

## MONONUCLEAR CARBONYL MANGANESE(I) AND MOLYBDENUM(II) COMPLEXES WITH CHELATING BIIMIDAZOLE, BIBENZIMIDAZOLE OR TETRAMETHYLBIIIMIDAZOLE LIGANDS \*

M.P. GAMASA, E. GARCIA, J. GIMENO\*

*Departamento de Química Inorgánica, Universidad de Oviedo, Oviedo (Spain)*

and C. BALLESTEROS

*Departamento de Química Inorgánica, Universidad de Zaragoza, Zaragoza (Spain)*

(Received December 10th, 1985)

### Summary

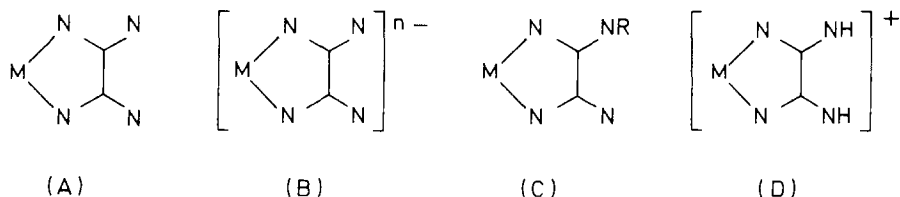
The preparations and properties are described of novel anionic and neutral mononuclear biimidazolate (biim), bibenzimidazolate (bibzim), or tetramethylbiimidazolate (tmbiim) manganese(I) and molybdenum(II) complexes of the type  $[\text{Et}_4\text{N}][\text{Mn}(\text{CO})_2\text{L}_2(\text{bibzim})]$  ( $\text{L} = \text{P}(\text{OMe})_3, \text{P}(\text{OEt})_3$ );  $[\text{Et}_4\text{N}][\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{N-N})_2]$  ( $(\text{N-N})_2^{2-} = \text{biim}^{2-}, \text{bibzim}^{2-}, \text{tmbiim}^{2-}$ );  $[\text{Mn}(\text{CO})_{4-n}\text{L}_n\{\text{H}(\text{N-N})_2\}]$  ( $n = 1$ ;  $\text{H}(\text{N-N})_2^- = \text{Hbibzim}^-$ ;  $\text{L} = \text{P}(\text{OMe})_3, \text{PEt}_3$ , ( $n = 2$ ;  $\text{H}(\text{N-N})_2^- = \text{Hbiim}^-$ ,  $\text{Hbibzim}^-$ ;  $\text{L} = \text{P}(\text{OPh})_3, \text{P}(\text{OMe})_3, \text{P}(\text{OEt})_3, \text{P}(\text{O}^i\text{Pr})_3$ );  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{H}(\text{N-N})_2)]$  ( $\text{H}(\text{N-N})_2^- = \text{Hbiim}^-, \text{Hbibzim}^-, \text{Htmbiim}^-$ ), in which the heterocyclic anions act as bidentate chelate groups. Treatment of the anionic complexes with MeI gives neutral derivatives of general formula  $[\text{Mn}(\text{CO})_2\text{L}_2(\text{Mebibzim})]$  ( $\text{L} = \text{P}(\text{OMe})_3, \text{P}(\text{OEt})_3$ ) and  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\{\text{Me}(\text{N-N})_2\}]$  ( $\text{Me}(\text{N-N})_2^- = \text{Mebiiim}^-, \text{Mebibzim}^-, \text{Metmbiim}^-$ ). Cationic manganese(I) complexes of the type  $[\text{Mn}(\text{CO})_{4-n}\text{L}_n\{\text{H}_2(\text{N-N})_2\}][\text{ClO}_4]$  ( $n = 1$ ;  $\text{H}_2(\text{N-N})_2 = \text{H}_2\text{bibzim}$ ;  $\text{L} = \text{P}(\text{OMe})_3, \text{PEt}_3$ , ( $n = 2$ ;  $\text{H}_2(\text{N-N})_2 = \text{H}_2\text{biim}, \text{H}_2\text{bibzim}$ ;  $\text{L} = \text{P}(\text{OPh})_3, \text{P}(\text{OMe})_3, \text{P}(\text{OEt})_3, \text{P}(\text{O}^i\text{Pr})_3$ ) have also been obtained by treating the corresponding neutral complexes with  $\text{HClO}_4$ . The structures of the complexes have been elucidated by molecular weight determinations, conductance data, and IR spectroscopy.

### Introduction

In recent years we have extensively studied the coordination chemistry of biimidazolate ( $\text{biim}^{2-}$ ) and bibenzimidazolate ( $\text{bibzim}^{2-}$ ) anions, demonstrating

\* Dedicated to Professor Rafael Usón on the occasion of his 60th birthday.

their ability to act as bridging ligands and to form a large number of bi-, tri- and tetranuclear complexes [1–6]. In contrast, mononuclear complexes with the heterocyclic anionic ligands acting as bidentate chelates are relatively much scarcer. They fall into two types: (a) neutral complexes (**A**)  $[M(\text{dppe})(\text{N-N})_2]$  ( $M = \text{Pd}, \text{Pt}$ ;  $(\text{N-N})^{2-} = \text{biim}^{2-}, \text{bibzim}^{2-}$ ;  $\text{dppe} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$ ) [4]; (b) anionic complexes (**B**)  $[\text{Et}_4\text{N}]_2[\text{M}(\text{CO})_4(\text{N-N})_2]$  ( $M = \text{Cr}, \text{Mo}, \text{W}$ ) [7]. A few neutral complexes containing the analogous  $\text{Hbiim}^-$  and  $\text{Hbibzim}^-$  anions (**C**) ( $R = \text{H}$ ) are also known  $M = \text{Pd}$  [5],  $M = \text{Rh}, \text{Ir}$  [6,8].

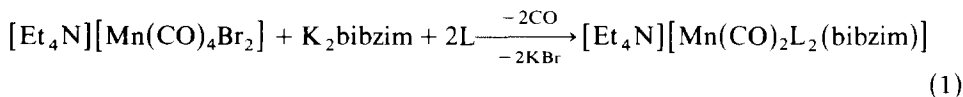


We describe here the synthesis and properties of new mononuclear manganese(I) or molybdenum(II) carbonyl complexes with the aforementioned chelating heterocyclic anionic ligands of the types **B** ( $n = 1$ ; complexes I–V) and **C** ( $R = \text{Me}$ , complexes VI, VII, XVII–XIX;  $R = \text{H}$ , complexes VIII–XVI, XX–XXII) along with cationic manganese(I) carbonyl complexes of the type **D** (XXIII–XXXI) obtained by protonation of the corresponding neutral derivatives.

## Results and discussion

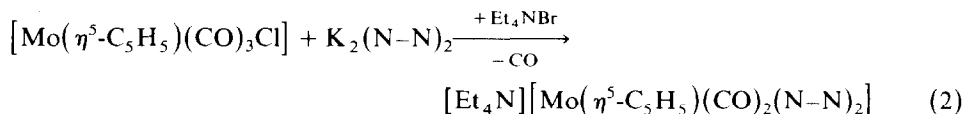
### (a) Anionic complexes I–V

Reaction between equimolar amounts of  $[\text{Et}_4\text{N}][\text{Mn}(\text{CO})_4\text{Br}_2]$  and  $\text{K}_2\text{bibzim}$  (prepared from  $\text{H}_2\text{bibzim}$  and potassium hydroxide in 1/2.5 mol ratio in a ca. 1/1 dichloromethane/methanol mixture) followed by addition of an excess of trimethyl- or triethylphosphite to the resulting suspension leads, after refluxing for 3 h, to a yellow solution from which dicarbonyl derivatives I and II can be obtained (see eq. 1).



( $\text{L} = \text{P}(\text{OMe})_3$  (I),  $\text{P}(\text{OEt})_3$  (II))

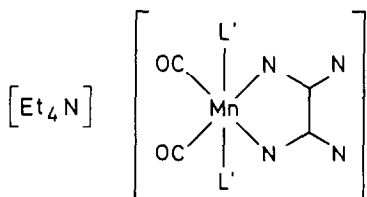
$[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cl}]$  reacts similarly with the appropriate potassium salts under the same conditions. Addition of  $\text{Et}_4\text{NBr}$  to the resulting red solution gives solutions of the corresponding anionic complexes (eq. 2).



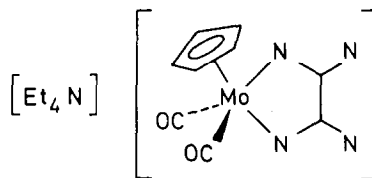
(( $\text{N-N}$ ) $_2^{2-} = \text{biim}^{2-}$  (III),  $\text{bibzim}^{2-}$  (IV),  $\text{tmbiim}^{2-}$  (V))

Crystalline complexes (III–V) can be isolated from the dichloromethane solutions by evaporation to dryness followed by several extractions of the resulting solid residue.

All the anionic complexes (I–V) and their solutions are highly moisture sensitive, so that, only for complex I could a good elemental analysis be obtained. The  $^1\text{H}$  NMR spectra in  $\text{CDCl}_3$  exhibit the expected resonances for the ligands. Conductance data (acetone or nitromethane solutions) show the complexes to be 1:1 electrolytes, and the infrared spectra of all the complexes in dichloromethane show two CO stretching bands (see Experimental). They readily undergo protonation at the non-coordinated N atoms to give the corresponding neutral or cationic complexes (see below).



(I,  $L' = \text{P}(\text{OMe})_3$ ;  $L^{2-} = \text{bibzim}^{2-}$ ;  
II,  $L' = \text{P}(\text{OEt})_3$ ;  $L^{2-} = \text{bibzim}^{2-}$ )



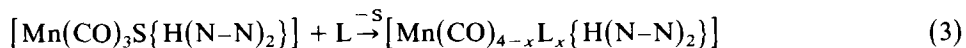
(III,  $L^{2-} = \text{biim}^{2-}$ ;  
IV,  $L^{2-} = \text{bibzim}^{2-}$ ;  
V,  $L^{2-} = \text{tmbiim}^{2-}$  (\*);  
(\* )  $\text{H}_2\text{tmbiim} = 4,4,4',4'$ -  
- tetramethylbiimidazole)

### (b) Neutral complexes

Anionic complexes I–V display a marked nucleophilic reactivity, since they react at room temperature with methyl iodide in dichloromethane giving rise within a few minutes to the methylated derivatives VI, VII and XVII–XIX, which can be isolated as air stable crystalline solids after partial evaporation of the solvent. The neutral character of the dicarbonyl complexes is shown by the expected shifting of the two IR  $\nu(\text{CO})$  bands towards higher energy (5–10 and 10–30  $\text{cm}^{-1}$ , respectively, for the manganese and molybdenum complexes) (Table 1). A similar shift is observed upon addition of aqueous perchloric acid, indicating the formation in solution of protonated neutral and cationic species (see Experimental) which can also be prepared by a more selective method.

Thus, refluxing solutions of  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cl}]$  in THF or  $\text{MeOH}/\text{CH}_2\text{Cl}_2$  react in 1/1 mol ratio with  $\text{H}_2(\text{N-N})_2$  in the presence of potassium hydroxide to give red air-stable complexes (XX–XXII).  $[\text{Mn}(\text{CO})_4(\mu\text{-Br})_2]$  reacts (eq. 3) similarly with  $\text{H}_2(\text{N-N})_2$  in 1/2 mol ratio to give orange-yellow solutions, which probably contain solvated tricarbonyl species of the type  $[\text{Mn}(\text{CO})_3\text{S}\{\text{H}(\text{N-N})_2\}]$  as indicated by the observed IR  $\nu(\text{CO})$  stretching bands which are characteristic for a *fac*-tricarbonyl moiety. In these reactions only one of the anionic hydrogens of  $\text{H}_2(\text{N-N})_2$  is dissociated, since the corresponding anionic complexes are only formed when an excess of KOH is used (see above).

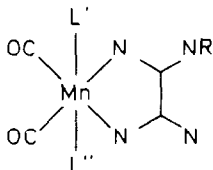
Treatment with P-donor ligands of solutions of the manganese tricarbonyl derivatives formed in situ results in displacement of one CO group and/or the coordinated solvent molecule to give tri- or dicarbonyl derivatives (eq. 3).



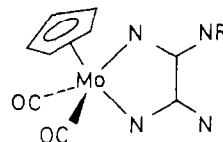
(S = THF or MeOH;  $x = 1$  or  $2$ ; L = P-donor ligands)

Thus, additions of P-donor ligands (1/1) at room temperature give solutions, whose IR  $\nu(\text{CO})$  pattern show three strong absorption bands, as expected for the new *fac*-tricarbonyl derivatives. However, only complexes VIII and IX could be isolated pure since for the biim derivatives or other P-ligands dicarbonyl species are formed at the same time (IR spectra) even when stoichiometric amounts are used.

The solvated tricarbonyl complexes react with an excess of the P-donor ligands in refluxing THF to give yellow dicarbonyl complexes (X–XVI). The greater the  $\pi$ -acceptor ability of the ligand the shorter is the reaction time (20–90 min), as indicated by monitoring the  $\nu(\text{CO})$  pattern in the IR spectra. For  $\text{L} = \text{PPh}_3$  and the more basic alkyl phosphines, prolonged treatment leads to either decomposition or non crystallizable oils.



- (VI,  $\text{L}' = \text{L}'' = \text{P}(\text{OMe})_3$ ;  $\text{RL}^- = \text{Mebibzim}^-$ ;  
 VII,  $\text{L}' = \text{L}'' = \text{P}(\text{OEt})_3$ ;  $\text{RL}^- = \text{Mebibzim}^-$ ;  
 VIII,  $\text{L}' = \text{CO}$ ;  $\text{L}'' = \text{P}(\text{OMe})_3$ ;  $\text{RL}^- = \text{Hbibzim}^-$ ;  
 IX,  $\text{L}' = \text{CO}$ ;  $\text{L}'' = \text{PEt}_3$ ;  $\text{RL}^- = \text{Hbibzim}^-$ ;  
 X,  $\text{L}' = \text{L}'' = \text{P}(\text{OPh})_3$ ;  $\text{RL}^- = \text{Hbiim}^-$ ;  
 XI,  $\text{L}' = \text{L}'' = \text{P}(\text{OMe})_3$ ;  $\text{RL}^- = \text{Hbiim}^-$ ;  
 XII,  $\text{L}' = \text{L}'' = \text{P}(\text{OEt})_3$ ;  $\text{RL}^- = \text{Hbiim}^-$ ;  
 XIII,  $\text{L}' = \text{L}'' = \text{P}(\text{O}^i\text{Pr})_3$ ;  $\text{RL}^- = \text{Hbiim}^-$ ;  
 XIV,  $\text{L}' = \text{L}'' = \text{P}(\text{OPh})_3$ ;  $\text{RL}^- = \text{Hbibzim}^-$ ;  
 XV,  $\text{L}' = \text{L}'' = \text{P}(\text{OMe})_3$ ;  $\text{RL}^- = \text{Hbibzim}^-$ ;  
 XVI,  $\text{L}' = \text{L}'' = \text{P}(\text{OEt})_3$ ;  $\text{RL}^- = \text{Hbibzim}^-$ )



- (XVII,  $\text{RL}^- = \text{Mebiiim}^-$ ;  
 XVIII,  $\text{RL}^- = \text{Mebibzim}^-$ ;  
 XIX,  $\text{RL}^- = \text{Metmbiiim}^-$ ;  
 XX,  $\text{RL}^- = \text{Hbiim}^-$ ;  
 XXI,  $\text{RL}^- = \text{Hbibzim}^-$ ;  
 XXII,  $\text{RL}^- = \text{Htmbiiim}^-$ )

Infrared spectra ( $\text{CH}_2\text{Cl}_2$  solutions) of dicarbonyl complexes X–XVI and XX–XXII exhibit two strong CO stretching bands (Table 1) along with a broad band at  $3000\text{--}2300\text{ cm}^{-1}$  (Nujol mulls) assigned to the N–H bond. This relatively low energy absorption as well as the molecular weights determined osmotically in chloroform (see Experimental), which are higher than the calculated values, suggest that there is intermolecular association in the solid state via hydrogen bonds. The  $^1\text{H}$  NMR spectra in  $\text{CDCl}_3$  show resonances characteristic of the protons of the ligands (see Experimental) although no structural information can be obtained, except from the data for the manganese complexes VI, XI and XV ( $\text{L} = \text{P}(\text{OMe})_3$ ). For these complexes triplets for the methyl groups of VI, XI and XV appear at  $\delta$  3.1, 3.4 and 3.2 ppm respectively, as expected for virtual coupling to two *trans* phosphorus atoms [9] and consistent with the proposed arrangements of the manganese dicarbonyl complexes.

### (c) Cationic complexes

Addition of stoichiometric amounts of perchloric acid to dichloromethane solu-

TABLE 1  
COLOURS, ANALYTICAL, AND  $\nu(\text{CO})$  INFRARED SPECTRAL DATA FOR THE COMPLEXES

Complex	Colour	Analyses (Found (calcd.) (%))			$\nu(\text{CO})$ ( $\text{cm}^{-1}$ ) ( $\text{CH}_2\text{Cl}_2$ )
		C	H	N	
I	yellow	49.33 (49.97)	6.74 (6.38)	9.52 (9.70)	1939s, 1858s
VI	yellow	46.41 (45.58)	4.81 (4.78)	9.40 (9.24)	1948s, 1870s
VII	yellow	50.37 (50.47)	5.94 (5.94)	8.18 (8.11)	1941s, 1861s
VIII	orange	47.98 (48.40)	4.39 (3.65)	10.75 (11.28)	2045s, 1957s, 1918s
IX	yellow	56.52 (56.53)	5.24 (4.93)	11.31 (11.42)	2029s, 1937s, 1903s
X	yellowish	61.46 (61.12)	4.39 (4.08)	6.40 (6.48)	1965s, 1892s
XI	yellowish	34.19 (34.16)	4.76 (4.70)	11.44 (11.38)	1947s, 1870s
XII	yellowish	42.22 (41.67)	6.47 (6.12)	9.91 (9.72)	1943s, 1864s
XIII	yellow	48.01 (47.27)	7.98 (7.17)	8.68 (8.48)	1936s, 1854s
XIV	yellow	64.84 (64.73)	4.98 (4.07)	5.44 (5.80)	1966s, 1893s
XV	yellow	44.33 (44.60)	4.58 (4.59)	9.41 (9.45)	1949s, 1871s
XVI	yellow	49.44 (49.71)	6.38 (5.81)	8.01 (8.28)	1941s, 1864s
XVII	red	46.14 (46.17)	3.28 (3.32)	15.60 (15.38)	1963s, 1863s
XVIII	orange-red	56.89 (56.92)	3.62 (3.45)	12.26 (12.06)	1959s, 1872s
XIX	orange	51.51 (51.31)	5.15 (5.02)	13.69 (13.30)	1957s, 1863s
XX	orange-red	44.53 (44.59)	2.98 (2.88)	15.66 (15.99)	1964s, 1868s
XXI	red	52.21 (52.41) <sup>a</sup>	3.17 (3.07) <sup>a</sup>	11.15 (11.37) <sup>a</sup>	1963s, 1874s
XXII	orange	45.15 (46.84) <sup>a</sup>	4.09 (4.27) <sup>a</sup>	12.01 (12.48) <sup>a</sup>	1957s, 1862s
XXIII	yellow	40.24 (40.25)	3.66 (3.21)	9.00 (9.38)	2050s, 1968s, 1930s
XXIV	yellow	47.21 (46.75)	4.93 (4.26)	9.54 (9.48)	2043s, 1952s, 1918s
XXV	yellowish	54.39 (54.75)	4.26 (3.76)	6.15 (5.80)	1980s, 1910s
XXVI	yellowish	28.50 (28.37)	4.48 (4.08)	9.51 (9.45)	1962s, 1885s
XXVII	yellow	35.75 (35.49)	5.88 (5.36)	8.52 (8.27)	1954s, 1878s
XXVIII	yellow	40.29 (41.03)	7.03 (6.35)	7.21 (7.36)	1949s, 1870s
XXIX	yellow	58.30 (58.63)	4.50 (3.78)	5.72 (5.26)	1979s, 1909s

continued

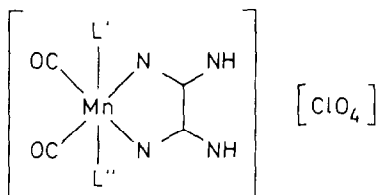
TABLE 1 (continued)

Complex	Colour	Analyses (Found (calcd.) (%))			$\nu(\text{CO})$ ( $\text{cm}^{-1}$ ) ( $\text{CH}_2\text{Cl}_2$ )
		C	H	N	
XXX	orange	38.39	4.86	8.48	1959s, 1884s
		(38.14)	(4.07)	(8.08)	
XXXI	orange	43.06	5.24	6.96	1954s, 1878s
		(43.28)	(5.19)	(7.21)	

<sup>a</sup> Calculated with  $\text{CH}_2\text{Cl}_2$  of crystallization (0.5 mol).

tions of neutral manganese complexes VIII–XVI leads to protonation of the basic nitrogen atom to give cationic complexes XXIII–XXXI in form of perchlorate salts, which can be precipitated as yellow-orange air-stable solids by addition of hexane to the partially evaporated solutions.

The IR spectra of the solids show a broad absorption band at  $3300\text{--}3150\text{ cm}^{-1}$  assignable to the N–H stretching vibration, along with the expected split absorptions for the perchlorate anion at ca.  $1100$  and  $620\text{ cm}^{-1}$ . We have previously observed [6] splitting in similar cationic perchlorate complexes, and attributed this to a distortion of the  $T_d$  symmetry because of  $\text{N-H} \cdots \text{OCIO}_3$  hydrogen bonding. The  $\nu(\text{CO})$  stretching bands are listed in Table 1 and appear, as should be expected, at higher energy than in the corresponding precursor neutral complexes.



- (XXIII,  $L' = \text{CO}$ ;  $L'' = \text{P}(\text{OMe})_3$ ;  $\text{H}_2\text{L} = \text{H}_2\text{bibzim}$ ;  
 XXIV,  $L' = \text{CO}$ ;  $L'' = \text{PEt}_3$ ;  $\text{H}_2\text{L} = \text{H}_2\text{bibzim}$ ;  
 XXV,  $L' = L'' = \text{P}(\text{OPh})_3$ ;  $\text{H}_2\text{L} = \text{H}_2\text{biim}$ ;  
 XXVI,  $L' = L'' = \text{P}(\text{OMe})_3$ ;  $\text{H}_2\text{L} = \text{H}_2\text{biim}$ ;  
 XXVII,  $L' = L'' = \text{P}(\text{OEt})_3$ ;  $\text{H}_2\text{L} = \text{H}_2\text{biim}$ ;  
 XXVIII,  $L' = L'' = \text{P}(\text{O}^i\text{Pr})_3$ ;  $\text{H}_2\text{L} = \text{H}_2\text{biim}$ ;  
 XXIX,  $L' = L'' = \text{P}(\text{OPh})_3$ ;  $\text{H}_2\text{L} = \text{H}_2\text{bibzim}$ ;  
 XXX,  $L' = L'' = \text{P}(\text{OMe})_3$ ;  $\text{H}_2\text{L} = \text{H}_2\text{bibzim}$ ;  
 XXXI,  $L' = L'' = \text{P}(\text{OEt})_3$ ;  $\text{H}_2\text{L} = \text{H}_2\text{bibzim}$ )

Treatment of the neutral carbonyl molybdenum complexes with perchloric acid gives solutions whose IR spectra also show similar shifts of the  $\nu(\text{CO})$  bands, but no attempts were made to isolate the corresponding cationic complexes (see Experimental).

Table 1 lists the colours, analytical data and  $\nu(\text{CO})$  stretching bands (dichloromethane solutions) for the isolated complexes. Other relevant information on conductivity data, molecular weights, IR and  $^1\text{H}$  NMR spectra are given in the Experimental section.

## Experimental

Infrared spectra in the  $\nu(\text{CO})$  stretching region were recorded on a Perkin–Elmer 577 spectrophotometer using dichloromethane solutions or Nujol mulls between NaCl plates. Conductivities were measured at room temperature in acetone or nitromethane ( $5 \times 10^{-4}$  M solutions) with a Metrohm AG. E382 conductimeter. Carbon, hydrogen and nitrogen analyses were carried out with a Perkin–Elmer 240 microanalyser. Molecular weights were determined with a Knauer vapour-pressure-osmometer ( $2 \times 10^{-3}$  M solutions). Proton NMR spectra were recorded on a Varian FT-80A spectrometer at 79.54 MHz, using  $\text{SiMe}_4$  as internal standard reference.

All reactions were carried out under argon and the solvents were dried before use. The ligands were used as purchased.  $\text{H}_2\text{biim}$ ,  $\text{H}_2\text{bibzim}$  and  $\text{H}_2\text{tmbiim}$  were prepared as described elsewhere [10,11].

### Preparation of the complexes

#### Anionic complexes

$[\text{Et}_4\text{N}][\text{Mn}(\text{CO})_2\text{L}_2(\text{bibzim})]$  ( $\text{L} = \text{P}(\text{OMe})_3$  (I),  $\text{P}(\text{OEt})_3$  (II)). To a suspension of  $\text{K}_2\text{bibzim}$  in 30 ml of a ca. 3/1  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  mixture (obtained by stirring 0.5 mmol of  $\text{H}_2\text{bibzim}$  with 1.25 mmol of KOH for 30 min at room temperature) was added  $[\text{Et}_4\text{N}][\text{Mn}(\text{CO})_4\text{Br}_2]$  [12] (0.102 g, 0.5 mmol). After 1 h stirring at room temperature an excess of the ligand (ca. 1.5 mmol) was added and the mixture was heated under reflux for 3 h. Solvents were removed in vacuo and the residue was washed with hexane then extracted with  $\text{CH}_2\text{Cl}_2$ . Partial evaporation of the solvent and addition of hexane gave yellow solids. Yields: I: 65%; II: 60%.  $\Lambda_M$  ( $\text{S cm}^2 \text{mol}^{-1}$ ) (acetone): I: 122; II: 125.

Complex II: colour: yellow; IR  $\nu(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$ ): 1935s, 1854s  $\text{cm}^{-1}$ .

$[\text{Et}_4\text{N}][(\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{N-N})_2)]$  ( $(\text{N-N})_2^{2-} = \text{biim}^{2-}$  (III),  $\text{bibzim}^{2-}$  (IV),  $\text{tmbiim}^{2-}$  (V)). A mixture of  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cl}]$  [13] (0.28 g, 1 mmol) and  $\text{K}_2(\text{N-N})_2$  (obtained as described above, from 1 mmol of the corresponding heterocyclic ligand) in 40 ml of THF and 10 ml of MeOH was stirred at room temperature for 45 min. After filtration under argon  $\text{Et}_4\text{NBr}$  (0.21 g, 1 mmol) was added, and the resulting red solution was stirred for 1 h then evaporated to dryness, and the residue was extracted with  $\text{CH}_2\text{Cl}_2$ . Red solids were obtained by adding hexane to the concentrated dichloromethane solution then cooling. Yields: III: 32%; IV: 52%; V: 65%.  $\Lambda_M$  ( $\text{S cm}^2 \text{mol}^{-1}$ ) (nitromethane): III: 95; IV: 87; V: 90. Colours: III: red; IV: red; V: red. IR  $\nu(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$ ): III: 1952s, 1852s  $\text{cm}^{-1}$ ; IV: 1942s, 1842s  $\text{cm}^{-1}$ ; V: 1935s, 1835s  $\text{cm}^{-1}$ .

#### Neutral complexes

$[\text{Mn}(\text{CO})_2\text{L}_2(\text{Mebibzim})]$  ( $\text{L} = \text{P}(\text{OMe})_3$  (VI),  $\text{P}(\text{OEt})_3$  (VII)) and  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\{\text{Me}(\text{N-N})_2\}]$  ( $\text{Me}(\text{N-N})_2^- = \text{Mebiim}^-$  (XVII),  $\text{Mebibzim}^-$  (XVIII),  $\text{Metmbiim}^-$  (XIX)). General procedure. A solution of the anionic complexes I–V (1 mmol) (or the corresponding molybdenum potassium salts, prepared in situ as described above) and an excess of MeI (ca. 2 mmol) was stirred at room temperature until the two  $\nu(\text{CO})$  absorptions in the IR spectra were completely replaced by

two new ones of higher energy (ca. 1 h). The corresponding complexes were isolated (70–80% yields) from the filtered solutions as follows:

*VI–VII*: partial evaporation and addition of hexane.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ): *VI*:  $\delta$  7.7 (m, 8H, bibzim), 4.5 (s, 3H, N- $\text{CH}_3$ ), 3.1 (t, 18H, OMe) ppm; *VII*:  $\delta$  7.7 (m, 8H, bibzim), 4.5 (s, 3H, N- $\text{CH}_3$ ), 3.5 (m, 12H,  $\text{CH}_2$ ), 0.8 (t, 18H,  $\text{CH}_3$ ) ppm.

*XVII–XIX*: evaporation to dryness and recrystallization from cold toluene.  $^1\text{H NMR}$ : *XVII*: (in  $(\text{CD}_3)_2\text{CO}$ )  $\delta$  6.8, 7.3 (m, 4H, biim), 5.4 (s, 5H,  $\text{C}_5\text{H}_5$ ), 4.1 (s, 3H, N- $\text{CH}_3$ ) ppm; *XVIII*: (in  $\text{CDCl}_3$ )  $\delta$  7.5 (m, 8H, bibzim), 5.6 (s, 5H,  $\text{C}_5\text{H}_5$ ), 4.5 (s, 3H, N- $\text{CH}_3$ ) ppm; *XIX*: (in  $\text{CDCl}_3$ )  $\delta$  5.4 (s, 5H,  $\text{C}_5\text{H}_5$ ), 3.4 (s, 3H, N- $\text{CH}_3$ ), 2.3 (s, 3H, *exo*  $\text{CH}_3$  ring), 2.2 (s, 3H, *endo*  $\text{CH}_3$  ring) ppm.

$[\text{Mn}(\text{CO})_3\text{L}(\text{Hbibzim})]$  ( $\text{L} = \text{P}(\text{OMe})_3$  (*VIII*),  $\text{P}(\text{OEt})_3$  (*IX*)). A mixture of  $\text{H}_2$ -bibzim (1 mmol) and KOH (2 mmol) in 30 ml of methanol/dichloromethane (1/1) was stirred for 2 h and  $[\text{Mn}(\text{CO})_4(\mu\text{-Br})]_2$  (0.5 mmol) was added. After 15 min refluxing 1 mmol of ligand was added and refluxing continued for 30 min. The solutions were evaporated to dryness and the residues extracted with dichloromethane. Addition of hexane and cooling yielded yellow microcrystalline solids. Yields: *VIII*: 35%; *IX*: 58%. IR  $\nu(\text{N-H})$  (KBr pellet): 3000–2300 (s, br)  $\text{cm}^{-1}$ . MW ( $\text{CHCl}_3$ ): Found (calcd.): *VIII*: 578 (496); *IX*: 619 (490).

$\text{L} = \text{P}(\text{OPh})_3$ ,  $\text{P}(\text{OEt})_3$ ,  $\text{P}(\text{O}^i\text{Pr})_3$ . The IR spectra of the reaction solutions in the  $\nu(\text{CO})$  stretching region show absorptions corresponding to a mixture of tri- and dicarbonyl complexes; these could not be separated.

$[\text{Mn}(\text{CO})_2\text{L}_2\{\text{H}(\text{N-N})_2\}]$  ( $\text{H}(\text{N-N})_2^- = \text{Hbiim}^-$ ,  $\text{L} = \text{P}(\text{OPh})_3$  (*X*),  $\text{P}(\text{OMe})_3$  (*XI*),  $\text{P}(\text{OEt})_3$  (*XII*),  $\text{P}(\text{O}^i\text{Pr})_3$  (*XIII*);  $\text{H}(\text{N-N})_2^- = \text{Hbibzim}^-$ ,  $\text{L} = \text{P}(\text{OPh})_3$  (*XIV*),  $\text{P}(\text{OMe})_3$  (*XV*),  $\text{P}(\text{OEt})_3$  (*XVI*)). A mixture of  $\text{H}_2(\text{N-N})_2$  (1 mmol) and KOH (2 mmol) in 30 ml of THF was stirred for 2 h at room temperature and then  $[\text{Mn}(\text{CO})_4(\mu\text{-Br})]_2$  (0.5 mmol) was added. After 15 min refluxing the suspension was cooled to room temperature and the relevant ligand (ca. 2 mmol) was added. Evolution of CO occurred, and the mixture was then refluxed until the IR spectra in the  $\nu(\text{CO})$  stretching region showed two absorptions characteristic of a *cis*-dicarbonyl system. THF was removed under vacuum and the yellow residue extracted with dichloromethane. Partial evaporation under reduced pressure and addition of hexane led to the precipitation of yellow microcrystalline solids. Reaction times and yields: *X*: 45 min, 60%; *XI*: 20 min, 57%; *XII*: 25 min, 33%; *XIII*: 25 min, 56%; *XIV*: 75 min, 52%; *XV*: 60 min, 54%; *XVI*: 30 min, 35%. MW (in  $\text{CHCl}_3$ ): Found (calcd.): *X*: 1101 (865); *XI*: 655 (492); *XII*: 731 (576); *XIII*: 770 (661); *XIV*: 803 (965); *XV*: 758 (592); *XVI*: 837 (676).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ): *XI*:  $\delta$  7.4 (m, 4H, biim), 3.4 (t, 6H,  $\text{OCH}_3$ ) ppm; *XV*:  $\delta$  7.7 (m, 8H, bibzim), 3.2 (t, 6H,  $\text{OCH}_3$ ) ppm.

$[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\{\text{H}(\text{N-N})_2\}]$  ( $\text{H}(\text{N-N})_2^- = \text{Hbiim}^-$  (*XX*),  $\text{Hbibzim}^-$  (*XXI*),  $\text{Htmbiim}^-$  (*XXII*)). A mixture of  $\text{H}_2(\text{N-N})_2$  (1 mmol) and KOH (2 mmol) in 30 ml of THF/MeOH (4/1) was stirred for 30 min and  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cl}]$  (0.28 g, 1 mmol) was added. After 45 min stirring at room temperature solvents were removed under vacuum and the residue extracted with dichloromethane. Addition of hexane and partial evaporation under reduced pressure gave red microcrystalline solids. Yields: *XX*: 94%; *XXI*: 95%; *XXII*: 90%. IR  $\nu(\text{N-H})$  (KBr pellet): 3000–2500  $\text{cm}^{-1}$ . MW ( $\text{CHCl}_3$ ): Found (calcd.): *XX*: 584 (350); *XXI*: 675 (450); *XXII*: 629 (406).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ): *XX*:  $\delta$  7.2 (m, 4H, biim), 5.4 (s, 5H,  $\text{C}_5\text{H}_5$ ) ppm; *XXI*:  $\delta$  7.5 (m, 8H, bibzim), 5.6 (s, 5H,  $\text{C}_5\text{H}_5$ ) ppm; *XXII*:  $\delta$  5.4 (s, 5H,  $\text{C}_5\text{H}_5$ ), 2.2 (s, 3H, *exo*  $\text{CH}_3$  ring), 2.1 (s, 3H, *endo*  $\text{CH}_3$  ring) ppm.



### Cationic complexes

$[Mn(CO)_3L(H_2bibzim)][ClO_4]$  ( $L = P(OMe)_3$  (XXIII),  $PEt_3$  (XXIV)) and  $[Mn(CO)_2L_2\{H_2(N-N)_2\}][ClO_4]$  ( $H_2(N-N)_2 = H_2biim$ ;  $L = P(OPh)_3$  (XXV),  $P(OMe)_3$  (XXVI),  $P(OEt)_3$  (XXVII),  $P(O^iPr)_3$  (XXVIII);  $H_2(N-N)_2 = H_2bibzim$ ;  $L = P(OPh)_3$  (XXIX),  $P(OMe)_3$  (XXX),  $P(OEt)_3$  (XXXI)). A solution of neutral complexes VIII–XVI (1 mmol) in 30 ml of dichloromethane was treated with 0.06 ml of 60%  $HClO_4$  and stirred at room temperature for 1 h. After filtration through Celite the filtrate was concentrated under reduced pressure. Complexes XXIII–XXXI were precipitated as yellow microcrystalline solids by addition of hexane. Yields and  $\Lambda_M$  ( $S\text{ cm}^2\text{ mol}^{-1}$ ) (acetone): XXIII: 71%, 117; XXIV: 81%, 111; XXV: 79%, 111; XXVI: 85%, 135; XXVII: 75%, 126; XXVIII: 62%, 128; XXIX: 82%, 100; XXX: 88%, 120; XXXI: 63%, 113.

Complexes XXX and XXXI could also be obtained by treating a dichloromethane solution of the anionic salts I or II, respectively, with an excess of 60%  $HClO_4$ . They were identified by comparison of the IR spectra in the  $\nu(CO)$  stretching region with those of original samples.

### Reactions of $[Mo(\eta^5-C_5H_5)(CO)_2\{H(N-N)_2\}]$ (XX–XXII) with aq. $HClO_4$

A solution of XX–XXII (0.1 mmol) in 10 ml of dichloromethane was treated with an excess of 60%  $HClO_4$  and stirred at room temperature. The reaction was monitored by periodical scans of IR spectra in the  $\nu(CO)$  stretching region, which revealed new two absorptions at higher energy (ca.  $30\text{ cm}^{-1}$ ).

### Acknowledgement

We thank the Spanish C.A.I.C.Y.T. for financial support.

### References

- 1 R. Usón and J. Gimeno, *J. Organomet. Chem.*, 220 (1981) 173.
- 2 R. Usón, J. Gimeno, J. Forniés, F. Martínez and C. Fernández, *Inorg. Chim. Acta*, 54 (1981) L95; 63 (1982) 91.
- 3 R. Usón, J. Gimeno, J. Forniés and F. Martínez, *Inorg. Chim. Acta*, 50 (1981) 173.
- 4 R. Usón, J. Gimeno, L.A. Oro, M.A. Aznar and J.A. Cabeza, *Polyhedron*, 2 (1983) 163.
- 5 R. Usón, J. Gimeno, L.A. Oro, J.M. Martínez, J.A. Cabeza, A. Tiripicchio and M. Tiripicchio Camellini, *J. Chem. Soc., Dalton Trans.*, (1983) 1729.
- 6 R. Usón, L.A. Oro, J. Gimeno, M.A. Ciriano, J.A. Cabeza, A. Tiripicchio and M. Tiripicchio Camellini, *J. Chem. Soc., Dalton Trans.*, (1983) 323.
- 7 W. Beck, F. Götzfried und M. Riederer, *Z. Anorg. Allg. Chem.*, 423 (1976) 97.
- 8 J.W. Kaiser, R.B. Saillant, W.N. Butler and P.G. Rasmussen, *Inorg. Chem.*, 17 (1976) 2681.
- 9 J.M. Jenkins and B.L. Shaw, *J. Chem. Soc. (A)*, (1966) 770.
- 10 B.F. Fieselmann, D.N. Hendrickson and G.B. Stucky, *Inorg. Chem.*, 17 (1978) 2078.
- 11 R. Kuhn and W. Blann, *Liebigs Ann. Chem.*, 605 (1975) 32.
- 12 R.J. Angelici, *Inorg. Chem.*, 3 (1964) 1099; E.B. Abel and J.S. Butler, *J. Chem. Soc.*, (1964) 434.
- 13 T.S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 3 (1956) 104.