

Synthesis, characterization and olefin hydroformylation reactions of *mer*-[Mo(CO)₃(*p*-C₅H₄N-CN)₃]

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Abstract *Mer*-[Mo(CO)₃(*p*-C₅H₄N-CN)₃] was prepared by UV-irradiation of a THF solution of Mo(CO)₆ and *p*-cyanopyridine under heating. The complex was characterized by FT-IR, MS, ¹H and ¹³C NMR and showed catalytic activity for olefin hydroformylation (1-hexene, cyclohexene and 2,3-dimethyl-2-butene as model olefins; 600 psi synthesis gas (pCO/pH₂ = 1); 100 °C; 24 h; toluene). An examination of the complex catalyzed hydroformylation of a real naphtha cut (El Palito refinery, Venezuela), under the same conditions, also showed activity in the conversion to oxygenated products.

Introduction

In recent years, there has been an upsurge of interest in catalysis by transition metal organometallic complexes [1–3]. In this sense, one of the obvious aspects to investigate is the choice of metal centre. Among the transition metals, molybdenum is often useful since its coordination and organometallic chemistry are among the most varied, complex and interesting among the transition metals. Surprisingly, however, there have only been a few reports concerning the use of Mo complexes in such reactions [4–6]. Recently, our group reported the synthesis of *trans*-[Mo(CO)₄(*p*-PySO₃Na)₂] [7], a catalytic precursor that was evaluated for the biphasic hydroformylation of a variety of olefins and light naphtha cuts [8]. In this work, we report

the synthesis, characterization and catalytic hydroformylation reactions of a new Mo complex, *mer*-[Mo(CO)₃(*p*-C₅H₄N-CN)₃].

Experimental

Materials and methods

Mo(CO)₆ (Strem); *p*-cyanopyridine, 1-hexene, cyclohexene and 2,3-dimethyl-2-butene (Aldrich) were all used without further purification. Ar, CO, H₂ (Gases Industriales de Venezuela) were obtained commercially and used as received. THF, toluene and other organic solvents were purified as described in the literature [9].

Synthesis of *mer*-[Mo(CO)₃(*p*-C₅H₄N-CN)₃]

A solution of Mo(CO)₆ (0,500 g, 1.90 mmol) in THF (15 mL) was irradiated with an UV lamp for 4 h (PASCO Scientific Model OS-9286 Mercury Vapor Light Source, 115 V, 30 W). To the resultant, dark yellow solution was added dropwise a solution of *p*-cyanopyridine (0,600 g, 5.8 mmol) in THF (10 mL), giving after 2 h of UV irradiation a dark brown solution. This was heated to 50 °C, in the absence of UV light, for 118 h to yield a dark brown precipitate. Sublimation, under vacuum, at 50 °C followed by washing with diethyl ether gave the desired air-stable product (yield 80%, decomposes at 90 °C, soluble in H₂O, DMSO, THF and toluene; partly soluble in chloroform).

Physical measurements

Vibrational spectra (5,000–400 cm⁻¹, KBr pellet) were taken with a Fourier Transform Perkin-Elmer 1725X

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spectrophotometer. Room temperature ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded as $\text{DMSO-}d_6$ solutions using a Bruker Avance DRX 400-MHz spectrometer. Chemical shifts are expressed in ppm downfield from external TMS. Mass spectra (EI) were obtained on a Hewlett-Packard 5988 GC/MS spectrometer.

Catalytic runs

Catalytic trials were performed in a 125 mL Parr reactor with internal glass liner, heating unit, temperature and stirring control and sampling valve. Conditions for a typical trial were toluene (60 mL), olefin or olefin mixtures (1 mL), Mo complex (4.0 mg, 8.1×10^{-3} mmol), substrate/catalyst = *ca.* 1,000:1, H_2 pressure (300 psi), CO pressure (300 psi), temperature (50, 100 y 120 °C), 1,600 rpm, 24 h reaction time. Reaction products were analyzed with a Perkin-Elmer Autosystem GC, using a 3-m column (0.6 cm diameter) of 10% tricresyl phosphate on Chromosorb P (80–100 mesh), with H_2 carrying gas and a TC detector.

Results and discussion

The FTIR spectrum of $\text{mer-}[\text{Mo}(\text{CO})_3(\text{p-C}_5\text{H}_4\text{N-CN})_3]$, shows three sharp bands, at 2,072 (w), 1,927 (s) and 1,880 (s) cm^{-1} , assigned to the $\text{C}\equiv\text{O}$ groups bonded to the Mo center. One sharp band observed at 2,224 cm^{-1} (w) is assigned to the stretching $\text{C}\equiv\text{N}$ from the cyano groups on the pyridine rings and two broad bands at 1,675 (s) and 1,608 (m) cm^{-1} are associated with the vibrations of the $\text{C}=\text{N}$ and $\text{C}=\text{C}$ groups of the pyridine rings. By comparing the above results with the FTIR spectrum of the free cyanopyridine, it is observed that the bands assigned to the vibrations of the $\text{C}=\text{N}$ and $\text{C}=\text{C}$ groups of the cyanopyridine are shifted by 45 and 15 cm^{-1} , respectively, upon coordination to the metal center, whereas those corresponding to the $\text{C}\equiv\text{N}$ group remained unaltered, therefore suggesting bonding through the pyridyl nitrogen instead of the cyano nitrogen. We therefore propose a six coordinated structure (ideal C_{3v} symmetry, see Fig. 1a) for the complex. Another argument that supports our proposition comes from simple group theory comparison of the $\nu(\text{CO})$ modes of the *mer*-complex with the alternative *fac*- isomer. For the *mer*-isomer, three ν_{CO} ($2a_1 + b_2$) IR active bands are predicted as shown for analogous Mo complexes, whereas for the *fac*-isomer two CO stretching bands are expected for three mutually *cis* carbonyl groups [10].

The ^1H NMR spectrum of the complex presents two major groups of resonances (see Fig. 1a) at δ 8.99 (*d*, 4.8 Hz, H_c) and 7.89 (*d*, 4.8 Hz, H_d) ppm assigned to the *o*- and *m*-pyridine protons of the equatorial 4-cyanopyridine

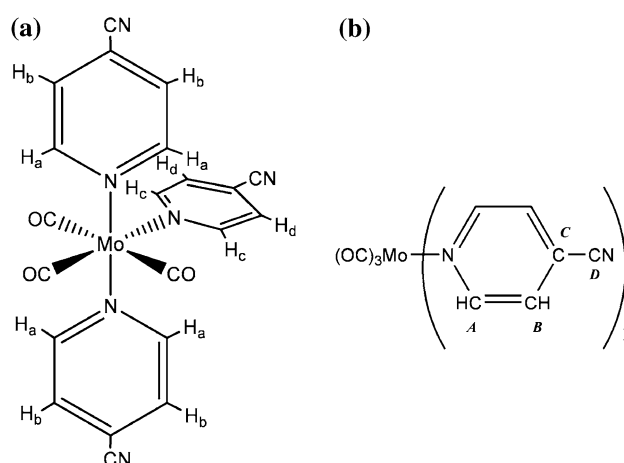


Fig. 1 Proposed structure for complex (1), $\text{mer-Mo}(\text{CO})_3(\text{p-C}_5\text{H}_4\text{N-CN})_3$ according to **a** ^1H -NMR and **b** ^{13}C -NMR

ligand and at 8.85 (*d*, 4.8 Hz, H_a) and 7.76 (*d*, 4.8 Hz, H_b) ppm assigned to the *o*- and *m*-pyridine protons of the two axial 4-cyanopyridine ligands. The ^{13}C NMR (Fig. 1b) shows peaks corresponding to CH carbon atoms rings at δ 155.3 (C_A) and 150.4 (C_B) ppm, one peak assigned to the quaternary carbon atom at 149.8 ppm (C_C) and one peak assigned to the cyano group carbon at 124.9 ppm (C_D).

The positive ion mass spectrum shows an ion at m/z 492, assigned to the molecular ion $[\text{Mo}(\text{CO})_3(\text{p-C}_5\text{H}_4\text{N-CN})_3]^+$. In the range m/z 490–497, the spectrum displays a series of peaks that are consistent with the isotopic pattern of Mo calculated with the Sheffield Chemputer program (<http://winter.group.shef.ac.uk/chemputer/>). Three major ions are also observed among them corresponding to successive losses of CO, a typical behavior of metallic carbonyl compounds, assigned to the fragments $[\text{Mo}(\text{CO})_2(\text{p-C}_5\text{H}_4\text{N-CN})_3]^+$ (m/z 464), $[\text{Mo}(\text{CO})(\text{p-C}_5\text{H}_4\text{N-CN})_3]^+$ (m/z 436) and $[\text{Mo}(\text{p-C}_5\text{H}_4\text{N-CN})_3]^+$ (m/z 408). Likewise, the loss of cyanopyridine ligands is evidenced by two peaks at m/z 304 and 200, corresponding to the fragments $[\text{Mo}(\text{p-C}_5\text{H}_4\text{N-CN})_2]^+$ and $[\text{Mo}(\text{p-C}_5\text{H}_4\text{N-CN})]^+$. Exploration of an area up to m/z 2000 shows no evidence of the presence of metal clusters.

Finally, the analysis of the spectroscopic evidence and the proposed *mer*-structure are consistent with both the minimum energy structure and the carbonyl groups frequencies calculated for this complex with PC Spartan Plus software [11] using the method RHF/PM3D, basis functions 141, 75 shells: 43 s shells, 31 p shells, 1 5 D shell, No. electrons 150.

Hydroformylation reactions

At 100 °C and 600 psi of total pressure ($\text{pCO}/\text{pH}_2 = 1$), $\text{mer-}[\text{Mo}(\text{CO})_3(\text{p-C}_5\text{H}_4\text{N-CN})_3]$ catalyses the hydroformylation of different olefins, namely 1-hexene, 2,3-

Table 1 Hydroformylation of organic substrates with *mer*-[Mo(CO)₃(p-C₅H₄N-CN)₃]

Substrate/solvent	Conversion (%)	Selectivity (%)
1-hexene/toluene	95	<i>n</i> -heptanal (59) 2-methylhexanal (33) 2-ethylpentanal (8)
1-hexene/ <i>n</i> -heptane	60	<i>n</i> -heptanal (55) 2-methylhexanal (32) 2-ethylpentanal (13)
2,3-dimethyl-2-butene/toluene	17	2,2,3-trimethylbutanal (42) 2,2,3-trimethylbutanol (58)
Cyclohexene/toluene	12	Cyclohexanecarboxaldehyde (60) Cyclohexylmethanol (40)
Naphtha ^b	15 ^a	Oxygenated products (32)

Substrate: 1.0 cm³, solvent: 30 cm³, Catalyst: 4.0 mg total pressure: 600 psi, ratio P_{CO}/H₂ = 1/1, stirring: 1,600 rpm, T: 100 °C, time: 24 h

^a Calculated from the total initial content of olefins present in the naphtha

^b No-solvent

dimethyl-2-butene, cyclohexene and of a real naphtha cut from a refinery. As shown in Table 1, for 1-hexene as substrate the highest conversion yield is reached in toluene (95%) and the products obtained are the linear isomer *n*-heptanal (major product), the branched aldehydes 2-methyl-hexanal and 2-ethyl-pentanal (minor product), the latter being a hydroformylation product of 2-hexene (itself produced from an initial isomerization of 1-hexene). The selectivity toward these products remains near constant in heptane. Regarding the other olefinic substrates, the favorable alcohol formation over the aldehyde product is rationalized by considering additional reduction of the initially produced aldehyde, a process that is probably favored by thermodynamics. Additionally, hydroformylation experiments performed either in the absence of the complex or in the presence of Mo(CO)₆ show no catalytic activity. One of our goals in this study was to evaluate the Mo catalytic system in the hydroformylation reaction of the complex olefinic mixture present in a real naphtha cut, in order to partially reduce its olefin content and to produce in situ oxygenated compounds, therefore improving gasoline formulations. The result obtained after testing the new complex in the hydroformylation of naphtha, shows evidence for the production of a variety of oxygenated compounds, mainly aldehydes and alcohols.

Conclusions

The new molybdenum complex *mer*-[Mo(CO)₃(p-C₅H₄N-CN)₃] was synthesized and characterized by spectroscopic techniques. Under moderate reaction conditions, this complex catalyses the hydroformylation of olefins such as 1-hexene in toluene to give the expected oxo-products. The

system favors the production of linear aldehydes and some alcohols, and the substrates showed the following reactivity order: 1-hexene > cyclohexene > 2,3-dimethyl-2-butene and real naphtha. The reactivity exhibited with the real naphtha shows promising results that could be an indication of the potential of this catalytic system to improve gasoline quality.

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