



STUDIES ON THE REACTIVITY OF THE BIS-(η -CYCLOPENTADIENYL) MOLYBDENUM (OR TUNGSTEN) SYSTEM. SOME NEW COMPLEXES WITH NITROGEN AND NITROGEN AND OXYGEN DONOR ATOM LIGANDS

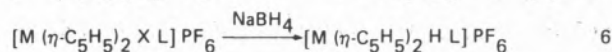
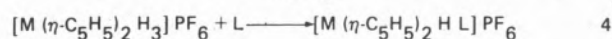
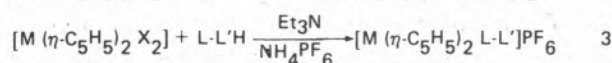
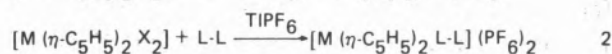
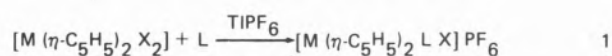
This paper describes the synthesis of complexes $[M(\eta\text{-C}_5\text{H}_5)_2(\text{L-L})](\text{PF}_6)_2$ (1) ($M = \text{Mo}, \text{W}$; $\text{L-L} = \text{bipyridil}, o\text{-phenanthroline}$), $[M(\eta\text{-C}_5\text{H}_5)_2(\text{L-L}')]\text{PF}_6$ (2) ($M = \text{Mo}, \text{W}$; $\text{L-L}' = 8\text{-quinolinato}, \text{pyridine-2-carboxylato}, 2\text{-pyridolato}$) and $[M(\eta\text{-C}_5\text{H}_5)_2\text{XL}]\text{PF}_6$ (3) ($\text{L} = \text{pyridine}$; $M = \text{Mo}$, $\text{X} = \text{H}, \text{Cl}, \text{I}$; $M = \text{W}$, $\text{X} = \text{H}, \text{Cl}, \text{Br}$).

The new compounds were identified by analytical and spectroscopic methods (IR, electronic and ^1H nmr) and their reactivity was studied with special emphasis on the substitution reactions of complexes (3).

1 — INTRODUCTION

The study of the reactivity of the bent bis- η -cyclopentadienyl metal complexes has received much attention due mainly to the variety of their reactions and to their potential use as catalyst precursors. As part of a general study on the reactivity of this type of compounds being carried out in these laboratories we have prepared, characterized and studied the reactions of some new complexes with nitrogen and nitrogen and oxygen donor atom ligands.

The general procedures used for the synthesis of the new compounds were the following:



where $M = \text{Mo}, \text{W}$; $\text{X} = \text{halogen}$; $\text{L} = \text{pyridine}$; $\text{L-L} = 2,2'\text{-bipyridil}$ or $o\text{-phenanthroline}$ and $\text{L-LH} = 8\text{-hydroxyquinoline}$, picolinic acid or 2-hydroxypyridine .

Although procedures 3 and 7 have been extensively used before [1, 2], methods 1, 2, 4 and 5 have only recently begun to be explored and are proving to be very convenient. The use of procedure 6 has been reported before [2] but its mechanism may involve a nucleophilic attack on the cyclopentadienyl ring and is now being investigated [3, 4].

2 — RESULTS AND DISCUSSION

The bidentate neutral ligands 2,2'-bipyridil and $o\text{-phenanthroline}$ reacted with $[M(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]\text{PF}_6$ and $[M(\eta\text{-C}_5\text{H}_5)_2\text{X}_2]$ (in the presence of TIPF_6) in refluxing acetone to give the dication complexes $[M(\eta\text{-C}_5\text{H}_5)_2\text{L-L}]^{2+}$, which were isolated as the hexa-

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fluorophosphate salts (I, II). Refluxing $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{I}_2]$ with 2,2'-bipyridil in acetone solution for 8hrs in the absence of TIPF_6 failed to yield the dication a different result from the one obtained with the ligand dppe (diphenylphosphinoethane) [3]. In the same way, after refluxing $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$ with 2,2'-bipyridil in acetone for 30hrs the starting materials were recovered. The analogous molybdenum dihydride complex was refluxed with *o*-phenanthroline in acetone for 25hrs and the starting material was recovered together with a small amount of a green compound very unstable which may be the known complex $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{O}]$. After refluxing $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H I}]$ with *o*-phenanthroline in acetone for 14hrs the complex decomposed and the ligand was recovered.

The monocation complexes $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{L-L'}]^+$ were obtained by refluxing the compound $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{X}_2]$ with 8-hydroxyquinoline, picolinic acid and 2-hydroxypyridine, respectively, in ethanol in the presence of triethylamine and were isolated as the hexafluorophosphate salts (III – V).

Refluxing $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{X}_2]$ in pyridine in the presence of TIPF_6 yielded the monocations $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{Xpy}]^+$ which were also isolated as the PF_6 salts (VI). Treatment of the halide pyridine complexes with sodium borohydride in toluene/acetone at room temperature gave the hydride pyridine complexes VI-a and VI-b. When the reaction was carried out in refluxing THF the known dihydride $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$ was obtained. Complexes VI-a and VI-b were also prepared by the direct reaction of the trihydride complex $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]\text{PF}_6$ with pyridine.

All chemical and photochemical attempts to prepare the bispyridine complex were unsuccessful probably due to stereochemical reasons.

Substitution reactions on the trihydride complex may involve as a first step the elimination of H_2 , formally a reductive elimination; with bidentate ligands a second step follows in which the hydride ligand is substituted.

All the new compounds described are well crystallised solids and are stable in air for prolonged periods; they are also thermally stable up to about 200-300 °C. The analytical and conductimetric evidence for the proposed structures (fig. 1) is given in Table I, the spectroscopic evidence (IR and electronic) is given in Table II and the ^1H n.m.r. spectra are described in Table III.

The electronic spectra are of the type usually found for the bent sandwich complexes [9].

The infrared spectra show the characteristic bands of

the anion, PF_6^- , of the cyclopentadienyl ring and those of the other ligands. The shifts of the bands of the pyridine ligand, namely at 1580, 1220, 991, 601 and 403 cm^{-1} are the ones usually associated with coordination through the nitrogen atom [16, 17, 18].

With the ligands 8-hydroxyquinoline, picolinic acid and 2-hydroxypyridine it was observed that the band associated with O-H stretching is absent in the complexes. In the complexes of the picolinic acid it was observed that the shift of the $> \text{C}=\text{O}$ frequency is the opposite of the one observed in the complexes where the coordination is only through the carboxylate group [15].

In the ^1H n.m.r. spectra is observed a general move of the chemical shifts of the protons of the pyridinic ligands to lower fields which is more pronounced for the *ortho* and *para* positions and small or non-existent for the *meta* protons. In the octahedral complexes dicyanobis(*o*-phenanthroline) iron (II) [19], tris(*o*-phenanthroline) iron (II) [20, 21], tris-(2,2'-bipyridil) iron (II) [22] and ethylenediamine bis(*o*-phenanthroline) ruthenium (II) [23] an increased shielding of the protons of the ligand in the regions where a ligand lies directly above the other has been observed; this effect is obviously absent in our monochelate complexes, in the bis(ethylenediamine) *o*-phenanthroline ruthenium (II) which also shows ABCM spectrum [23] and in the 2,2'-bipyridil (N, N'-dimethyl-1,2-diaminopropane) platinum (II) [24]. Also, the metal-protons (2,9) interaction invoked by MILLER and PRINCE [21] does not seem to be important here. The observed coupling constants, namely $J_{5,6} \approx 5\text{ Hz}$, $J_{3,4} \approx 9\text{ Hz}$ for the 2,2'-bipyridil complex and $J_{2,3} \approx 5\text{ Hz}$, $J_{4,3} \approx 9\text{ Hz}$ for the *o*-phenanthroline complex seem to be fairly characteristic in the reported *o*-phenanthroline and bipyridil complexes [19, 23, 25] and support our assignment.

Also, upon irradiation of the resonance corresponding to protons 5 and 6, a positive Overhauser effect was observed in the bands assigned to protons 4 and 7, which provides further support to our assignment.

The mono- and dication complexes with bidentate ligands (I–IV) are stable in concentrated NaOH but are decomposed by concentrated acids (HCl and HNO_3). Unlike what happens with the ligand dppe [3] reaction with NaBH_4 did not give a cyclopentadiene complex but yielded instead very unstable species, not characterized, probably due to a nucleophilic attack on the nitrogen ligand instead of an attack on the cyclopentadienyl ring.

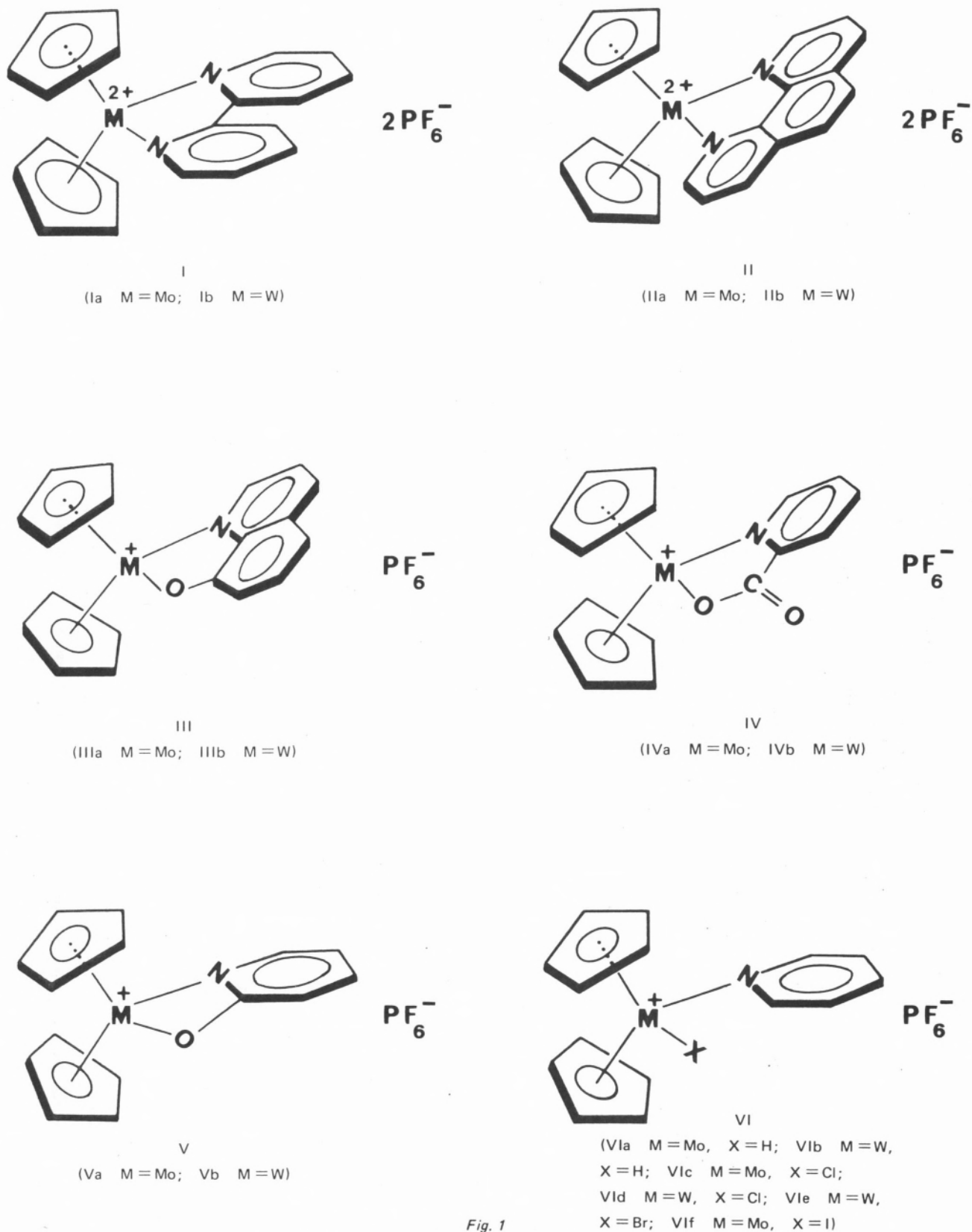


Fig. 1

Proposed structures for the new complexes synthesized

Table I

Compound	Colour	Dec °C	Method of Prep.	Analysis % req. (found)				Molar Conductivity
				C	H	N	M	
Ia - [Mo (η -C ₅ H ₅) ₂ bpy] (PF ₆) ^b	red	240	2,5	35.63 (35.47)	2.99 (2.69)	4.16 (3.89)	14.23 (14.00)	250
Ib - [W (η -C ₅ H ₅) ₂ bpy] (PF ₆) ²	red	230	2,5	31.52 (32.15)	2.64 (2.79)	3.68 (3.82)	—	204
IIa - [Mo (η -C ₅ H ₅) ₂ phen] (PF ₆) ^c	red	320	2,5	37.84 (37.78)	2.89 (2.46)	4.01 (3.97)	13.74 (13.95)	210
IIb - [W (η -C ₅ H ₅) ₂ phen] (PF ₆) ²	red	270	2,5	33.61 (33.64)	2.56 (2.42)	3.56 (3.54)	23.38 (24.29)	184
IIIa - [Mo (η -C ₅ H ₅) ₂ 8-hq] PF ₆ ^d	orange red	270	3	44.29 (44.23)	3.13 (3.20)	2.72 (2.79)	18.62 (19.12)	94
IIIb - [W (η -C ₅ H ₅) ₂ 8-hq] PF ₆	orange red	260	3	37.84 (37.71)	2.67 (2.84)	2.32 (2.28)	30.48 (29.24)	92
IVa - [Mo (η -C ₅ H ₅) ₂ pic] PF ₆ ^e	red	250	3	38.96 (39.64)	2.86 (2.91)	2.84 (3.25)	—	94
IVb - [W (η -C ₅ H ₅) ₂ pic] PF ₆	red	250	3	33.07 (33.00)	2.43 (2.52)	2.41 (2.59)	—	86
Va - [Mo (η -C ₅ H ₅) ₂ 2-hpy] PF ₆ ^f	redish brown	260	3	38.73 (38.92)	3.03 (3.01)	3.01 (2.96)	—	91
Vb - [W (η -C ₅ H ₅) ₂ 2-hpy] PF ₆	redish brown	280	3	32.57 (32.48)	2.55 (2.46)	2.53 (2.90)	—	78
VIa - [Mo (η -C ₅ H ₅) ₂ H py] PF ₆ ^g	orange	110	4,6	39.93 (40.39)	3.57 (3.71)	3.10 (2.91)	21.26 (21.76)	90
VIIb - [W (η -C ₅ H ₅) ₂ H py] PF ₆	orange	130	4,6	33.42 (33.16)	2.99 (3.01)	2.60 (2.52)	—	93
VIIIc - [Mo (η -C ₅ H ₅) ₂ Cl py] PF ₆	green	210	1	37.10 (36.70)	3.11 (3.18)	2.88 (2.85)	—	85
VIId - [W (η -C ₅ H ₅) ₂ Cl py] PF ₆	brown	160	1	31.41 (31.64)	2.64 (3.06)	2.44 (2.45)	—	95
VIIf - [W (η -C ₅ H ₅) ₂ Br py] PF ₆ ^h	brown	190	1,7	29.15 (28.77)	2.45 (2.65)	2.27 (2.10)	—	83
VIIIf - [Mo (η -C ₅ H ₅) ₂ I py] PF ₆ ⁱ	green	170	1	31.22 (32.03)	2.62 (2.95)	2.43 (2.23)	—	78

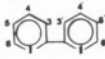





a ohm⁻¹ cm² mol⁻¹, c = 10⁻³M in nitromethane; b bpy = 2,2'-bipyridil; c phen = o-phenanthroline; d 8-hq = 8-quinolinolato; e pic = pyridine-2-carboxilato; f 2-hpy = pyridolato; g py = pyridine; h the analogous complex [Mo (η -C₅H₅)₂ py Br] PF₆ was prepared in this work but it had been previously prepared by method 7 [2]; i the analogous tungsten complex was also prepared although it was not possible to purify it well enough to obtain good analysis.

Table II

Compound	Infrared data: main bands cm^{-1}		Electronic spectra.	
			Positions of the bands ν (ϵ) ^(a)	
Ia	1605 s, 770 s, 730 m, 420 w ^b 840 s, 560 s ^c 3120 s ^d		31.4 (9.7×10^3), 30.4 (9.7×10^3), 26.5 sh (207), 19 (97)	
Ib	1605 s, 770 s, 730 m, 430 vw ^b 840 s, 560 s ^c 3120 s ^d		29.8 (7.4×10^3), 28.8 (7.4×10^3), 25.5 sh (185), 16 (74)	
IIb	1430 s, 1520 s, 1585 m, 1605 m, 1635 m ^e 840 s, 560 s ^c 3120 s ^d		43 (3×10^4), 35 (3×10^4), 32 sh (9.9×10^3), 31 sh (3×10^3), 29 sh (1.8×10^3), 28 sh (1.5×10^3), 19.5 (139)	
IIb	1430 s, 1520 s, 1585 m, 1605 m, 1635 m ^e 840 s, 560 s ^c 3120 s ^d		36.5 (3.2×10^4), 34.5 (3.2×10^4), 31.5 sh (7.8×10^3), 29.5 sh (4.4×10^3), 26.2 sh (1.2×10^3), 16.5 (130)	
IIIa	1575 m, 1500s, 1110 m ^f 840 s, 560 s ^c 3120 s ^d		37 (3×10^4), 30.8 sh (2.1×10^3), 29.4 (1.6×10^3), 23.5 (4.2×10^3)	
IIIb	1575 m, 1500 s, 1110 s ^f 840 s, 560 s ^c 3120 s ^d		39 (1.5×10^4), 36 (1.5×10^4), 30 (670), 22 (2.4×10^3)	
IVa	1680 s, 1610 s, 1020 m, 620 vw ^g 840 s, 560 s ^c 3115 s ^d		37 (7.8×10^4), 26.7 sh (283), 20.4 (127)	
IVb	1690 s, 1610 s, 1020 m, 660 vw ^g 840 s, 560 s ^c 3115 s ^d		36.4 (8.4×10^4), 30.3 (355), 21.5 (213)	
Va	1610 s, 1120 m, 1020 m, 750 m ^h 840 s, 560 s ^c 3120 s ^d		39.2 (6.1×10^4), 30.8 (1.5×10^3), 22.2 (81), 18.2 (52)	
Vb	1610 s, 1125 m, 1025 m, 750 m ^h 840 s, 560 s ^c 3120 s ^d		40.8 (8.4×10^3), 31.7 (2.3×10^3), 22.7 (152)	
VIa	1610 s, 1240 m, 1010 m, 640 vw, 420 sh ⁱ 840 s, 560 s ^c 3115 s ^d 1850 m ^j		38.5 sh (5.9×10^3), 37 sh (3.9×10^3), 30.8 sh (440), 21.3 sh (108)	
VIb	1610 s, 1240 w, 1005 m, 645 vw, 425 vw ⁱ 840 s, 560 s ^c 3115 s ^d 1925 m ^j		37 sh (8.3×10^4), 35 sh (3.6×10^4), 22.8 (98)	
VIc	1610 s, 1230 m, 1015 m, 640w, 420 sh ⁱ 840 s, 560 s ^c 3115 s ^d 300 m ^k		34.5 sh (6×10^4), 29.4 (380), 24.4 (175), 16.4 (90)	
VId	1610 s, 1230 m, 1015 w, 640 w ⁱ 840 s, 560 s ^c 3115 s ^d 300 m ^k		37 sh (1.7×10^4), 34.5 sh (7×10^3), 24 sh (320), 19.2 sh (140)	
VIe	1610 s, 1230 m, 1015 m, 640 vw ⁱ 840 s, 560 s ^c 3110 m ^d		37 (3.9×10^3), 22 (239)	
VIIf	1610 s, 1230 m, 1015 m, 640vw, 410 sh ⁱ 840 s, 560 s ^c 3115 s ^d		30.8 (1.6×10^3), 25 sh (540), 20.8 sh (197), 15.6 (138)	

a $\text{kK} (\text{mol}^{-1} \text{cm}^{-1})$, in acetonitrile; b bands characteristic of coordinated bipy free bpy: 1580, 760 (splits into two upon coordination), 620 (disappears upon coordination), 405 [12, 13, 14]; c bands characteristic of PF_6^- ; d bands characteristic of $\eta\text{-C}_5\text{H}_5$; e bands characteristic of coordinated *o*-phenanthroline (free phen: 1420, 1520, 1560, 1590, 1615) [10, 11]; f bands characteristic of coordinated 8-quinolinolato (free 8-hq: 1580, 1500); g bands of coordinated pyridine-2-carboxylato (free picolinic acid 1600, 1590, 990, 515) [15]; h bands characteristic of coordinated 2-pyridolato (free 2-hpy: 1580, 1100, 985, 730); i characteristic bands of coordinated pyridine (free py: 1580, 1220, 991, 601, 403) [16, 17, 18]; j $\nu (\text{M-H})$; k $\nu (\text{M-Cl})$.

Table III

Compound	¹ H n.m.r. data ^a				
	b 1.33 (D, 2); b, c 1.19 (C, 4);	c 1.50 (D, 2); d 1.49 (T, 2);	d 2.07 (T, 2); e 2.25 (T, 2);	e 2.59 (T, 2); f 3.64 (S, 10);	
Ib	b 0.64 (D, 2);	c 1.20 (D, 2);	d 1.41 (T, 2);	e 2.20 (T, 2);	f 3.74 (S, 10)
	g 0.87 (D, 2);	h 1.57 (D, 2);	i 2.06 (S, 2);	j 2.26 (Q, 2)	
IIa	g 0.72 (D, 2);	h 0.85 (D, 2);	i 1.60 (S, 2);	j 1.90 (Q, 2);	f 3.66 (S, 10)
IIb	g 0.24 (D, 2);	h 0.75 (D, 2);	i 1.60 (S, 2);	j 1.82 (Q, 2);	f 3.70 (S, 10)
	k 1.08–2.85 (C)				
IIIa	k 0.45–2.62 (C, 6);		f 3.85 (S, 10)		
IIIb	k 0.69–3.12 (C, 6);		f 4.06 (S, 10)		
	l 1.15 (D, 1);	m, n 1.82 (C, 2);	o 2.24 (T, 1)		
IVa	l 1.30 (D, 1);	m 1.48 (T, 1);	n 1.78 (D, 1);	o 2.06 (T, 1);	f 3.91 (S, 10); (solv. d ⁶ DMSO)
IVb	l 0.82 (D, 1);	m 1.39 (T, 1);	n 1.75 (D, 1);	o 2.04 (T, 1);	f 3.93 (S, 10); (solv. d ⁶ DMSO)
	t 1.76 (S, 1);				
Va	l, m 2.30 (C, 2);	o 3.24 (T, 1);	n, f 3.91 (C, 11);	(sol. d ⁶ Me ₂ CO/D ₂ O)	
Vb	l 2.02 (D, 1);	m 2.12 (T, 1);	o 3.09 (T, 1);	n 3.80 (D, 1);	f 3.87 (S, 10); (solv. d ⁶ DMSO)
	p 1.39 (D, 2);	q 2.19 (T, 1);	r 2.57 (T, 2)		
VIa	p 1.20 (D, 2);	q 2.02 (T, 1);	r 2.64 (T, 2);	f 4.59 (S, 10);	s 19.02 (S, 1)
VIb	p 0.87 (D, 2);	q 1.98 (T, 1);	r 2.75 (T, 2);	f 4.76 (S, 10);	s 22.18 (T, 1)
VIc	p 0.99 (D, 2);	q 1.87 (T, 1);	r 2.47 (T, 2);	f 4.00 (S, 10)	
VId	p 0.70 (D, 2);	q 1.80 (T, 1);	r 2.44 (T, 2);	f 4.04 (S, 10)	
VIe	p 0.54 (D, 2);	q 1.83 (T, 1);	r 2.49 (T, 2);	f 4.02 (S, 10)	
VIIf	p 0.75 (D, 2);	q 1.90 (T, 1);	r 2.57 (T, 2);	f 3.93 (S, 10)	

a solvent d⁶ —acetone except where stated otherwise, reference TMS, chemical shifts in τ scale, (multiplicity, relative intensity), S singlet, D doublet, T triplet, Q quadruplet, C complex; b $\tau_{6,6'}$; $J_{6,5}$ (Ib) \cong 5 Hz; c $\tau_{3,3'}$; $J_{3,4}$ (Ib) \cong 9 Hz; d $\tau_{4,4'}$; e $\tau_{5,5'}$; f $\tau_{\eta-C_6H_5}$; g $\tau_{2,9}$; $J_{2,3}$ (IIa) \cong 5 Hz; $J_{2,3}$ (IIb) \cong 5 Hz; h $\tau_{4,7}$; $J_{4,3}$ (IIa) \cong 9 Hz; $J_{4,3}$ (IIb) \cong 9 Hz; i $\tau_{5,6}$; j $\tau_{3,8}$; k $\tau_{2,7}$; l τ_1 ; m $\tau_{3,5}$; n τ_4 ; o τ_2 ; p $\tau_{1,1'}$; q τ_3 ; r $\tau_{2,2'}$; s $J_{W-H} \cong$ 35 Hz; t τ_{O-H} .

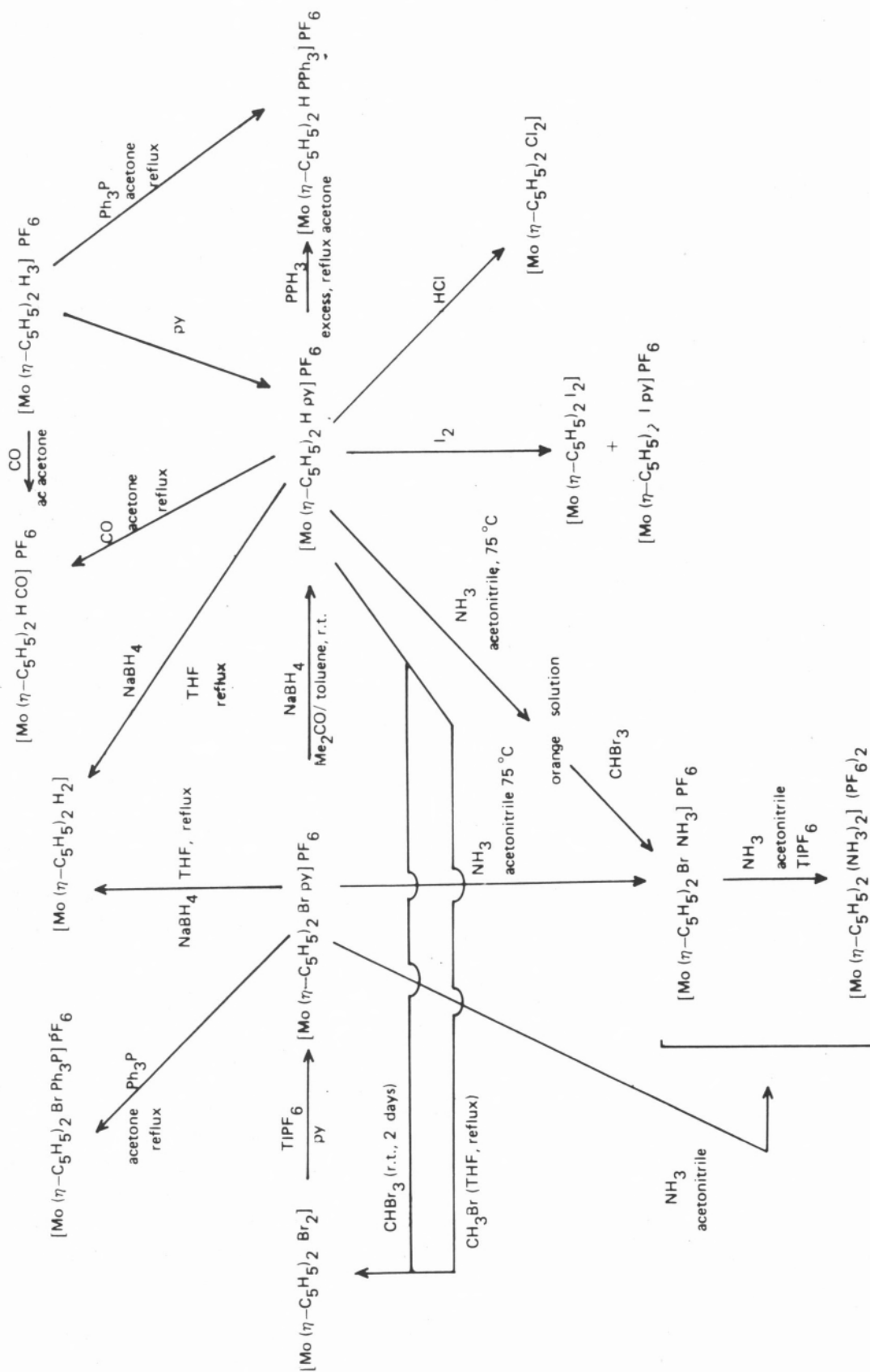


Fig. 2
Reaction scheme for the pyridine and related complexes

In the compound $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br py}]\text{PF}_6$ the pyridine ligand was replaced by triphenylphosphine by refluxing the complex with the phosphine in acetone, a slower process than the related photochemical reaction [5]. Thermal substitution of pyridine by NH_3 was also obtained: bubbling NH_3 through a acetonitrile solution of the complex at 75°C yielded $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br NH}_3]\text{PF}_6$; in the presence of TIPF_6 the known complexes $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br NH}_3]\text{PF}_6$ and $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{NH}_3)_2](\text{PF}_6)_2$ [4-6] were obtained. The latter complex was also obtained by reaction on the monoamino complex with further NH_3 in the presence of TIPF_6 .

The complex VIa is stable in concentrated NaOH but reacts with a series of compounds giving either the pyridine substituted analogue $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H L}]\text{PF}_6$ ($\text{L} = \text{Ph}_3\text{P}$, CO , NH_3) or the dihalide $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{X}_2]\text{PF}_6$. The hydrideamino complex was not isolated as such but further reaction of the orange solution obtained with bromoform yielded the bromoamino complex. Reaction with CH_3CN gave a red oil which was not characterized; the related photochemical reaction gives the complex $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{NCCH}_3)]\text{PF}_6$ [5]. The chemical studies done in this work with the pyridine complexes are summarized in fig. 2.

3 - EXPERIMENTAL

All preparations and further manipulations were carried out under nitrogen unless otherwise stated. The compounds $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{X}_2]$, $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]\text{PF}_6$, $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]\text{PF}_6$ and $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{Br SMe}_2]\text{PF}_6$ ($\text{M}=\text{Mo}; \text{W}; \text{X}=\text{Cl}, \text{Br}, \text{I}$) were prepared as described [7, 8, 9, 2]. ^1H n.m.r. spectra were determined on a Japan Electron Optics Laboratory Co. instrument model JNM 100 PFT. Infrared spectra were determined on a Perkin-Elmer 457 instrument in KBr pellets and were calibrated with polystyrene. Conductivity measurements were made at 25°C using a Radiometer CDM₃ Conductivity Meter instrument calibrated with standard KCl solution. Electronic spectra were measured in solution in a UNICAM SP700 and in a CARY 17 instrument. C, H, N analysis were carried out at the Inorganic Chemistry Laboratory, Oxford and the metal analysis were carried out in our laboratories by atomic absorption spectroscopy.

Bis-(η -cyclopentadienyl) bipyridilmolybdenum (or tungsten) hexafluorophosphate

Procedure 2

- The compound $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}_2]$ (0.8g ~ 2 mmol) in acetone (40 ml) was refluxed for 6hrs with 2,2'-bipyridil (0.35g ~ 2 mmol) in the presence of TIPF_6 (1.5g ~ 4 mmol). The reaction mixture was filtered and pumped to dryness under vacuum. The residue was extracted with acetone, water was added and upon removal of the acetone under vacuum red needles precipitated. Yield ca 60 %.
- The tungsten analogue was prepared in a similar way except that the acetone solution of the residue was chromatographed on an alumina column. Elution with acetone/ethanol (1.1) gave a first band, yellow, which was discarded. To the second band, pink, NH_4PF_6 was added after reducing the volume. The compound was recrystallised as before giving red needles. Yield ca 10 %.

Procedure 5

- The compound $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]\text{PF}_6$ (0.3g ~ 0.8 mmol) in acetone (40ml) was refluxed for 10hrs with 2,2'-bipyridil (0.3g ~ 2 mmol). The reaction mixture was filtered and treated as described for the tungsten complex in method 2. Yield ca 10 %.
- The tungsten analogue was prepared in a similar way. Yield ca 10 %.

Bis-(η -cyclopentadienyl) o-phenanthrolinemolybdenum (or tungsten) hexafluorophosphate

Procedure 2

- The compound $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{I}_2]$ (0.5g ~ 1 mmol) in acetone (40 ml) was refluxed for 4hrs with o-phenanthroline hydrate (0.4g ~ 2 mmol) in the presence of TIPF_6 (1.4g ~ 4 mmol). The reaction mixture was filtered and the filtrate was pumped to dryness under vacuum. The residue was extracted with acetone and chromatographed on an acid alumina column using acetone/ethanol (1.1) as eluent. The pink band obtained was filtered, pumped to dryness under vacuum and the residue was recrystallised from acetone/water giving red needles. Yield ca 5 %.
- The tungsten analogue was prepared in a similar way giving red needles. Yield ca 5 %.

Procedure 5

g. The compound $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]\text{PF}_6$ (3g ~ 8 mmol) in acetone (50 ml) was refluxed for 20hrs with *o*-phenanthroline (2g ~ 10 mmol). The solution was filtered, the volume was reduced under vacuum and a small volume of saturated aqueous solution of NH_4PF_6 was added. The remaining acetone was removed under vacuum leading to the precipitation of red needles which were recrystallised from acetone/water. Yield ca 90 %.

h. The analogous tungsten complex was prepared as in d. Yield ca 5 %.

Bis-(η -cyclopentadienyl) 8-quinolinolatomolybdenum (or tungsten) hexafluorophosphate

i. The compound $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}_2]$ (0.8g ~ 2mmol) was refluxed in ethanol (40ml) with 8-hydroxyquinoline (0.6g ~ 4mmol) and triethylamine (1.5ml ~ mmol) for 2hrs. The solvent was pumped to dryness and the residue was extracted with water and NH_4PF_6 was added to the solution. The brick coloured precipitate was recrystallised from acetone/water giving big red-orange needles. Yield ca 80 %.

j. The analogous tungsten compound was prepared in a similar way. Yield ca 70 %.

Bis-(η -cyclopentadienyl) (pyridine-2-carboxylato) molybdenum (or tungsten) hexafluorophosphate

k. The molybdenum compound was prepared as in i. It was recrystallised from hot acetonitrile giving red crystals. Yield ca 80 %.

l. The tungsten compound was prepared as in j giving red crystals. Yield ca 80 %.

Bis-(η -cyclopentadienyl) 2-pyridolatomolybdenum (or tungsten) hexafluorophosphate

m. The molybdenum compound was prepared as in i giving reddish-brown crystals. Yield ca 70 %.

n. The tungsten compound was prepared as in j giving reddish-brown crystals. Yield ca 70 %.

Bis-(η -cyclopentadienyl) hydridepyridinemolybdenum (or tungsten) hexafluorophosphate

Procedure 4

o. The compound $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]\text{PF}_6$ (720 mg~

~2 mmol), was refluxed in pyridine (5 ml) for 20hrs. The solution was filtered, the volume was reduced under vacuum and ether was added. The orange-brown precipitate obtained was extracted with acetone and repeatedly recrystallised from acetone/water giving orange crystals. Yield ca 70 %.

p. The analogous tungsten compound was prepared in a similar way. Yield ca 50 %.

Procedure 6

q. The compound $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br py}]\text{PF}_6$ (150mg ~ 0.28 mmol) in acetone/toluene (1:1) (30 ml) was treated with excess NaBH_4 at room temperature for 9 min. The orange solution obtained was pumped to dryness. The residue was extracted with acetone and recrystallised from acetone/water. Yield ca 10 %.

Bis-(η -cyclopentadienyl) halidepyridinemolybdenum (or tungsten) hexafluorophosphate

Procedure 1

r. A typical preparation is described. The compound $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{X}_2]$ (1 mmol) in pyridine (5 ml) was refluxed with TIPF_6 (1 mmol) for 4hrs. The solution was pumped to dryness under vacuum. The residue was extracted with acetone and recrystallised from acetone/water. Yield varied from 30 % for the iodide to 90 % for the chloride.

Procedure 7

As described [2] for the molybdenum analogue $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br py}]\text{PF}_6$

Reaction of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H py}]\text{PF}_6$ with CO

A solution of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H py}]\text{PF}_6$ in acetone was refluxed for 3.5hrs in CO atmosphere. A red solution was obtained and its volume was reduced under vacuum. Upon addition of ethyl ether to this solution a brown solid precipitated. This was extracted with acetone, ethanol was added and upon removal of the acetone under vacuum yellow crystals precipitated. These proved to be the compound $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H CO}]\text{PF}_6$ by comparison of its infrared spectrum with that of a genuine sample.

Reaction of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H py}]\text{PF}_6$ with I_2

A solution of iodine in acetone was added to a solution of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H py}]\text{PF}_6$ in the same solvent. The reaction mixture was stirred for 25 min at room temperature. The volume of the solution was reduced under vacuum and ethyl ether added. The infrared spectrum of the precipitate shows that it is a mixture of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{I}_2]$ and $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{I py}]\text{PF}_6$.

Reaction of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H py}]\text{PF}_6$ with CH_3Br
Methyl bromide was added to a suspension of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H py}]\text{PF}_6$ in THF and the mixture was refluxed for 4hrs. The mixture was filtered and the volume of the filtrate was reduced under vacuum precipitating a brown solid. This was recrystallised from acetone/ethanol giving crystals which were identified as being $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}_2]$ by comparison of its infrared spectrum with that of a genuine sample.

Reaction of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H py}]\text{PF}_6$ with CHBr_3
A few drops of bromoform were added to a solution of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H py}]\text{PF}_6$ in acetone at 40°C . After 20 min the solution turned green. Water was added to the solution and when the acetone was removed under vacuum green crystals precipitated which were identified as $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br py}]\text{PF}_6$ by comparison of its infrared spectrum with that of a genuine sample. When the reaction was repeated at room temperature the colour change was observed after two days. The compound isolated was identified by its infrared spectrum as being $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}_2]$.

Reaction of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H py}]\text{PF}_6$ with NaBH_4
 NaBH_4 was added to a suspension of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H py}]\text{PF}_6$ in dry THF and the mixture was refluxed for 4hrs. Upon filtration an orange solution was obtained which after reducing the solvent and cooling gave the starting complex. The remaining solution was pumped to dryness under vacuum. The residue was extracted with dry toluene giving a yellow solution. Removing the solvent under vacuum yellow crystals were obtained which were identified as $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$ by its infrared spectrum.

Reaction of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H py}]\text{PF}_6$ and

$[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br py}]\text{PF}_6$ with Ph_3P

An excess of triphenylphosphine (260mg ~ 1 mmol) was added to a solution of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H py}]\text{PF}_6$ (220mg ~ 0.5 mmol) and the mixture refluxed for 6hrs.

The solution was filtered, the solvent reduced under vacuum and ethanol added. Yellow crystals precipitated which were identified as $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H Ph}_3\text{P}]\text{PF}_6$ by comparison of its infrared spectrum with that of a genuine sample.

The reaction of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br py}]\text{PF}_6$ with Ph_3P gave purple crystals of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br Ph}_3\text{P}]\text{PF}_6$ in the above conditions.

Reaction of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br py}]\text{PF}_6$ with NaBH_4 in TiF_4

A suspension of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br py}]\text{PF}_6$ in dry THF was treated with NaBH_4 at room temperature for 1hr. The solution was filtered and the solvent was removed under vacuum. The residue was extracted with acetone and recrystallised from acetone/ethanol. The yellow crystals obtained were identified as $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$ by its infrared spectrum.

Reaction of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br py}]\text{PF}_6$ with NH_3

NH_3 was bubbled for 2hrs through a solution of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br py}]\text{PF}_6$ in acetonitrile in the presence of TiPF_6 at 50°C . The solution was filtered, water was added and the volume was reduced under vacuum. Green crystals precipitated which were identified as $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br NH}_3]\text{PF}_6$ by comparison of its infrared spectrum with that of a genuine sample. Further evaporation of the solvent yielded red crystals (about 1/8 of the previous ones) which were also identified by comparison of its infrared spectrum with that of a genuine sample as being $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{NH}_3)_2](\text{PF}_6)_2$.

NH_3 was bubbled for 3hrs through a solution of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br py}]\text{PF}_6$ in acetonitrile at 75°C and treated as described above. Green crystals were obtained which were identified as being $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br NH}_3]\text{PF}_6$ by its infrared spectrum.

NH_3 was bubbled for 30 min through a solution of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br NH}_3]\text{PF}_6$ in acetonitrile in the presence of TiPF_6 at 70°C . The solution was treated as described above and red crystals were obtained which were identified as $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{NH}_3)_2](\text{PF}_6)_2$ by its infrared spectrum.

Reaction of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H py}]\text{PF}_6$ with NH_3

NH_3 was bubbled for 3hr through a solution of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H py}]\text{PF}_6$ in acetonitrile at 75°C . CHBr_3 was added to the orange solution, which turned green after 20 min. (~ 40°C). The volume was reduced

under vacuum, after filtration and diethyl ether was added. Green crystals precipitated which were identified as $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{BrNH}_3]\text{PF}_6$ by comparison of its infrared spectrum with that of a genuine sample.

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RESUMO

Descreve-se a síntese dos complexos $[\text{M}(\eta\text{-C}_5\text{H}_5)_2(\text{L-L})](\text{PF}_6)_2$ (1) ($\text{M} = \text{Mo}$, W ; $\text{L-L} = \text{bipiridilo}$, o -fenantrolina), $[\text{M}(\eta\text{-C}_5\text{H}_5)_2(\text{L-L}')]\text{PF}_6$ (2) ($\text{M} = \text{Mo}$, W ; $\text{L-L}' = 8$ quinolinato, piridina-2-carboxilato, 2-piridolato) e $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{LX}]\text{PF}_6$ (3) ($\text{L} = \text{piridina}$; $\text{M} = \text{Mo}$, $\text{X} = \text{H}$, Cl , I ; $\text{M} = \text{W}$, $\text{X} = \text{H}$, Cl , Br).

Os novos compostos foram caracterizados por métodos analíticos e espectroscópicos (IR, electrónico e ^1H rmn) e a sua reactividade foi estudada com particular ênfase para as reacções de substituição dos complexos (3).