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# Seven-Coordinate Molybdenum(II) Carbonyl Complexes Containing Two Different Bidentate Ligands (2,2′-Bipyridyl and $Ph_2PCH_2PPh_2$ or $Ph_2PCH_2CH_2PPh_2$)

FRANCISCO J. ARNAÍZ, CARLOS S. BARTOLOMÉ, GABRIEL GARCÍA* and MERCEDES PÉREZ

*Departamento de Química Inorgánica, Colegio Universitario de Burgos, 09002 Burgos, Spain*

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## Abstract

The complexes $MoX_2(CO)_3(bipy)$ (X = Cl, Br, I) undergo substitution of a single CO ligand by $Ph_2PCH_2PPh_2$ (dppm) and $Ph_2PCH_2CH_2PPh_2$ (dppe) to give seven-coordinate complexes $MoX_2(CO)_2(bipy)(L–L)$ (X = Cl, Br, I; L–L = dppm, dppe). Spontaneous isomerization to $[MoX(CO)_2(bipy)(dppm)]X$ was observed for X = I in dichloromethane at room temperature. However $MoCl_2(CO)_2(bipy)(dppm)$ led to $MoCl_2(CO)(bipy)(dppm)$ by sunlight irradiation. The cationic species $[MoX(CO)_2(bipy)(L–L)]BPh_4$ (X = Cl, Br; L–L = dppm and X = Cl, Br, I; L–L = dppe) were also prepared by use of $NaBPh_4$. Reactions of $MoX_2(CO)_3(bipy)$ (X = Cl, Br) with dppe in molar ratios 2/1 (complex/ligand) afforded the slightly soluble compounds formulated as dimers, $Mo_2X_4(CO)_4(bipy)_2(\mu\text{-dppe})$. We also report the possibility of preparing $MoCl_2(CO)_3(bipy)$ by direct halogenation of $Mo(CO)_4(bipy)$ at room temperature in dichloromethane.

## Introduction

The complexes of Mo(II) and W(II) have received considerable attention recently not only with regard to their reactivity [1] but also for the seven-coordination displayed by these compounds [2, 3]. In a previous paper [4] we have reported several mono and dicarbonyl complexes of Mo(II) containing 2,2′-bipyridyl (bipy) and bis(diphenylphosphino)methane (dppm) as bidentate ligands. In order to further investigate on complexes containing two different bidentate ligands, we have explored in this work the reactions of $MoX_2(CO)_3(bipy)$ (X = Cl, Br, I) with both 1,2-bis(diphenylphosphino)ethane (dppe) and dppm.

## Experimental

All preparations were carried out under nitrogen or argon following conventional Schlenk techniques. Solvents were dried and degased before use. The compound $Mo(CO)_4(bipy)$ [5] was prepared as described in the literature. IR spectra were recorded using a Perkin-Elmer 577 spectrophotometer. $^{31}P\{^1H\}$ NMR spectra were obtained with a Varian FT80A instrument and were measured in $CDCl_3$ solution at room temperature ($\delta$ values to high frequency of external 85% $H_3PO_4$). Conductivity measurements were made with a WTW conductivity bridge LBR at 3 KHz; the cell constant of the glass conductivity probe was determined by use of 0.01 mol $dm^{-3}$ KCl solution. Elemental analysis for C, H, N were determined with a Carlo Erba 1106 or Perkin-Elmer 240 instrument.

### *Preparation of $MoX_2(CO)_3(bipy)$ (X = Cl, Br, I)*

The procedure was that described by Stiddard [5] for X = Br, I with small modifications.

To a stirred solution of $Mo(CO)_4(bipy)$ (0.4 g, 1.1 mmol) in 90 $cm^3$ of dichloromethane at room temperature was added the stoichiometric amount of $X_2$ (1.1 mmol) dissolved in carbon tetrachloride. Concentration to *ca.* 25 $cm^3$ and addition of an equal volume of hexane afforded the solids with yields 85–90%.

### *Preparation of $MoX_2(CO)_2(bipy)(L–L)$ (L–L = dppm, X = Cl, Br; L–L = dppe, X = Cl, Br, I)*

A typical preparation for $MoCl_2(CO)_2(bipy)(dppm)$ is described. To a stirred solution of $Mo(CO)_4(bipy)$ (0.1 g, 0.27 mmol) in 20 $cm^3$ of dichloromethane was added a solution of chlorine in carbon tetrachloride until the formation of $MoCl_2(CO)_3(bipy)$ was completed (IR $\nu$(CO)). To the resulting mixture, dppm (0.104 g, 0.27 mmol) was added and the solution stirred for 10 min. Concentration near to dryness and addition of hexane afforded the solid (0.18 g, 86%). The product was

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*Author to whom correspondence should be addressed.

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washed with diethylether and recrystallized from $CH_2Cl_2$–hexane.

### *Preparation of [MoX(CO)$_2$(bipy)(L–L)] BPh$_4$ (X = Cl, Br, I; L–L = dppe and X = Cl, Br; L–L = dppm)*

A typical preparation for [MoI(CO)$_2$(bipy)(dppe)] BPh$_4$ is described. To a solution of MoI$_2$(CO)$_2$(bipy)(dppe) (0.085 g, 0.09 mmol) in 20 cm$^3$ of dichloromethane was added NaBPh$_4$ (0.04 g, 0.1 mmol) and the mixture stirred for 4 h. The suspension was filtered and concentrated under vacuum to a half of the volume. Addition of hexane (*ca.* 20 cm$^3$) and concentration yielded 0.07 g (68%) of the product.

### *Preparation of [MoI(CO)$_2$(bipy)(dppm)] I*

A solution of MoI$_2$(CO)$_3$(bipy) (0.27 mmol) in 40 cm$^3$ of dichloromethane was prepared as described above. To this solution was added dppm (0.135 g, 0.35 mmol). After stirring for 8 h the mixture was filtered. Concentration to *ca.* 15 cm$^3$ and addition of diethylether afforded the complex as a red powder which was recrystallized from $CH_2Cl_2$–hexane. Yield 0.18 g (70%).

### *Preparation of MoCl$_2$(CO)(bipy)(dppm)*

The procedure was the same as that used for the bromo-derivative described elsewhere [4].

### *Preparation of Mo$_2$X$_4$(CO)$_4$(bipy)(μ-dppe) (X = Cl, Br)*

The procedure for the bromo-derivative is described. To a solution of MoBr$_2$(CO)$_3$(bipy) (0.27 mmol) prepared as described above, was added dppe (0.05 g, 0.13 mmol). After stirring for 0.5 h the orange precipitate was washed with hexane and diethylether respectively. Yield 0.1 g (60%).

## Results and Discussion

The reactions of Mo(CO)$_4$(bipy) with $X_2$ in chloroform to give MoX$_2$(CO)$_3$(bipy) (X = Br, I) were described by Stiddard [5] in 1962. We have employed the same procedure but dichloromethane was used instead of chloroform. Recently [6] MoI$_2$(CO)$_3$(bipy) has been prepared by treatment of MoI$_2$(CO)$_3$(NCCH$_3$)$_2$ with 2,2′-bipyridyl.

The reactions of Mo(0) carbonyl compounds with chlorine lead in general to a higher oxidation state than Mo(II) unless low temperatures are used [7, 8]. We have found that it is possible to prepare MoCl$_2$(CO)$_3$(bipy) in good yields by treatment of Mo(CO)$_4$(bipy) in dichloromethane with a solution of chlorine in carbon tetrachloride at room temperature. An alternative synthetic route consists in the reaction of MoCl$_2$(CO)$_4$ with bipyridine [9], but the synthesis of MoCl$_2$(CO)$_4$ involves the use of low temperatures.

Although it was possible to isolate all the tricarbonyls they were prepared and used 'in situ' by carefully monitoring of the halogenation reaction by IR spectroscopy.

### *Reactions of MoX$_2$(CO)$_3$(bipy) with dppm*

The tricarbonyl MoCl$_2$(CO)$_3$(bipy) reacted with dppm in dichloromethane, in molar ratio 1:1, to give the light sensitive dicarbonyl MoCl$_2$(CO)$_2$(bipy)(dppm) (**1**). The $^{31}P\{^1H\}$ NMR of **1** in CDCl$_3$ at room temperature showed two signals at +42 ppm(d) and −27 ppm(d) with $^2J(PP) = 23$ Hz. These values are similar to the chemical shifts observed for the dppm attached to molybdenum via only one phosphorus ligand [10]. Further reaction of **1** with NaBPh$_4$ in dichloromethane led to the cationic [MoCl(CO)$_2$(bipy)(dppm)] BPh$_4$ (**2**). The orange solution of complex **1** in dichloromethane turned slowly dark green when exposed to sunlight at room temperature under nitrogen. This allowed us to isolate the monocarbonyl MoCl$_2$(CO)(bipy)(dppm) (**3**) which underwent further reaction with CO to give [MoCl(CO)$_2$(bipy)(dppm)] Cl (**2a**). This complex characterized by IR spectroscopy in solution, was transformed into **2** by treatment with NaBPh$_4$.

The same behaviour had been shown by the analogous bromo-derivative [4] but the rate of substitution increased from bromine to chlorine.

The reaction of MoI$_2$(CO)$_3$(bipy) with dppm afforded, in a first step, MoI$_2$(CO)$_2$(bipy)(dppm) which was detected by IR spectroscopy [ν(CO) bands at 1942 and 1865 cm$^{-1}$). However, this compound isomerized into the ionic complex [MoI(CO)$_2$(bipy)(dppm)] I (**4**) in dichloromethane solution.

From these results and those reported for the bromo-derivatives [4] it was possible to conclude that the rate of the reactions of MoX$_2$(CO)$_3$(bipy) with dppm to give MoX$_2$(CO)$_2$(bipy(dppm) increased in the order $I < Br < Cl$. On the contrary, for the isomerization process of MoX$_2$(CO)$_2$(bipy)(dppm) to the ionic complexes [MoX(CO)$_2$(bipy)(dppm)] X the rate increased in the same order, $Cl < Br < I$, as the steric hindrance. For X = I the ionization occurred spontaneously and for X = Cl and Br it was necessary to employ NaBPh$_4$ leading to **2** and [MoBr(CO)$_2$(bipy)(dppm)] BPh$_4$ after stirring at room temperature 20 and 7 h respectively.

The reactions of MoX$_2$(CO)$_3$(bipy) with dppm in molar ratio 2:1 did not afford the dimeric species formed with dppe as discussed below.

### *Reactions of MoX$_2$(CO)$_3$(bipy) with dppe*

Treatment of MoX$_2$(CO)$_3$(bipy) (X = Cl, Br, I) with dppe in molar ratios 1:1 in dichloromethane at room temperature led to the formation of MoX$_2$(CO)$_2$(bipy)(dppe) (**5**, **6** and **7**). These complexes

TABLE I. Analytical Data (C, H, N), Colour and Melting Points of the Complexes

| Complex | | Analysis: found (calculated) (%) | | | Melting point[a] (°C) | Colour |
|---|---|---|---|---|---|---|
| | | C | H | N | | |
| $MoCl_2(CO)_2(bipy)(dppm)$ | 1 | 57.7(58.2) | 4.1(4.0) | 3.5(3.7) | 141 | orange |
| $[MoCl(CO)_2(bipy)(dppm)]BPh_4$ | 2 | 68.8(70.0) | 4.6(4.8) | 2.8(2.7) | 178 | red |
| $MoCl_2(CO)(bipy)(dppm)$ | 3 | 57.7(58.8) | 3.9(4.1) | 3.7(3.8) | 180 | dark green |
| $[MoI(CO)_2(bipy)(dppm)]I$ | 4 | 45.9(47.0) | 3.2(3.2) | 2.9(3.0) | 194 | red |
| $MoCl_2(CO)_2(bipy)(dppe)$ | 5 | 57.8(58.7) | 3.9(4.1) | 3.5(3.6) | 114 | red |
| $MoBr_2(CO)_2(bipy)(dppe)$ | 6 | 51.4(52.7) | 3.7(3.7) | 3.0(3.2) | 99 | orange–red |
| $MoI_2(CO)_2(bipy)(dppe)$ | 7 | 46.6(47.5) | 3.2(3.3) | 2.7(2.9) | 70 | orange |
| $[MoCl(CO)_2(bipy)(dppe)]BPh_4$ | 8 | 70.0(70.2) | 4.7(4.9) | 2.4(2.6) | | yellow |
| $[MoBr(CO)_2(bipy)(dppe)]BPh_4$ | 9 | 66.2(67.3) | 4.7(4.7) | 2.4(2.5) | | yellow |
| $[MoI(CO)_2(bipy)(dppe)]BPh_4$ | 10 | 63.3(64.6) | 4.3(4.5) | 2.4(2.4) | | dark red |
| $Mo_2Cl_4(CO)_4(bipy)_2(\mu\text{-dppe})$ | 11 | 51.3(51.9) | 3.5(3.5) | 4.7(4.8) | 139 | orange |
| $Mo_2Br_4(CO)_4(bipy)_2(\mu\text{-dppe})$ | 12 | 44.8(45.0) | 2.9(3.0) | 4.0(4.2) | 194 | orange |

[a] All melted with decomposition.

TABLE II. Infrared, Conductivity, Yields and Times of Reaction Data

| Complex | | $\nu$(CO)[a] ($cm^{-1}$) | $\Lambda_M$[c] ($S\ cm^2\ mol^{-1}$) | Yield (%) | Time of reaction (h) |
|---|---|---|---|---|---|
| $MoCl_2(CO)_2(bipy)(dppm)$ | 1 | 1943, 1858 | 5.0 | 86 | 0.2 |
| $[MoCl(CO)_2(bipy)(dppm)]BPh_4$ | 2 | 1959, 1896 | 115.4 | 84 | 24 |
| $MoCl_2(CO)(bipy)(dppm)$ | 3 | 1786 | 4.0 | 73 | 1 |
| $[MoI(CO)_2(bipy)(dppm)]I$ | 4 | 1957, 1877 | 106.0 | 70 | 8 |
| $MoCl_2(CO)_2(bipy)(dppe)$ | 5 | 1943, 1857 | 20.5 | 86 | 0.2 |
| $MoBr_2(CO)_2(bipy)(dppe)$ | 6 | 1948, 1861 | 32.0 | 76 | 0.5 |
| $MoI_2(CO)_2(bipy)(dppe)$ | 7 | 1945, 1863 | 65.5 | 75 | 1.5 |
| $[MoCl(CO)_2(bipy)(dppe)]BPh_4$ | 8 | 1955, 1870 | 95.0 | 78 | 20 |
| $[MoBr(CO)_2(bipy)(dppe)]BPh_4$ | 9 | 1954, 1871 | 102.5 | 65 | 6 |
| $[MoI(CO)_2(bipy)(dppe)]BPh_4$ | 10 | 1953, 1875 | 122.5 | 68 | 4 |
| $Mo_2Cl_4(CO)_4(bipy)_2(\mu\text{-dppe})$ | 11 | 1940, 1847[b] | | 62 | 0.2 |
| $Mo_2Br_4(CO)_4(bipy)_2(\mu\text{-dppe})$ | 12 | 1942, 1856[b] | | 60 | 0.5 |

[a] In dichloromethane solution. [b] In KBr pellets. [c] In acetone solution *ca.* $10^{-3}$ M.

when exposed to the sunlight, unlike the dppm derivatives, only led to decompositions. However the behaviour of these dicarbonyls with $NaBPh_4$ was analogous, yielding the cationic $[MoX(CO)_2(bipy)(dppe)]BPh_4$ (X = Cl (**8**), Br (**9**), I (**10**)], with rates of substitution increasing in the same order as that for dppm (see below Table II).

The high conductivity exhibited by the neutral dicarbonyls suggested that the equilibrium

$$MoX_2(CO)_2(bipy)(dppe) \rightleftharpoons [MoX(CO)_2(bipy)(dppe)]X$$

was present in acetone solution. In spite of that, the complexes were formulated as neutral because the $\nu$(CO) frequencies showed lower values than for the ionic compounds (see below Table II).

The reactions of $MoX_2(CO)_3(bipy)$ (X = Cl, Br) with dppe in molar ratios 2:1 allowed us to isolate the complexes $[Mo_2X_4(CO)_4(bipy)_2(\mu\text{-dppe})]$ (X = Cl (**11**), Br (**12**)]. Formulation as dimers was based in their low solubility and elemental analysis. Attempts to carry out molecular weight determinations were always unsuccessful.

The reaction rates with dppe were faster than with dppm due probably to the lower steric hindrance of the dppe [11].

All of the complexes described above were air and light sensitive especially in solution. Yellow or orange solutions in dichloromethane turned purple when they were not conveniently protected. Melting points, analytical data, conductivity and $\nu$(CO) frequencies for the prepared compounds are given in Tables I and II.

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