

MARIA J. CALHORDA
ALBERTO R. DIAS*

Centro de Química Estrutural
Complexo I
Instituto Superior Técnico
1096 Lisboa Codex, Portugal



METAL COMPLEXES WITH DIAZINES AND 4,4' — BIPYRIDYL LIGANDS

Complexes $[M(\eta^5-C_5H_5)_2X_2]$ ($M=Mo, W$; $X=halogen$) and $[Mo(\eta^5-C_5H_5)_2HI]$ react with nitrogen donor atom ligands pyridazine, pyrimidine, pyrazine and 4,4'—bipyridyl to give new complexes which were fully characterized.

1 — INTRODUCTION

We have been interested for some time in the coordination of nitrogen donor atom ligands and nitrogen and oxygen donor atom ligands to the early transition metals. In previous articles [1] we have described the synthesis, characterization and reactivity of new complexes containing the $M(\eta^5-C_5H_5)_2$ ($M=Ti, Mo, W$) moiety and some of these ligands. We now report the results of related studies with ligands pyridazine (**I**, pyrd), pyrimidine (**II**, pyrm), pyrazine (**III**, pyr_z) and 4,4'-bipyridyl (**IV**, 4-bipy).

2 — RESULTS AND DISCUSSION

The compounds $[M(\eta^5-C_5H_5)_2Br_2]$, $[M(\eta^5-C_5H_5)_2HI]$ and $[M(\eta^5-C_5H_5)_2H_3] [PF_6]$ ($M=Mo$ and, sometimes, W) reacted under various conditions with the nitrogen donor atom ligands pyridazine (**I**, pyrd), pyrimidine (**II**, pyrm), pyrazine (**III**, pyr_z) and 4,4'—bipyridyl (**IV**, 4-bipy) to give the new compounds shown in fig. 1. The analytical and conductimetric evidence for the formulae proposed is given in Table 1, the 1H nmr spectra are described in Table 2 and the ir assignments are given in Tables 3-5.

Reaction of $[Mo(\eta^5-C_5H_5)_2Br_2]$ with pyridazine in refluxing acetone in the presence of one equivalent of $Tl[PF_6]$ gave an air stable dark brown crystalline compound. The elemental and conductimetric data (Table 1) together with the 1H nmr spectrum (three triplets and one singlet with relative areas 1:1:2:10) (Table 2), and the infrared spectrum (showing bands characteristic of the $\eta^5-C_5H_5$ ring, $[PF_6]$ anion and bands characteristic of the ligands, some of which shifted in relation to the free ligand) (Table 3), support the formula $[Mo(\eta^5-C_5H_5)_2Br(pyrd)][PF_6]$ (**Ia**). The analogous tungsten complex was prepared in the same way and was characterized in a similar fashion although the results of elemental analysis were not good even after repeated recrystallisations. Compound **Ia** reacts with $[NO][PF_6]$ in acetonitrile solution to give red crystals which were identified as being the known compounds $[Mo(\eta^5-C_5H_5)_2Br(MeCN)][PF_6]_2$ [2] by comparison of its ir spectrum with that of an authentic sample. When the reaction of **Ia** with $[NO][PF_6]$ was repeated in dry CH_2Cl_2 a dark blue compound was obtained.

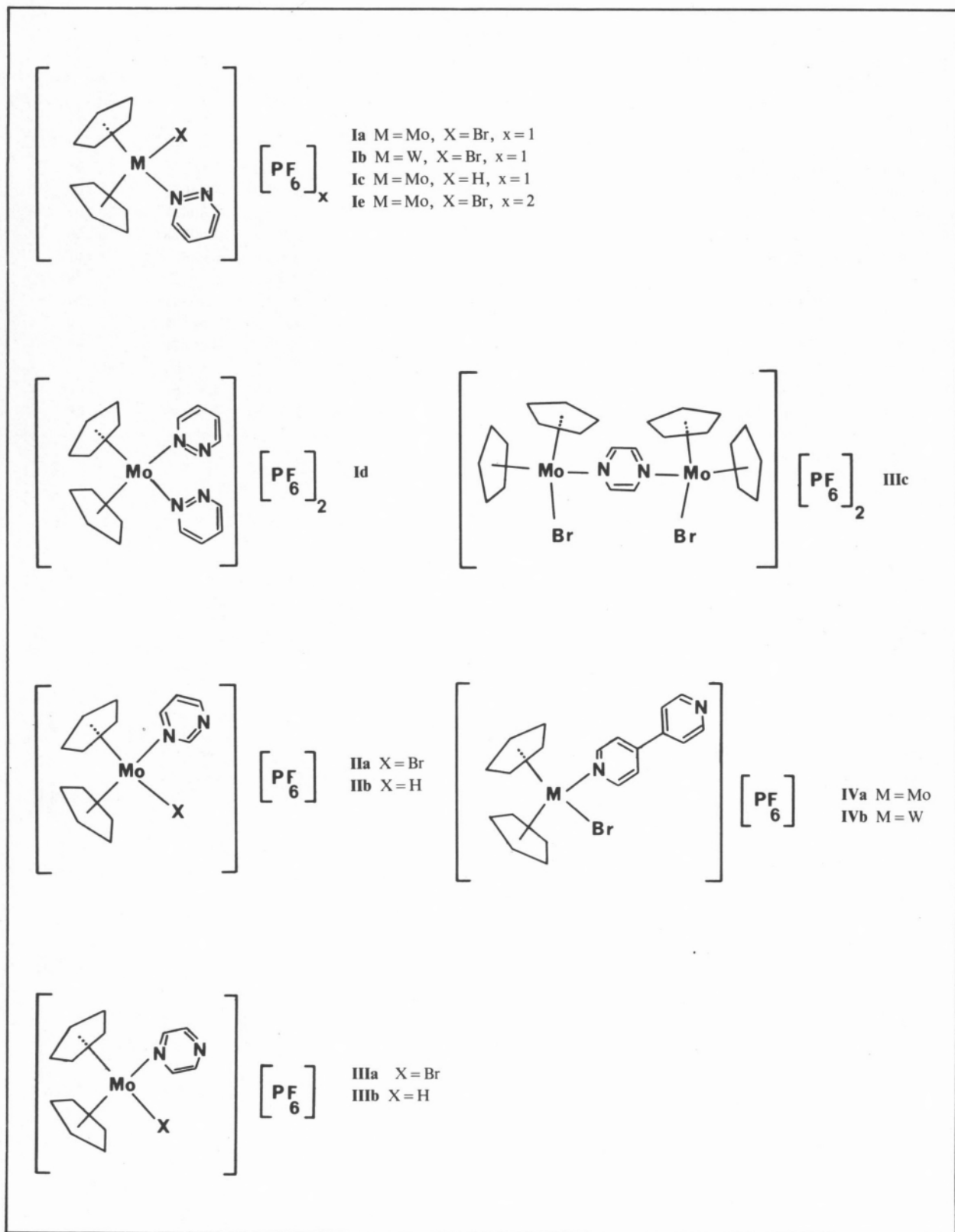


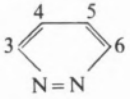
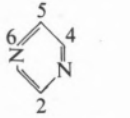
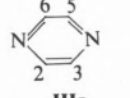
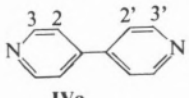
Fig. 1
Structural formulae of compounds I-IV

Table 1
Analytical and conductimetric data

COMPOUND	COLOUR	DEC/°C	ANALYSIS found (req)			MOLAR CONDUCTIVITY ^{a)}
			C	H	N	
Ia [Mo(η -C ₅ H ₅) ₂ Br(pyrd)][PF ₆]	brown	—	32.2(31.7)	2.7(2.7)	5.6(5.3)	91
Ib [W(η -C ₅ H ₅) ₂ Br(pyrd)][PF ₆]	red	180	28.3(27.2)	2.6(2.3)	4.8(4.3)	100
Ic [Mo(η -C ₅ H ₅) ₂ H(pyrd)][PF ₆]	red	140	37.15(37.2)	3.5(3.3)	6.1(6.2)	106
Id [Mo(η -C ₅ H ₅) ₂ (pyrd) ₂][PF ₆] ₂	red	180	32.6(32.0)	2.9(2.7)	7.8(8.3)	206
Ie [Mo(η -C ₅ H ₅) ₂ Br(pyrd)][PF ₆] ₂	dark blue	—	25.9(24.9)	2.4(2.1)	4.35(4.1)	440 ^{b)}
IIa [Mo(η -C ₅ H ₅) ₂ Br(pyrm)][PF ₆]	green	190	31.8(31.7)	2.6(2.7)	5.4(5.3)	76
IIb [Mo(η -C ₅ H ₅) ₂ H(pyrm)][PF ₆]	orange	140	37.2(37.2)	3.7(3.3)	5.4(6.2)	84
IIIa [Mo(η -C ₅ H ₅) ₂ Br(pyrz)][PF ₆]	green	230	31.7(31.7)	2.8(2.7)	5.6(5.3)	80
IIIb [Mo(η -C ₅ H ₅) ₂ H(pyrz)][PF ₆]	purplish-pink	130	37.0(37.2)	3.4(3.3)	4.7(6.2)	95
IIIc [Mo(η -C ₅ H ₅) ₂ Br ₂ (pyrz)][PF ₆] ₂	light-green	210	30.2(29.35)	2.6(2.5)	2.3(2.85)	—
IVa [Mo(η -C ₅ H ₅) ₂ Br(4-bipy)][PF ₆]	dark green	200	39.5(39.6)	3.2(3.0)	4.5(4.6)	—
IVb [W(η -C ₅ H ₅) ₂ Br(4-bipy)][PF ₆]	dark brown	190	34.2(34.6)	2.8(2.6)	3.4(4.0)	88

a) $\Lambda_M/\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ in CH₃NO₂; b) in CH₃CN.

Table 2
¹H nmr Data ^{a)}

Compound	τ (multiplicity ^{b)} , relative intensity)					
	3	4	5	6	η^5 -C ₅ H ₅	H ⁺
Ia	0.72(T,2) ^{c)}	2.30(T,2)				
Ib	—0.47(T,1)	1.96(T,2)		0.92(T,1)	3.99(S,10)	
Ic	—0.34(br,1)	1.89(br,2)		0.84(br,1)	4.04(S,10)	
Id	0.25(C,1)	2.20(C,2)		0.98(C,1)	4.63(S,10)	19.00(S,1)
	0.72(C,4) ^{c)}	1.97(C,4)			3.57(S,10)	
	2	4	5	6	η^5 -C ₅ H ₅	H ⁺
IIa	0.79(S,1)	1.17(D,2) ^{c)}	2.47(T,1)			
IIb	0.41(C,2) ^{c)}	0.94(D,2)	2.28(T,1)		3.86(S,10)	
	0.53(S,1)	1.12(D,2)	2.51(T,1)	0.84(D,1)	4.49(S,10)	19.04(S,1)
	2	3	5	6	η^5 -C ₅ H ₅	
IIIa	1.35(S) ^{d)}					
IIIb	0.81(D,2)	1.24(D,2)			3.88(S,10)	
IIIc	1.12(D,2)	1.40(D,2)			4.49(S,10)	19.17(S,1)
	1.20(S) ^{d,e)}				4.21(S)	
	3	3'	2,2'		η^5 -C ₅ H ₅	
IVa	1.21(D,2)		2,20(C,4)			
IVb	0.68(D,2)	1.12(D,2)	2.13(C,4)		3.91(S,10)	
	0.37(br,2)	1.12(br,2)	2.07(br,4)		3.95(S,10)	

a) solvent acetone-d₆ except where stated otherwise, internal reference TMS; b) S singlet, D doublet, T triplet, C complex; br broad; c) includes proton 6; d) includes all the ligand protons; e) solvent DMSO-d₆.

Table 3
Frequencies of some of the vibrational modes of pyridazine and its complexes *

Vibrational mode	Description [4]	Pyridazine [PF ₆]	[MoCp ₂ Br(pyrd)] [PF ₆]	[WCp ₂ Br(pyrd)] [PF ₆]	[MoCp ₂ H(pyrd)] [PF ₆]	[MoCp ₂ (pyrd) ₂] [PF ₆] ₂
8a	Ring	1575	1590	1590	1580 (shoulder)	1590
8b	Ring	1565	1575	1575	1570	1575
19a	Ring	1445	1450	1450	1450	1450
19b	Ring	1415	1425	1425	1425	1425
14	Ring	1285	—	—	—	—
9a		1160	1155	1155	—	—
15	Bending CH	1065	1065	1065	1065	1065
1	Ring	965	960	955	975	960,975
10a	Deformation CH	775	775	775	780	770
6a	Ring	620	640	645	640	640
6b	Ring	665	675	675	675	675
16b	Ring	375	395	—	400	395

* Cp = η^5 -C₅H₅

Although its complete characterization was not satisfactory due to its decomposition in solution, the data available support the formulation [Mo(η -C₅H₅)₂Br(pyrd)] [PF₆]₂ (**Id**).

Refluxing **Id** in acetone for 25 hrs in the presence of excess pyridazine and thallium hexafluorophosphate yielded a red crystalline compound. Its ir spectrum is very similar to that of complex **Ia** and the molar conductivity is characteristic of a 2:1 electrolyte. Together with elemental analysis results these data are compatible with the formulation [Mo(η -C₅H₅)₂(pyrd)₂] [PF₆]₂ (**Id**).

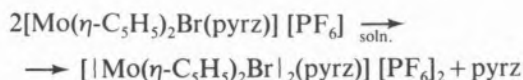
The ¹H nmr spectrum is puzzling: it shows three peaks with the relative areas 4:4:10; although the presence of only two peaks assignable to the pyridazine ligand seems to suggest a dimeric structure, the relative areas (pyridazine and η -C₅H₅) favour the monomeric structure **Id** in agreement with the elemental analysis results. No change was observed in the ¹H nmr spectrum on lowering the temperature down to -70°C. The equivalence of protons 3 and 6 (see Table 2) in the nmr spectrum may be due either to fluxional behaviour (coordination of the ligand to the metal changing from one nitrogen atom to the other) or to coordination through the N=N double bond. Further clarification of this problem must wait for an X-ray molecular structure determination. Under similar reaction conditions a very small amount of a reddish-brown crystalline compound was obtained from [W(η -C₅H₅)₂Br₂]; its characterization was not complete but the data

available suggest a structure similar to that of complex **Id**. The use of complexes [M(η -C₅H₅)₂(SR)₂] (M = Mo, W, Ta, Nb) as bidentate chelating ligands is well established [3]. Preliminary studies on the behaviour of complex **Id** as a bidentate ligand to transition metals proved promising and will be further investigated in the near future.

Reaction of [Mo(η -C₅H₅)₂H₃] [PF₆] with pyridazine in refluxing acetone or of [Mo(η -C₅H₅)₂HI] with the same ligand and in the same solvent but in the presence of Tl[PF₆] gave red crystals which were fully characterized as being the new hydride complex [Mo(η -C₅H₅)₂H(pyrd)] [PF₆] (**Ic**). This complex reacts with CHBr₃ in acetone to give complex (**Ia**) identified by comparison of its infrared spectrum with that of an authentic sample. Reaction of [Mo(η -C₅H₅)₂Br₂] with pyrimidine in refluxing acetone in the presence of one equivalent of Tl[PF₆] gave green crystals which were fully characterized as being the complex [Mo(η -C₅H₅)₂Br(pyrm)] [PF₆] (**Ila**). Starting from the complex [Mo(η -C₅H₅)₂HI] and working under the same conditions the related hydride complex [Mo(η -C₅H₅)₂H(pyrm)] [PF₆] (**Ilb**) was obtained.

Reaction of [Mo(η -C₅H₅)₂Br₂] with pyrazine in the presence of Tl[PF₆] in refluxing acetone during one hour gave a brownish-green crystalline compound which, on the basis of the evidence available, was formulated as being the complex [Mo(η -C₅H₅)₂Br(pyrz)] [PF₆] (**IIla**). It was also observed that the results of elemental analysis became worse with

successive recrystallisations. When a larger reaction time was used, a light-green crystalline compound formed which was insoluble in all the common solvents except DMSO. The ir spectrum shows the presence of the anions $\eta\text{-C}_5\text{H}_5^-$ and PF_6^- , as well as the peaks characteristic of the coordinated pyrazine. The ^1H nmr spectrum in DMSO-d_6 is not clean and suggests the presence of two compounds. After some time two of the peaks increased in area; based on their position and relative intensities we can assign one of them to four equivalent protons of one heterocycle and the other one to twenty protons of four $\eta\text{-C}_5\text{H}_5$ rings. Together with the values of elemental analysis we propose for this complex the formula $[\{\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}\}_2\text{pyrz}][\text{PF}_6]$ (**IIIc**) where the pyrazine is a bridging ligand, its favourite coordination mode [5]. The observations described suggest that the first product of the reaction of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}_2]$ with pyrazine is the mononuclear complex (**IIIa**) which slowly decomposes in solution to give the dinuclear complex (**IIIc**)



Pyrazine also reacts with $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{HI}]$ in refluxing acetone and in the presence of $\text{Ti}[\text{PF}_6]$ to give a reddish-pink crystalline compound which we tentatively identified as the hydride complex. $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{pyrz})][\text{PF}_6]$ **IIIb**; the analytical results are not very good as recrystallisation gives an

insoluble product probably a dimeric species equivalent to **IIIc**.

$[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{Br}_2]$ ($\text{M} = \text{Mo}, \text{W}$) reacts with 4,4'-bipyridyl in refluxing acetone to give crystalline compounds identified as $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{Br}(4\text{-bipy})][\text{PF}_6]$ ($\text{M} = \text{Mo}$ (**IVa**); $\text{M} = \text{W}$ (**IVb**), the tungsten compound being obtained only in very small yield. The formation of dimeric species was not observed even after 20 hrs reflux and a 2:1 metal/ligand ratio.

INFRARED SPECTRA The infrared and Raman spectra of ligands pyridazine, pyrimidine and pyrazine are described in the literature [4]. A complete study of the vibrational modes of 4,4'-bipyridyl has not been found.

Table 3 describes the frequencies of several vibrational modes of the free pyridazine [4] and of the coordinated ligand in complexes (**Ia-d**). Small shifts to higher frequencies in the bands corresponding to vibrational modes of the ring were observed. As in other cases where the ligand acts as monodentate [6,7], the band corresponding to stretching mode C-H was not observed as it comes under the corresponding mode of the cyclopentadienyl ring. Table 4 describes the frequencies of the free pyrimidine [4] and of the ligand in complexes (**IIa-b**). It was observed that the frequencies of the several vibrational modes are not much affected upon coordination to the metal. The largest shift was observed for the band corresponding to the vibrational modes 8a and 8b of the ring, which is

Table 4
Frequencies of some of the vibrational modes of pyrimidine and its complexes*

Vibrational mode	Description [4]	Pyrimidine	$[\text{MoCp}_2\text{Br}(\text{pyrm})][\text{PF}_6]$	$[\text{MoCp}_2\text{H}(\text{pyrm})][\text{PF}_6]$
2,13	Stretching C-H	3040	3090	3100
8a,8b	Ring	1570	1595,1560	1595
19a	Ring	1470	1470	1470
19b	Ring	1400	1410	1410
3	Deformation C-H	1230	1230	1235
15	Deformation C-H	1160	1180	1180
9a	Deformation C-H	1140	1135	1140
12	Ring	1075	1070	1070
1,5	Ring	995	995	—
11	Deformation C-H	815	—	825(?)
10b	Deformation C-H	720	705	710
4	Ring	680	685	690
6a	Ring	625	645	645
16b	Ring	350	390	400

* $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$

shifted from 1575 cm^{-1} in the free ligand to near 1600 cm^{-1} in **IIa** and split into two bands at 1599 and 1560 cm^{-1} in **IIb**. The band at 1400 cm^{-1} in the free ligand is shifted to higher frequencies upon coordination. These results are in agreement with those described in the literature for pyrimidine complexes of metals of the first transition series [7].

Table 5 describes the frequencies of the free pyrazine [4] and of the ligand in its complexes (**IIIa-c**). A new band at 950-1000 cm^{-1} was observed as it had been reported before [8] but it seems to be stronger in the case of bridging pyrazine.

Table 5
Frequencies of some of the vibrational modes of pyrazine and its complexes *

Vibrational mode	Description [4]	Pyrazine	$[\text{Mo}(\text{Cp}_2\text{Br})_2\text{pyrz}][\text{PF}_6]_2$	$[(\text{MoCp}_2\text{Br})_2\text{pyrz}][\text{PF}_6]_2$	$[\text{MoCp}_2\text{H}(\text{pyrz})][\text{PF}_6]$
2,13,20b	Stretching C-H	3060	3100,3040	3100,3050	—
8a	Ring	1585 [4]	1590	—	1590
19a	Ring	1495	1485	1480	1480
19b	Ring	1420	1415	1425(?)	1415
15	Deformation C-H	1145	1150	1150	1150
18a	Deformation C-H	1065	1050	1065	1050
1,12	Ring	1020	1020(?)	1025	1010(?)
11	Deformation C-H	790	—	—	780
16b	Ring	415	~ 400	~ 400	~ 400

* $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$

3 — EXPERIMENTAL

All preparations and further manipulation were carried out under dry nitrogen unless otherwise stated. The compounds $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3][\text{PF}_6]$, $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{Br}_2]$ and $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{HI}]$ ($\text{M} = \text{Mo}, \text{W}$) were prepared by the reported methods [9-11]. Pyridazine (Aldrich), pyrimidine (Merck), pyrazine (Fluka) and 4,4'-bipyridyl (Merck) were purchased and used without further purification.

^1H nmr spectra were determined on a JEOL JNM-PS-100 instrument. Infrared spectra were determined on a Perkin-Elmer 457 spectrophotometer in KBr pellets and were calibrated with polystyrene film. Conductivity measurements were made at 25°C using a Radiometer CDM 3 Conductivity Meter instrument calibrated with a standard KCl solution. C,H,N analyses were carried out in these laboratories.

The experimental conditions for some typical reactions are given below.

Preparation of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}(\text{pyrd})][\text{PF}_6]$

560 mg (~ 1.2 mmole) of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}_2]$ together with $\text{Tl}[\text{PF}_6]$ (700 mg ~ 2 mmole) and pyridazine (1 cm^3) were refluxed in acetone (50 cm^3) for 11 hrs. The brown mixture was filtered, the volume of the filtrate was reduced under vacuum and diethyl ether was added giving an oil. The solvent was decanted and the oil was taken to dryness under vacuum. Recrystallisation from acetone/ethanol gave dark brown crystals which were identified as being $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}(\text{pyrd})][\text{PF}_6]$. Yield ca. 80%.

Preparation of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{pyrd})_2][\text{PF}_6]_2$

400 mg (≈ 1 mmole) of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}_2]$ together with excess $\text{Tl}[\text{PF}_6]$ and pyridazine (2 cm^3) were refluxed in acetone (30 cm^3) for 10 hrs. The mixture was filtered, the volume of the filtrate was reduced and water was added. Removal of acetone under vacuum gave a red oil. This was crystallised from acetone/ethanol giving a mixture of brown and red crystals. This mixture was dissolved in acetone (40 cm^3) and an excess of $\text{Tl}[\text{PF}_6]$ and of pyridazine was added. The same mixture was refluxed for 25 hrs and then treated as above. Red crystals were obtained which were identified as being $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{pyrd})_2][\text{PF}_6]_2$. Yield ca. 70%.

Preparation of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{pyrd})][\text{PF}_6]$

450 mg (≈ 1.3 mmole) of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{HI}]$ together with 470 mg (≈ 1.3 mmole) of $\text{Tl}[\text{PF}_6]$ and 0.5 cm^3 of pyridazine were refluxed in acetone (40 cm^3) for 4 hrs. The mixture was filtered, the volume of the filtrate was reduced and chromatographed on an

alumina column, using acetone as eluent. A red solution was obtained; its volume was reduced under vacuum and slow addition of diethylether gave red crystals which were identified as being $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{pyrd})][\text{PF}_6]$ yield ca. 70%.

Preparation of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}(\text{pyrd})][\text{PF}_6]_2$
 $[\text{NO}][\text{PF}_6]$ (90 mg \approx 0.5 mmole) was added to a suspension of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}(\text{pyrd})][\text{PF}_6]$ (160 mg \approx 0.3 mmole) in dry CH_2Cl_2 (5 cm³). The mixture was stirred during 4 hrs at room temperature and then filtered. The dark blue solid was washed several times with dry diethyl ether and then dried. It was identified as being $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}(\text{pyrd})][\text{PF}_6]_2$. Yield ca. 50%.

Preparation of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}(\text{pyrz})][\text{PF}_6]_2$
 $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}_2]$ (400 mg \approx 1 mmole), $\text{Ti}[\text{PF}_6]$ (350 mg \approx 1 mmole) and pyrazine (10 mg \approx 1.5 mmole) were refluxed in acetone (30 cm³) during six hrs. The mixture was filtered, the volume of the green filtrate was reduced under vacuum and addition of diethyl ether gave a light green solid. This was insoluble in the common organic solvents except in DMSO where it decomposed.

The solid was identified as being $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}(\text{pyrz})][\text{PF}_6]_2$. Yield ca. 40%.

Preparation of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}(\text{pyrz})][\text{PF}_6]$
 $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}_2]$ (400 mg \approx 1.2 mmole), pyrazine (180 mg \approx 3 mmole) were refluxed in acetone (200 cm³) for 1 hr. The mixture was filtered. The volume of the filtrate was reduced and water was added giving green crystals which were identified as being $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}(\text{pyrz})][\text{PF}_6]$. Yield ca. 60%.

Received 13. February. 1981

REFERENCES

- [1] (a) — M. J. CALHORDA, A. R. DIAS, *Rev. Port. Quím.*, **20**, 77 (1978).
 (b) — idem, *J. Chem. Soc. Dalton*, 1443 (1980).
 (c) — idem, *J. Organometal. Chem.*, **197**, 291 (1980).
 (d) — ibid, **198**, 41 (1980).
- [2] M. J. CALHORDA, Doctoral Thesis, Lisbon (1980).
- [3] See for instance (a) A. R. DIAS, M. L. H. GREEN, *Rev. Port. Quím.*, **11**, 61 (1969).
 (b) — idem, *J. Chem. Soc. (A)*, 195 (1971).
 (c) — ibid, 2807 (1971).
 (d) — P. S. BRATERMAN, V. A. WILSON, K. K. JOSHI, *J. Chem. Soc. (A)*, 191 (1971).
 (e) — W. E. DOUGLAS, M. L. H. GREEN, *J. Chem. Soc. Dalton*, 1976 (1972).
 (f) — C. DAREN, K. PROUT, A. DE CIAM, M. L. H. GREEN, N. SINGAPORIA, *J. Organometal. Chem.*, **136**, C4 (1974).
- [4] R. C. LORD, A. L. MARSTON, F. A. MILLER, *Spectrosc. Acta*, **9**, 113 (1957).
- [5] W. M. CARMICHAEL, D. A. EDWARDS — *J. Inorg. Nucl. Chem.*, **32**, 1199 (1970).
- [6] M. HERBERHOLD, M. LEONHARD, *J. Organometal. Chem.*, **78**, 253 (1974).
- [7] J. R. FERRERO, J. ZIPPER, W. WOZNIK, *Appl. Spectrosc.*, **23**, 160 (1969).
- [8] W. M. CARMICHAEL, D. A. EDWARDS, *J. Inorg. Nucl. Chem.*, **34**, 1181 (1972).
- [9] M. L. H. GREEN, P. J. KNOWLES, *J. Chem. Soc. Perkin Trans. I*, 193 (1979).
- [10] R. L. COOPER, M. L. H. GREEN, *J. Chem. Soc. (A)*, 1155 (1967).
- [11] C. C. ROMÃO, Doctoral Thesis, Lisbon (1979).

RESUMO

Complexos metálicos com ligandos diazinas e 4,4'-bipiridilo.
 Descreve-se a síntese e caracterização de complexos obtidos por reacção de $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{X}_2]$ ($\text{M}=\text{Mo}$, W ; $\text{X}=\text{halogéneo}$) ou $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{HI}]$ com os ligandos piridazina, pirimidina e 4,4'-bipiridilo.