

DI- η^5 -CYCLOPENTADIENYLMETAL COMPLEXES WITH NITROGEN DONOR ATOM LIGANDS: NEW IMIDAZOLE, *N*-METHYLIMIDAZOLE, PYRAZOLE AND 2,2'-BISIMIDAZOLE COMPLEXES OF MOLYBDENUM AND TUNGSTEN

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Summary

Reactions of the tetrahedral metallocene derivatives $[M(\eta^5-C_5H_5)_2X_2]$, $[M(\eta^5-C_5H_5)_2HX]$ and $[M(\eta^5-C_5H_5)_2H_3][PF_6]$ ($M = Mo, W$; $X = \text{halogen}$) with ligands imidazole, *N*-methylimidazole, pyrazole and 2,2'-bisimidazole give a wide range of new mono- and bi-nuclear complexes. The pK_a values for some of the coordinated ligands and the ESR spectra of some molybdenum(V) complexes obtained by oxidation of their molybdenum(IV) analogues are also presented and discussed.

1. Introduction

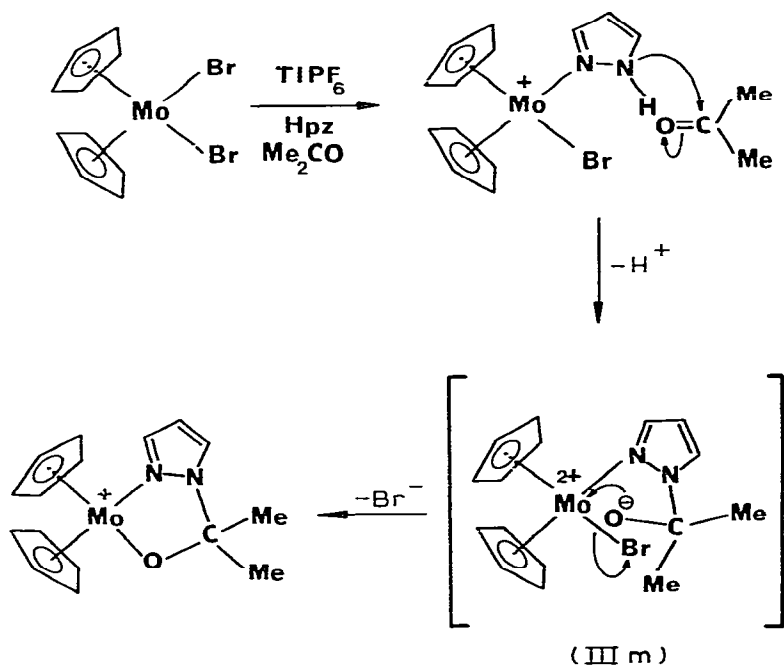
In previous articles we described the synthesis, characterization and reactivity of some complexes of the metallocenes $M(\eta^5-C_5H_5)_2$ ($M = Mo^{IV}, W^{IV}, Ti^{III}$ and Ti^{IV}) with nitrogen donor atom ligands [1,2]. We now report the extension of these studies to molybdenum and tungsten derivatives with ligands imidazole (I, Him), *N*-methylimidazole (II, Nmim), pyrazole (III, Hpz) and 2,2'-diimidazole (IV, H_2biim). Related studies of the titanium analogues with ligands III and IV have been reported recently [3,4]. Complexes containing these ligands are receiving increasing attention because of their biological significance [5] and also because of the ability of ligands I [6,10], III [3,7–9] and IV [1,10–12] to act as bridging ligands after deprotonation.

2. Results and discussion

The compounds $[M(\eta^5-C_5H_5)_2X_2]$, $[M(\eta^5-C_5H_5)_2HX]$ ($M = Mo, W$; $X = \text{halogen}$) and $[M(\eta^5-C_5H_5)_2H_3][PF_6]$ ($M = Mo, W$) reacted under various conditions

with the nitrogen donor atom ligands imidazole (I, Him), *N*-methylimidazole (II, Nmim), pyrazole (III, Hpz) and 2,2'-diimidazole (IV, H₂biim), to give the new complexes shown in Fig. 1. With thallium hexafluorophosphate in acetone solution replacement of one halide ligand by the neutral monodentate ligands was observed for both the dihalide and the halohydride complexes (except for M = W and X = Hpz); under the same conditions replacement of two halide ligands by the bidentate ligand H₂biim was observed for M = Mo. Reaction of [M(η -C₅H₅)₂Br₂] with an excess of the Him or Nmim as solvent, led to replacement of both halide ligands, but reaction of the tungsten analogue under the same conditions gave only monosubstitution.

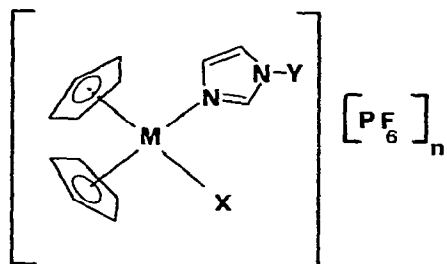
Reaction of excess pyrazole with [Mo(η -C₅H₅)₂Br₂] in the presence of Tl[PF₆] yielded, in addition to IIIc a second product which was formulated as [Mo(η -C₅H₅)₂{N₂C₃H₃C(CH₃)₂O}][PF₆] (III_m) on the basis of elementary analysis and ¹H NMR data: three non-equivalent peaks (τ 1.67, doublet; τ 3.20, triplet; τ 2.16, doublet) from the pyrazole ring protons, a singlet (τ 8.51) attributed to the CH₃ groups, and a singlet (τ 4.09) attributed to the η -C₅H₅ rings, in the integration ratio 3/6/10. We propose the following mechanism for the formation of this complex:



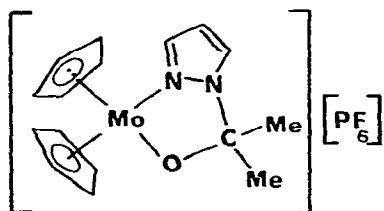
Another mechanism, involving coordination of the acetone molecule before the nucleophilic attack, cannot be excluded but we consider it less probable. While the available data are consistent with the structure assigned to complex III_m, a definitive structure proof will have to await the results of a single crystal X-ray determination, currently in progress.

An analogous compound was obtained, in very small yield, from the reaction of [W(η -C₅H₅)₂HBr] with pyrazole, but this was identified only by comparison of its IR spectrum with that of the molybdenum compound.

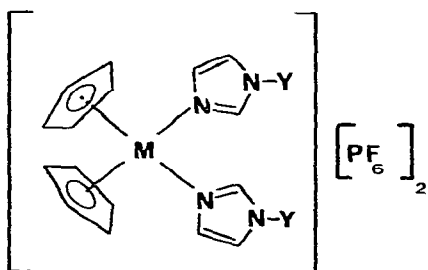
Reaction of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}_2]$ with excess of sodium imidazolate or pyrazolate (NaL) in dry THF gave the neutral complexes $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{L}_2]$; under the same conditions only monosubstitution was observed for the tungsten ana-



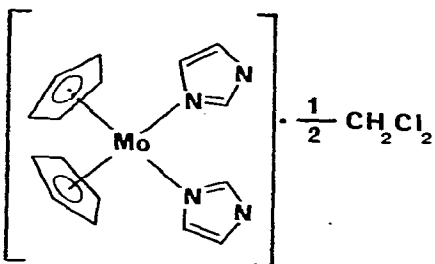
- (Ia, Y = H, M = Mo, X = H, n = 1;
 Ib, Y = H, M = Mo, X = Br, n = 1;
 Ic, Y = H, M = W, X = Br, n = 1;
 Id, Y = H, M = Mo, X = Br, n = 2;
 IIa, Y = CH₃, M = Mo, X = H, n = 1;
 IIb, Y = CH₃, M = Mo, X = Br, n = 1;
 IIc, Y = CH₃, M = W, X = H, n = 1;
 IId, Y = CH₃, M = W, X = Br, n = 1;
 IIf, Y = CH₃, M = Mo, X = Br, n = 2)



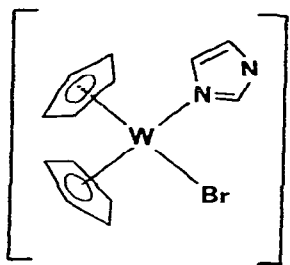
(IIIa)



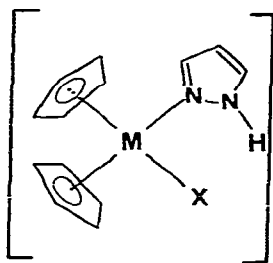
- (Ie, Y = H, M = Mo;
 IIf, Y = CH₃, M = Mo)



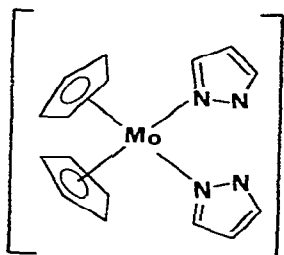
(If)



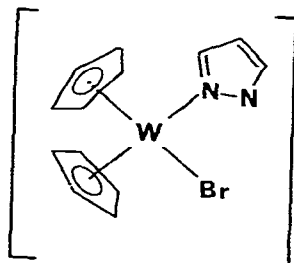
(I g)



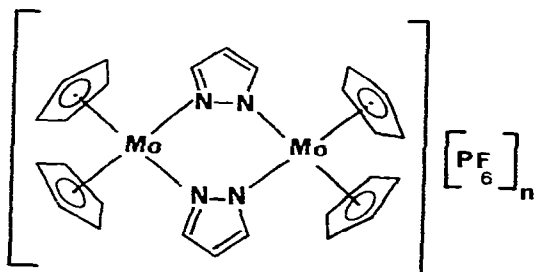
- (III a), M = Mo, X = H, n = 1
 III b, M = Mo, X = Cl, n = 1
 III c, M = Mo, X = Br, n = 1
 III d, M = Mo, X = I, n = 1
 III e, M = W, X = Cl, n = 1
 III f, M = W, X = Br, n = 1
 III g, M = W, X = I, n = 1
 III h, M = Mo, X = Br, n = 2)



(III i)



(III j)



- (III k, n = 2;
 III l, n = 3)

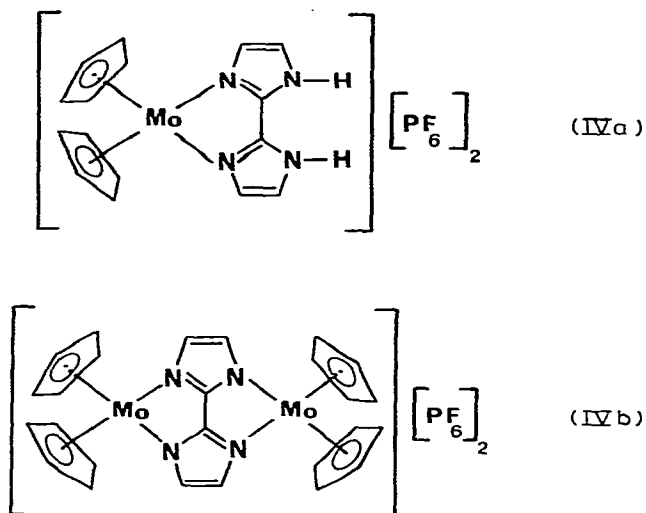


Fig. 1. Structural formulae of compounds I–IV.

logues. Reaction of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}_2]$ with sodium pyrazolate in the proportion 1/1 in THF gave the binuclear complex $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{Mo}(\text{pz})_2\text{Mo}(\eta\text{-C}_5\text{H}_5)_2]^{2+}$ (IIIk). Reaction of the same dibromide in the same solvent with $(\text{PMDTLi})_2\text{biim}$ ($\text{PMDT} = 1,1', 4,7,7'$ -pentamethyldiethylenetriamine) gave the binuclear complex $[(\eta\text{-C}_5\text{H}_5)_2\text{Mo}(\text{biim})\text{Mo}(\eta\text{-C}_5\text{H}_5)_2]^{2+}$ (IVb). Attempts to prepare metal(V) derivatives by oxidation of the metal(IV) parent compound with NOPF_6 in acetonitrile were successful for complexes Ib, Iib, IIIc, IIIk to give Id, IId, IIIh, IIIl, respectively. These molybdenum(IV) compounds could also be oxidised by nitric acid, but isolation of the molybdenum(V) compounds was very difficult in this case.

All the new compounds described give well defined crystals. The cationic complexes were isolated as the hexafluorophosphate salts. The mono- and di-cationic molybdenum(IV) and tungsten(IV) complexes are stable for long periods in the solid state and for several hours in solution. The molybdenum(V) complexes are extremely moisture sensitive both in the solid and in solution; they also react with the solvent acetonitrile to give the molybdenum(IV) precursor. The solid neutral complexes are moderately stable in dry air, and are also moderately stable in dry solvents.

The analytical, conductimetric and infrared spectroscopic evidence for the formulations proposed are given in Table 1.

The selected IR data presented in Table 1 show the M–H stretching frequencies (which appear at $1840\text{--}1855\text{ cm}^{-1}$ for the molybdenum complexes and at 1910 for the tungsten complexes) and the N–H stretching frequencies. These appear in general at 3410 cm^{-1} , lower frequencies being observed in the complexes $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{LL}']^+$ where hydrogen bonding can be expected; this is the case when $\text{L}' = \text{halogen}$ [20,21,23] $\nu 3300\text{ cm}^{-1}$ ($\text{M} = \text{Mo}$, $\text{L} = \text{pz}$, $\text{L}' = \text{Cl}$), $\nu 3280\text{ cm}^{-1}$ ($\text{M} = \text{W}$, $\text{L} = \text{pz}$, $\text{L}' = \text{Cl}$), $\nu 3290\text{ cm}^{-1}$ ($\text{M} = \text{Mo}$, $\text{L} = \text{pz}$, $\text{L}' = \text{Br}$), $\nu 3280\text{ cm}^{-1}$ ($\text{M} = \text{W}$, $\text{L} = \text{pz}$, $\text{L}' = \text{Br}$), $\nu 3260, 3290\text{ cm}^{-1}$ ($\text{M} = \text{Mo}$, $\text{L} = \text{pz}$, $\text{L}' = \text{I}$) and $\nu 3240, 3270\text{ cm}^{-1}$ ($\text{M} = \text{W}$, $\text{L} = \text{pz}$, $\text{L}' = \text{I}$). The only other case where

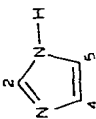
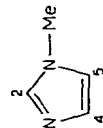
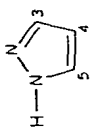
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TABLE 1. ANALYTICAL, CONDUCTOMETRIC AND IR SPECTROSCOPIC DATA

Compound	Colour	Decomp. (°C)	Analysis (found (calcd.)) (%)			Molar ^a conductivity	$\nu(\text{M}-\text{H})$	$\nu(\text{N}-\text{H})$ (cm^{-1})
			C	H	N			
Ia	yellow	180	34.9(35.5)	3.4(3.4)	6.35(6.4)	92	1845	3410
Ib	green	200	30.1(30.1)	2.8(2.7)	5.5(5.4)	106	—	3420
Ic	brownish-red	230	26.06(25.7)	2.5(2.3)	4.6(4.6)	96	—	3410, 3240
Id	red	135	23.5(23.5)	2.4(2.1)	5.0(4.2)	295 ^b	—	3410
Ie	reddish-orange	205	29.26(29.5)	2.8(2.8)	8.5(8.6)	216	—	3410, 3460
If	orange	140	49.4(49.1)	4.7(4.25)	13.9(13.9)	11	—	—
Ig	dark brown	180	34.3(33.9)	3.0(2.8)	6.4(6.1)	9	—	—
Ila	yellow	190	36.8(37.0)	3.9(3.8)	6.3(6.2)	102	1840	—
Ilb	brownish-green	225	32.2(31.5)	2.9(3.0)	5.1(5.25)	97	—	—
Ile	Yellow	230	31.2(31.0)	3.2(3.2)	5.1(5.2)	88	1910	—
Ild	red	210	27.2(27.1)	2.5(2.6)	4.6(4.5)	97	—	—
Ile	red	135	25.2(24.8)	2.2(2.4)	4.8(4.1)	270 ^b	—	—
Ilf	orange	170	31.5(31.2)	3.4(3.3)	7.9(8.2)	170	—	—
Ili	yellow	140	35.0(35.5)	3.6(3.4)	6.3(6.4)	80	1855	3400
Ilii	reddish-brown	220	33.0(32.9)	3.0(3.0)	5.7(5.9)	109	—	3300
Ilii	dark green	200	30.1(30.1)	2.9(2.7)	5.3(5.4)	79	—	3290
Ilii	green	200	28.0(27.6)	2.6(2.5)	4.7(5.0)	87	—	3260, 3290
Ilii	brown	210	28.2(27.7)	2.6(2.5)	4.95(5.0)	94	—	3280
Ilii	reddish-brown	210	25.7(25.7)	2.4(2.3)	3.9(4.6)	89	—	3280
Ilii	purple	150	24.3(23.8)	2.2(2.2)	4.5(4.3)	70	—	3240, 3270
Ilii	red	135	24.2(23.5)	2.3(2.1)	3.9(4.2)	250 ^b	—	3370
Ilii	red	190	53.2(53.3)	4.7(4.5)	15.7(15.6)	24	—	—
Ilii	dark brown	160	34.1(33.9)	3.0(2.8)	5.8(6.1)	8	—	—
Ilii	red	270	25.0(25.6)	3.4(3.0)	6.4(6.3)	170	—	—
Ilii	turquoise	175	30.3(30.6)	2.6(2.6)	3.9(5.5)	250	—	—
Ilii	orange	160	38.3(38.7)	3.85(3.85)	6.0(5.6)	89	—	—
Iva	orange	325	29.6(29.55)	2.6(2.5)	8.7(8.6)	190	—	3300, 3350
Ivb	orange	230	35.5(35.7)	2.8(2.8)	7.2(6.4)	184	—	—

^a ohm⁻¹ cm² mol⁻¹, ^c 10^{-3} M in nitromethane, ^b In acetonitrile, ^c Paramagnetic.

TABLE 2. 1H NMR DATA ^a

	H(2)	H(3)	H(4)	H(5)	Me/N-H	η -C ₅ H ₅	M-H
	2.28(S)	—	2.89(S,2)	—	—	—	—
Ia	2.02(S)	—	2.78(S)	3.13(S)	—	4.70(S,10)	18.55(S)
Ib	1.21(S)	—	2.63(S)	2.85(S)	—	4.11(S,10)	—
Ic	1.24(S)	—	2.51(S)	2.62(S)	1.11(S)	4.16(S,10)	—
Ie	1.86(T,2)	—	2.46(T,2)	2.94(T,2)	—	3.78(S,10)	— ^b
If	2.94(S,2)	—	3.11(S,2)	3.37(S,2)	—	4.32(S,10)	— ^b
Ig	2.24(S)	—	2.80(S)	3.21(S)	—	4.32(S,10)	—
	2.51(S)	—	2.94(S)	3.05(S)	6.31(S,3)	—	—
IIa	2.12(S)	—	2.89(S)	3.17(S)	6.29(S,3)	4.73(S,10)	18.62(S)
IIb	1.44(S)	—	2.70(S)	2.86(S)	6.16(S,3)	4.10(S,10)	—
IIc	1.88(S)	—	2.97(D,2)	—	6.26(S,3)	4.83(S,10)	21.98(T) ^c
IId	1.28(S)	—	2.51(S)	2.68(S)	5.96(S,3)	4.16(S,10)	—
IIe	1.97(S,2)	—	2.56(T,2)	3.03(T,2)	6.19(S,6)	3.81(S,10)	—
	—	2.33(S,2)	3.67(S)	—	—	—	—
IIIa	—	2.00(D)	3.58(S)	2.30(S)	-2.21(S)	4.70(S,10)	18.58(S)
IIIb	—	1.85(D)	3.39(T)	2.23(T)	—	4.02(S,10)	—
IIIc	—	1.88(D)	3.41(T)	2.09(D)	—	4.00(S,10)	—
IIId	—	1.74(D)	3.43(T)	1.92(D)	—	3.98(S,10)	—
IIIe	—	1.76(D)	3.36(T)	1.86(D)	—	4.05(S,10)	—
IIIf	—	1.69(D)	3.41(T)	1.90(D)	—	4.07(S,10)	—
IIIg	—	1.67(D)	3.46(S)	1.93(D)	—	4.05(S,10)	—
IIIh	—	2.54(S,2)	3.82(S,2)	2.62(D,2)	—	4.36(S,10)	— ^b
IIIj	—	1.60(D)	3.98(T)	2.64(D)	—	4.39(S,10)	— ^b
IIIk	—	2.11(D,4)	3.57(T,2)	—	—	3.98(S,20)	—
IIIm	—	1.67(D)	3.20(T)	2.16(D)	8.51(S,6)	4.09(S,10)	—

^a τ value (multiplet, relative intensity when different from 1); Me₂CO-*d*₆; internal reference TMS. ^b DMSO-*d*₆.

there is a suggestion of N—H...X hydrogen bonding is in the complex $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Br}(\text{Him})][\text{PF}_6]$ where a very intense and broad band at 3240 cm^{-1} was observed; previous observations [20] support this suggestion. As expected, no $\nu(\text{N—H})$ was observed in the neutral complexes in which the sp_3 nitrogen atom of the heterocycle has been deprotonated.

The ^1H NMR spectra (Table 2) also support the formulations proposed. For the imidazole complexes the two protons α to the N atom coordinated to the metal are shifted to lower field (particularly in the case of the bromides), this shift being more pronounced for the monocationic complexes than the dicationic complexes. The signal from the third proton is usually shifted to higher field. In the case of the neutral complexes, (bromide and imidazolate or pyrazolate ligands) there is no significant shift relative to the free ligand for tungsten derivatives, but for the molybdenum derivatives the signals from all the protons are moved to higher field. In the case of the other pyrazole complexes a shift to lower field was observed. The metal hydride resonances appear at τ ca. 18.6 for molybdenum complexes and at τ ca. 22 for tungsten complexes ($J(\text{W—H})$ 35 Hz).

The acid ionization constants of some of the coordinated ligands were determined by potentiometric titration in acetone/water (1/1) and the values are given in Table 3. In agreement with published data there is a general increase in the acidity of the ligands upon coordination. The electronegativity of the halogen coordinated in the adjacent position seems not to play any role in the acidity of the nitrogen donor atom ligand. As reported earlier [2], the acidity of the ligands coordinated to the tungsten atom is considerably higher than the acidity of the same ligands when coordinated to the molybdenum atom of the $(\eta\text{-C}_5\text{H}_5)_2\text{M}$ moiety, which seems to suggest the following order for the bond strengths: $\bar{D}(\text{W—N}) > \bar{D}(\text{Mo—N})$. Although the bond-enthalpy contributions, $\bar{D}(\text{M—N})$, have not yet been determined for this system, it has been found for other ligands L (L = H, CH_3 , Cl, Br, I) that $\bar{D}(\text{W—L})$ is about 50 kJ higher than $\bar{D}(\text{Mo—L})$ [24].

The ESR spectra of the molybdenum(V) complexes were recorded both in the solid state and as glasses in DMSO at 77 K; g values are given in Table 4. The spectra of the compounds Id, Iie and IIIh in the solid state show no structure; the pattern observed in the glass spectra is probably due to the anisotropy

TABLE 3
ACID IONIZATION CONSTANTS ^a

Complex	pK_a^b	Complex	pK_a^b
$[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{BrHim}][\text{PF}_6]$	~10	—	—
$[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}(\text{Hpz})][\text{PF}_6]$	8.14 ± 0.06	$[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}(\text{Hpz})][\text{PF}_6]$	7.65 ± 0.03
$[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}(\text{Hpz})][\text{PF}_6]$	8.25 ± 0.03	$[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Br}(\text{Hpz})][\text{PF}_6]$	7.79 ± 0.03
$[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{I}(\text{Hpz})][\text{PF}_6]$	8.22 ± 0.04	—	—
$[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{H}_2\text{biim})][\text{PF}_6]_2$	4.81 ± 0.03	—	—
	9.61 ± 0.03		

^a $pK_a(\text{Him}) = 14.3$ [5]; $pK_a(\text{Hpz}) = 14$ [25]; $pK_{a_1}(\text{H}_2\text{biim}) > 11.5$ [26]. ^b Experimental error given by $\tau_m \cdot t$ where τ_m is the mean standard deviation for 95% probability and between 6 and 8 degrees of freedom.

TABLE 4
THE g VALUES OF THE MOLYBDENUM(V) COMPLEXES

Compound	g_{\min}	g_{med}	g_{\max}	
IId	[Mo(η -C ₅ H ₅) ₂ Br(Him)][PF ₆] ₂	1.988	2.060	DMSO glass at 77 K
			2.046	Solid state at 77 K
IIe	[Mo(η -C ₅ H ₅) ₂ Br(Nmim)][PF ₆] ₂	1.987	2.062	DMSO glass at 77 K
			2.040	Solid state at 77 K
IIIh	[Mo(η -C ₅ H ₅) ₂ Br(Hpz)][PF ₆] ₂	1.933	2.015	DMSO glass at 77 K
			2.010	Solid state at 77 K
IIIi	[Mo(η -C ₅ H ₅) ₂ (pz)] ₂ [PF ₆] ₃	1.962	1.988	DMSO glass at 77 K
			1.961	2.008

of the g tensor and to the molybdenum hyperfine splitting, which are probably of the same order of magnitude. The ligand hyperfine structure is not observed probably because the hyperfine constant of the ligands is much smaller than that of the metal, and is hidden under the signal observed. For compound IIIi both the solid state and the DMSO spectra show structure, but the general appearance of the spectra is similar to that observed for the mononuclear compounds. The data are insufficient to allow us to classify compound IIIi either as a Mo^{IV}—Mo^V or as a delocalized system, but further studies are in progress.

3. Experimental

All preparations and subsequent manipulations were carried out under nitrogen unless otherwise stated. Tetrahydrofuran and diethyl ether were distilled under nitrogen from sodium benzophenoneketyl, while dichloromethane and acetonitrile were dried from calcium hydride. Imidazole (Fluka), *N*-methylimidazole (Fluka), pyrazole (Aldrich) and nitrosonium hexafluorophosphate (Aldrich) were commercial products and were used without further purifications. 2,2'-Diimidazole was prepared from glyoxal and concentrated ammonia by a published method [13]. (PMDTLi)₂biim was prepared as reported in the literature [4].

The compounds [M(η -C₅H₅)₂X₂] (M = Mo, W; X = Cl, Br, I), [Mo(η -C₅H₅)₂H₃][PF₆] and [M(η -C₅H₅)₂HX] (M = Mo, X = I; M = W; X = Br), were prepared by published methods [14–16].

Hydrogen-1 NMR spectra were determined on a JEOL JNM 100 PFT instrument. ESR spectra were determined on a Bruker ER 200tt instrument. 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 CDM 3 Conductivity Meter instrument calibrated with standard KCl solutions. Ionization constants were determined by potentiometric titration of 10⁻³ M solutions of the metal complexes in acetone/water (1/1) with a 0.100 N aqueous potassium hydroxide solution at 20°C using a combined electrode Radiometer GK 2301C connected to a Radiometer pH meter 4. Potential values were converted into pH values by comparisons with a titration of 0.100 N HCl in the same mixed solvent with the same KOH solution. Calculations were based partly on Silva's procedure [17], using Irving and

Stacey's adaptation [18] of Bjerrum's method [19], and utilized 8, 9 or 10 experimental points.

C, H and N analyses were carried out in this laboratory. The conditions used for the preparation of the complexes are shown in Table 5. Typical methods of synthesis are described below:

Method 1: Preparation of [Mo(η -C₅H₅)₂H(Him)][PF₆] (Ia). A solution of [Mo(η -C₅H₅)₂HI] (340 mg, ~1 mmol), Tl[PF₆] (350 mg, ~1 mmol) and imidazole (70 mg, ~1 mmol) in acetone was refluxed for 5 h. The mixture was filtered and a precipitate was obtained by addition of ethanol to the filtrate and removal of the acetone. The precipitate was recrystallized several times from acetone/diethyl ether giving yellow crystals: Yield ca. 60%.

Method 2: Preparation of [Mo(η -C₅H₅)₂Br(Him)][PF₆] (Ib). A solution of [Mo(η -C₅H₅)₂Br₂] (400 mg, ~1 mmol), Tl[PF₆] (350 mg, ~1 mmol) and imidazole (140 mg, ~2 mmol) in acetone was refluxed for 3 h. The mixture was filtered and the filtrate chromatographed on alumina column. Elution with acetone gave a green band, which was removed and treated with ~2 ml of a

TABLE 5
EXPERIMENTAL CONDITIONS FOR THE PREPARATION OF THE COMPLEXES

Com-pound	Method	Reactants	Solvent	Conditions	Yield (%)
Ia	1	[Mo(η -C ₅ H ₅) ₂ HI], Him, TlPF ₆	Acetone	Reflux, 5 h	~60
Ib	2	[Mo(η -C ₅ H ₅) ₂ Br ₂], Him, TlPF ₆	Acetone	Reflux, 3 h	~80
Ic	2	[W(η -C ₅ H ₅) ₂ Br ₂], Him, TlPF ₆	Acetone	Reflux, 1.5 h	~60
Id	3	Ib, NOPF ₆	Acetonitrile	r.t., 2 min	~80
Ie	6	If, NH ₄ PF ₆	Acetone/H ₂ O	r.t., 2 days	~90
If	4	[Mo(η -C ₅ H ₅) ₂ Br ₂], Kim	THF	Reflux, 4 h	~30
Ig	4	[W(η -C ₅ H ₅) ₂ Br ₂], Kim	THF	Reflux, 3.5 h	~5
IIa	7	[Mo(η -C ₅ H ₅) ₂ H ₃][PF ₆], Nmim	Acetone	Reflux, 20 h	~30
2b	2	[Mo(η -C ₅ H ₅) ₂ Br ₂], Nmin, TlPF ₆	Acetone	Reflux, 6 h	~70
IIc	1	[W(η -C ₅ H ₅) ₂ HBr], Nmin, TlPF ₆	Acetone	Reflux, 10.5 h	~30
IId	2	[W(η -C ₅ H ₅) ₂ Br ₂], Nmim, TlPF ₆	Acetone	Reflux, 6 h	~50
IIe	3	IIb, NOPF ₆	Acetonitrile	r.t., 5 min	~80
IIf	7	[Mo(η -C ₅ H ₅) ₂ H ₃][PF ₆], Nmin	Acetone	Reflux, 20 h	~40
	8	[Mo(η -C ₅ H ₅) ₂ Br ₂], Nmim	—	200°C, 5 h	~90
IIIa	1	[Mo(η -C ₅ H ₅) ₂ HI], Hpz, TlPF ₆	Acetone	Reflux, 4 h	~30
IIIb	2	[Mo(η -C ₅ H ₅) ₂ Cl ₂], Hpz, TlPF ₆	Acetone	Reflux, 1 h	~50
IIIc	2	[Mo(η -C ₅ H ₅) ₂ Br ₂], Hpz, TlPF ₆	Acetone	Reflux, 7 h	~60
IIId	2	[Mo(η -C ₅ H ₅) ₂ Cl ₂], Hpz, TlPF ₆	Acetone	Reflux, 1 h	~60
IIIe	2	[W(η -C ₅ H ₅) ₂ Cl ₂], Hpz, TlPF ₆	Acetone	Reflux, 3 h	~70
IIIf	2	[W(η -C ₅ H ₅) ₂ Br ₂], Hpz, TlPF ₆	Acetone	Reflux, 4 h	~60
IIIg	2	[W(η -C ₅ H ₅) ₂ I ₂], Hpz, TlPF ₆	Acetone	Reflux, 3 h	~5
IIIh	3	IIIc, NOPF ₆	Acetonitrile	r.t., 5 min	~80
IIIi	4	[Mo(η -C ₅ H ₅) ₂ Br ₂], Napz	THF	Reflux, 4 h	~20
IIIj	4	[W(η -C ₅ H ₅) ₂ Br ₂], Napz	THF	Reflux, 4 h	~5
IIIk	5	[Mo(η -C ₅ H ₅) ₂ Br ₂], Napz (1/1)	THF	Reflux, 3 h	~60
IIIl	3	IIIk, NOPF ₆	Acetonitrile	r.t., 5 min	~60
IIIIm	10	[Mo(η -C ₅ H ₅) ₂ Br ₂], TlPF ₆ , excess Hpz	Acetone	Reflux, 20 h	~40
IVa	2	[Mo(η -C ₅ H ₅) ₂ Br ₂], TlPF ₆ , H ₂ biim (1/2/1)	Acetone	Reflux, 20 h	~70
IVb	9	[Mo(η -C ₅ H ₅) ₂ Br ₂] (PMDTLi) ₂ biim	THF	Reflux, 3 h	~60

saturated solution of $[\text{NH}_4][\text{PF}_6]$. Removal of the acetone gave a green precipitation, which was recrystallised from acetone/water, giving green crystals. Yield ca. 80%.

Method 3: Preparation of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}(\text{Him})][\text{PF}_6]_2$ (Id). $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}(\text{Him})][\text{PF}_6]$ (180 mg \sim 0.3 mmol) was dissolved in dry acetonitrile (20 ml) and $[\text{NO}][\text{PF}_6]$ (190 mg \sim 0.5 mmol) was added. The green solution immediately turned red and was filtered without delay. After concentration of the solution under vacuum, rapid addition of dry diethyl ether gave red crystals. Yield ca. 80%.

Method 4: Preparation of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{im})_2]$ (If). A solution of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}_2]$ (400 mg, \sim 1 mmol) and potassium imidazolate (350 mg, \sim 3 mmol) in dry THF were refluxed for 4 h. The mixture was evaporated to dryness under vacuum and the residue extracted with dry dichloromethane. Addition of diethyl ether to the extract gave an oily orange precipitate, which after repeated recrystallisations from dichloromethane/diethyl ether gave orange crystals. Yield ca. 30%.

Method 5: Precipitation of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{pz})_2][\text{PF}_6]_2$ (IIIk). A solution of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}_2]$ (1, 2 mg, \sim 3 mmol) and sodium pyrazolate (350 mg, \sim 4 mmol) in dry THF was refluxed for 3 h. The mixture was pumped to dryness under vacuum and extraction of the residue with dry dichloromethane yielded the compound $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{pz})_2]$ (IIIi). To the solution obtained by further extraction of the residue with water, excess $[\text{NH}_4][\text{PF}_6]$ was added to give a pink precipitate. This was recrystallised twice from acetone/water to give red crystals. Yield ca. 60%.

Method 6: Preparation of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{Him})_2][\text{PF}_6]_2$ (Ie). The compound $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{im})_2]$ (180 mg, \sim 0.5 mmol) was dissolved in a mixture of acetone/water and excess $[\text{NH}_4][\text{PF}_6]$ was added. The solution was left to stand for two days in contact with air; the red crystals formed were filtered off, washed with water, ethanol and ether and dried and were identified as being the compound $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{Him})_2][\text{PF}_6]_2$. Yield ca. 90%.

Method 7: Preparation of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{Nmim})][\text{PF}_6]$ (IIa) and $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{Nmim})_2][\text{PF}_6]_2$ (IIf). A solution of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3][\text{PF}_6]$ (380 mg, \sim 1 mmol) in acetone (50 cm³) containing *N*-methylimidazole (1.5 cm³) was refluxed for 20 h to give a brownish orange solution. This was filtered, some solvent was removed under vacuum, and the remaining solution was chromatographed on an alumina column. Elution with acetone gave first a yellow band (A), then a small blue band which was discarded, and then an orange band (B). Addition of diethyl ether to band (A) gave yellow crystals, which were recrystallised from acetone/ethanol and were identified as $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{Nmim})][\text{PF}_6]$; Yield ca. 30%. Addition of diethyl ether to band (B) gave an orange precipitate which was recrystallised from acetone/ethanol and identified as $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{Nmim})_2][\text{PF}_6]_2$; yield ca. 40%.

Method 8: Preparation of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{Nmim})_2][\text{PF}_6]_2$ (IIf). $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}_2]$ (400 mg, \sim 1 mmol) was stirred with *N*-methylimidazole (2 cm³) at 200°C for 5 h. The viscous mixture was extracted with water and addition of $[\text{NH}_4][\text{PF}_6]$ to the filtrate gave an orange precipitate. This was recrystallised from acetone/ethanol to give red crystals which were identified as $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{Nmim})_2][\text{PF}_6]_2$; yield ca. 90%.

Method 9: Preparation of $[\{Mo(\eta-C_5H_5)_2\}_2biim][PF_6]_2$ (IVb). A solution of $[Mo(\eta-C_5H_5)_2Br_2]$ (600 mg, ~ 1.5 mmol) in dry THF (80 cm^3) was refluxed for 3 h in the presence of $(PMDTLi)_2biim$ (390 mg, ~ 0.75 mmol). The mixture was filtered and the residue was extracted with water to give an orange solution, to which excess $[NH_4][PF_6]$ was added to give orange crystals which were identified as $[\{Mo(\eta-C_5H_5)_2\}_2biim][PF_6]_2$; yield ca. 60%.

Method 10: Preparation of $[Mo(\eta-C_5H_5)_2\{N_2C_3H_3C(Me)_2O\}][PF_6]$ (IIIIn). Excess pyrazole and $Tl[PF_6]$ (700 mg, ~ 2 mmol) were added to a solution of $[Mo(\eta-C_5H_5)_2Br_2]$ (400 mg, ~ 1 mmol) in acetone (50 cm^3). The solution was refluxed for 20 h. The resulting brown solution was chromatographed on an alumina column with acetone as eluant. An orange solution was collected, from which orange crystals were obtained by addition of diethyl ether. These were further recrystallised from acetone/diethyl ether; yield ca. 40%.

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