M = Mn$  (**1a**),  $Re$  (**2a**)) were isolated as red solids in good yields (see Section 3). Similarly, the tetracarbonyl complex  $[Mo(CO)_4\{py-2-CH=NC_6H_4-m-(C\equiv CH)\}]$  (**3a** in Scheme 1) can be obtained from  $[Mo(CO)_4(pip)_2]$  via replacement of two piperidine ligands; and the dicarbonyl complex  $[Mo(CO)_2Cl(\eta^3-C_3H_4-Me-2)\{py-2-CH=NC_6H_4-m-(C\equiv CH)\}]$  (**4a** in Scheme 1) by substitution of two acetonitrile ligands from  $[MoCl(\eta^3-C_3H_4-Me-2)(NCMe)_2]$ . Starting from *p*-ethynylaniline, the same method afforded the corresponding compounds **1b**, **2b**, **3b** and **4b**, containing *p*-ethynyliminopyridine, as summarized in Scheme 1.

The new complexes were characterized by analytical and spectroscopic methods and their structures were determined by X-ray crystallography for **1a–b**, **2a–b**, **3b**, and **4a–b**. Crystal data and refinement details are collected in Table 1, and thermal ellipsoid plots are presented in Figs. 1–4.

Table 2 summarizes the relevant distances and angles for all complexes together for a better comparison. Bromotri-

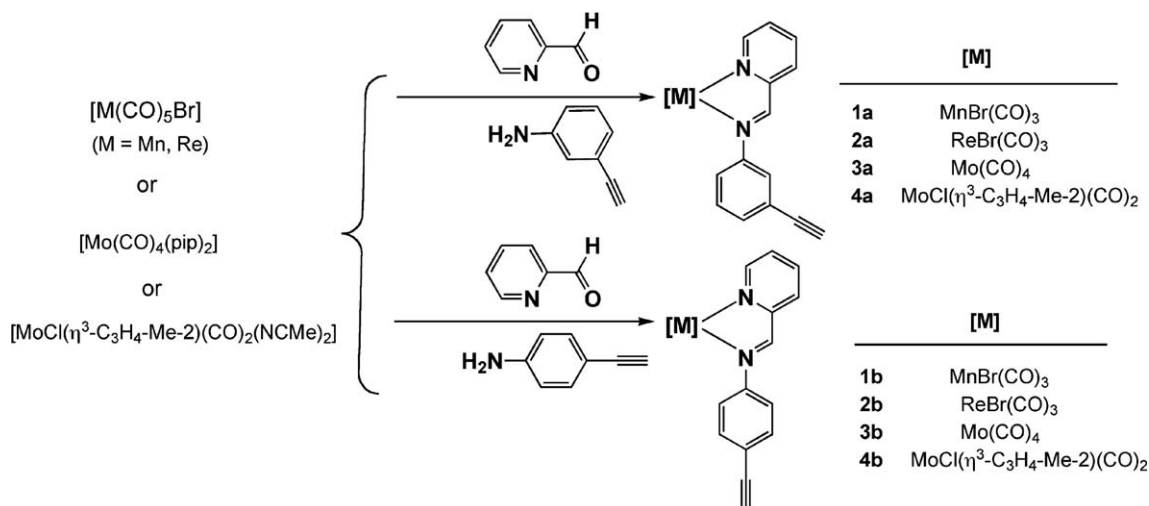
carbonyl compounds **1a** ( $M = Mn$ ) and **2a** ( $M = Re$ ) bearing 3-ethynylphenyliminopyridine are isostructural, as can be noticed from the plots in Fig. 1, and from the geometrical parameters in Table 2.

The same occurs to the pair **1b** and **2b** containing *p*-ethynylphenyliminopyridine (see Fig. 2). In fact the coordination environments of the metals in the four complexes are quite similar. The main distortion from the ideal octahedral geometry arises from the small bite angle  $N(1)-M-N(2)$  of the iminopyridine which falls in the range  $74.5(2)-78.47(16)^\circ$ . They all display the expected *facial*-tricarbonyl arrangement, with the chelate iminopyridine and bromo ligands in the opposite face of the octahedron. This geometry derives from the *cis*-labilization effect of Br directing the substitution of carbonyl ligands from  $[MnBr(CO)_5]$  [16].

The structure of the tetracarbonyl molybdenum complex **3b** (Fig. 3) is very close to those of the tricarbonyls **1a–b** and **2a–b**, with the Mo atom in an octahedral environment in which the main distortion is again the small bite angle of the iminopyridine ligand [ $72.48(7)^\circ$ ]. Methallyldicarbonyl molybdenum complexes **4a–b** display pseudooctahedral coordination geometry, with the distortions imposed by the diimine and the methallyl ligands (Fig. 4).

There is a consistent and significant variation of the  $M-X$ ,  $M-N$ , and  $M-C$  distances on passing from Mn to Re and (where applicable) to Mo complexes. This pattern has been observed for other families of complexes [17], and correlates well with the size of the metal center, estimated from their metallic radii (Mn 1.18 Å, Re 1.28 Å, Mo 1.30 Å [18]).

The spectroscopic properties of the complexes in solution correlate well with their solid state structures. IR spectra in dichloromethane display (see Table 3) the expected patterns of three active  $\nu(CO)$  normal modes for the tricarbonyls **1a–b**, and **2a–b**; four active  $\nu(CO)$  normal modes for the tetracarbonyls **3a–b**, and two active  $\nu(CO)$  normal modes for the dicarbonyls **4a–b** [19].



Scheme 1.

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