Bis(η-cyclopentadienyl)-molybdenum (and -tungsten or -titanium) Complexes with Chelate Imidazole Derivatives and Related Ligands

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The new compounds $[\mathrm{M}(\eta\text{-C}_5\mathrm{H}_5)_2(\mathrm{HL{-}L'})][\mathrm{PF}_6]_2$, $[\mathrm{Mo}(\eta\text{-C}_5\mathrm{H}_5)_2(\mathrm{L{-}L'})][\mathrm{PF}_6]$ (M = Mo or W), $[\mathrm{Ti}(\eta\text{-C}_5\mathrm{H}_5)_2(\mathrm{HL{-}L'})][\mathrm{PF}_6]$ [HL–L' = 2-(2'-pyridyl)imidazoline, 2-(2'-pyridyl)imidazole, 2-(2'-pyridyl)benzimidazole, or 8-aminoquinoline], and $[\mathrm{M}(\eta\text{-C}_5\mathrm{H}_5)_2(\mathrm{HL{-}L'})][\mathrm{PF}_6]$ and $[\mathrm{M}(\eta\text{-C}_5\mathrm{H}_5)_2(\mathrm{L{-}L'})]$ (M = Mo or W) [$\mathrm{H_2L{-}L'}$ = 2-(2'-hydroxyphenyl)imidazoline or 2-(2'-hydroxyphenyl)benzimidazole] have been prepared. The acid-ionisation constants of the co-ordinated ligands have been measured for the molybdenum and tungsten complexes. Some of the deprotonated complexes have been methylated, and dicationic titanium complexes $[\mathrm{Ti}(\eta\text{-C}_5\mathrm{H}_5)_2(\mathrm{L{-}L})][\mathrm{PF}_6]_2$ (L–L = 1,10-phenanthroline or 2,2'-bipyridyl) have also been prepared.

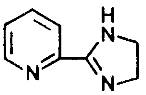
METAL complexes of imidazole derivatives have been prepared and studied by several workers.[1] Studies have concentrated on the deprotonation of the co-ordinated ligands, formation constants, analytical applications, and spectroscopic and magnetic properties. Some of this work has been prompted by the biological significance of some of these ligands.

To our knowledge no complexes of these ligands with titanium, molybdenum, or tungsten have been reported. In a previous note we described our preliminary results on the deprotonation reactions of some molybdenum and tungsten complexes with imidazole and imidazoline derivatives.[2] We now describe the synthesis, properties, and reactions of the complexes of the imidazole derivatives and related ligands shown below with the $\mathrm{M}(\eta\text{-C}_5\mathrm{H}_5)_2$ moiety where M = $\mathrm{Ti^{III}}$, $\mathrm{Mo^{IV}}$, or $\mathrm{W^{IV}}$; complexes of $\mathrm{Ti^{IV}}(\eta\text{-C}_5\mathrm{H}_5)_2$ with 1,10-phenanthroline (phen) and 2,2'-bipyridyl (bipy) are also described.

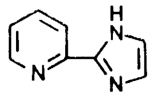
RESULTS AND DISCUSSION

The compounds $[\mathrm{M}(\eta\text{-C}_5\mathrm{H}_5)_2\mathrm{Br}_2]$ (M = Mo or W) reacted with the molten nitrogen-donor imidazole derivatives and 8-aminoquinoline ligands HL–L' [Hpyim, Hpym, Hpyb, or 8-aminoquinoline (Haquin)] to give either the dications $[\mathrm{M}(\eta\text{-C}_5\mathrm{H}_5)_2(\mathrm{HL{-}L'})]^{2+}$ or a mixture of the dication and the monocations $[\mathrm{M}(\eta\text{-C}_5\mathrm{H}_5)_2(\mathrm{L{-}L'})]^+$ which were then separated by treatment with either acid or base and isolated as the hexafluorophosphate salts.

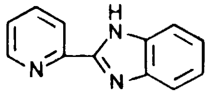
The dibromo-molybdenum and -tungsten complexes reacted also with the 2-hydroxyphenyl derivatives ($\mathrm{H_2}$hpim or $\mathrm{H_2}$hpb) in refluxing ethanol and in the presence of triethylamine (to remove the phenolic proton) to yield the monocations $[\mathrm{M}(\eta\text{-C}_5\mathrm{H}_5)_2(\mathrm{HL{-}L'})]^+$ which were also isolated as the hexafluorophosphate salts and which could be further deprotonated. In the case of the 2-(2'-hydroxyphenyl)imidazoline derivatives it was not possible to obtain satisfactory analytical results for the products of the second deprotonation, probably due to contamination with the parent compound. The deprotonated complexes $[\mathrm{M}(\eta\text{-C}_5\mathrm{H}_5)_2(\mathrm{L{-}L'})]^{0,1+}$ could be alkylated by reaction with alkyl halides. Similar alkylation reactions have been reported for the $[\mathrm{Ni(pym)_2}]^+$ complex.[1b] The ligands Hpyim, Hpym, Hpyb, and Haquin reacted with the titanium(III) dimer $[\{\mathrm{Ti}(\eta\text{-C}_5\mathrm{H}_5)_2\mathrm{Cl}\}_2]$ in dry tetrahydrofuran (thf) at room temperature to give the complexes $[\mathrm{Ti}(\eta\text{-C}_5\mathrm{H}_5)_2(\mathrm{HL{-}L'})]^+$. Attempts to deprotonate the co-ordinated ligands in these complexes lead to decomposition. Reaction of the titanium dimer with ligands $\mathrm{H_2}$hpim and $\mathrm{H_2}$hpb gave intractable species.



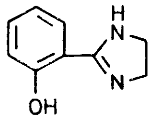
2-(2'-pyridyl)imidazoline
Hpyim



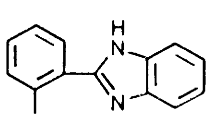
2-(2'-pyridyl)imidazole
Hpym



2-(2'-pyridyl)benzimidazole
Hpyb



2-(2'-hydroxyphenyl)imidazoline
$\mathrm{H_2}$hpim



2-(2'-hydroxyphenyl)benzimidazole
$\mathrm{H_2}$hpb

Attempts to oxidise the titanium(III) complexes prepared were unsuccessful and the complexes were decomposed by both $\mathrm{HNO_3}$ and $[\mathrm{NO}][\mathrm{PF}_6]$. However, we were able to oxidise the known related complexes $[\mathrm{Ti}(\eta\text{-C}_5\mathrm{H}_5)_2(\mathrm{bipy})]^+$ and $[\mathrm{Ti}(\eta\text{-C}_5\mathrm{H}_5)_2(\mathrm{phen})]^+$ with [NO]-

$[PF_6]$ obtaining the analogous titanium(IV) dications $[Ti(\eta\text{-}C_5H_5)_2(bipy)]^{2+}$ and $[Ti(\eta\text{-}C_5H_5)_2(phen)]^{2+}$. These are the first bis(η-cyclopentadienyl)titanium(IV) derivatives with neutral bidentate ligands to be isolated.

All the new compounds described are well crystallised solids and the cationic complexes were isolated as the hexafluorophosphate salts. The molybdenum and tungsten complexes are stable in air for prolonged periods but the titanium ones react readily with molecular oxygen, both in the solid state and in solution, to give yellow solids, presumably oxygen-bridged polymers. The complexes are thermally stable up to *ca.* 200—300 °C. The analytical and conductimetric evidence for the formulations proposed are given in Table 1.

TABLE 1

Analytical and conductimetric data

	Compound	Colour	Decomp. temperature (θ_c/°C)	Analysis (%) [a] C	H	N	Λ [b] Ω^{-1} cm^2 mol^{-1}
(1a)	$[Mo(\eta\text{-}C_5H_5)_2(Hpyim)][PF_6]_2$	Red	280	32.7 (32.6)	3.0 (2.9)	6.7 (6.3)	210
(1b)	$[Mo(\eta\text{-}C_5H_5)_2(pyim)][PF_6]$	Orange	270	42.2 (41.8)	4.3 (3.5)	7.8 (8.1)	94
(1c)	$[W(\eta\text{-}C_5H_5)_2(Hpyim)][PF_6]_2$	Red	260	28.7 (28.8)	2.4 (2.5)	6.2 (5.6)	245
(1d)	$[W(\eta\text{-}C_5H_5)_2(pyim)][PF_6]$	Orange	300	35.8 (35.7)	3.5 (3.0)	6.9 (7.0)	91
(1e)	$[Ti(\eta\text{-}C_5H_5)_2(Hpyim)][PF_6]$	Mauve	210	45.2 (46.0)	3.8 (4.1)	8.2 (9.0)	104
(1f)	$[Mo(\eta\text{-}C_5H_5)_2(1\text{-}Mepyim)][PF_6]_2$	Pink	290	32.9 (32.5)	3.2 (3.2)	6.4 (6.3)	185
(2a)	$[Mo(\eta\text{-}C_5H_5)_2(Hpym)][PF_6]_2$	Orange	290	32.9 (32.7)	2.4 (2.6)	6.8 (6.4)	200
(2b)	$[Mo(\eta\text{-}C_5H_5)_2(pym)][PF_6]$	Dark yellow	275	41.7 (42.0)	3.2 (3.1)	8.0 (8.2)	88
(2c)	$[W(\eta\text{-}C_5H_5)_2(Hpym)][PF_6]_2$	Red	300	28.9 (28.9)	2.4 (2.3)	5.9 (5.6)	215
(2d)	$[W(\eta\text{-}C_5H_5)_2(pym)][PF_6]$	Yellowish orange	290	35.1 (35.8)	2.7 (2.7)	7.3 (7.0)	90
(2e)	$[Ti(\eta\text{-}C_5H_5)_2(Hpym)][PF_6]$	Purple	160	46.1 (46.2)	4.1 (3.7)	8.7 (9.0)	82
(2f)	$[Mo(\eta\text{-}C_5H_5)_2(1\text{-}Mepym)][PF_6]_2$	Salmon pink	310	33.0 (33.8)	2.8 (2.8)	5.8 (6.2)	150
(2g)	$[W(\eta\text{-}C_5H_5)_2(1\text{-}Mepym)][PF_6]_2$	Salmon pink	315	29.75 (29.9)	2.8 (2.5)	5.5 (5.5)	150
(3a)	$[Mo(\eta\text{-}C_5H_5)_2(Hpyb)][PF_6]_2$	Red	310	36.7 (37.15)	2.7 (2.7)	6.1 (5.9)	215
(3b)	$[Mo(\eta\text{-}C_5H_5)_2(pyb)][PF_6]$	Carrot	270	46.5 (46.7)	3.2 (3.2)	7.3 (7.4)	82
(3c)	$[W(\eta\text{-}C_5H_5)_2(Hpyb)][PF_6]_2$	Red	315	33.1 (33.1)	2.5 (2.4)	5.5 (5.3)	176
(3d)	$[W(\eta\text{-}C_5H_5)_2(pyb)][PF_6]$	Carrot	290	40.5 (40.45)	2.8 (2.8)	6.3 (6.4)	80
(3e)	$[Ti(\eta\text{-}C_5H_5)_2(Hpyb)][PF_6]$	Purplish blue	260	50.2 (51.0)	3.9 (3.7)	8.2 (8.1)	98
(3f)	$[Mo(\eta\text{-}C_5H_5)_2(1\text{-}Mepyb)][PF_6]_2$	Pink	290	37.6 (38.1)	3.0 (2.9)	5.8 (5.8)	165
(4a)	$[Mo(\eta\text{-}C_5H_5)_2(Haquin)][PF_6]_2$	Red	250	34.6 (34.6)	2.9 (2.75)	4.3 (4.2)	191
(4b)	$[Mo(\eta\text{-}C_5H_5)_2(aquin)][PF_6]$	Mauve	240	45.1 (44.4)	3.4 (3.3)	5.7 (5.45)	72
(4c)	$[W(\eta\text{-}C_5H_5)_2(Haquin)][PF_6]_2$	Orange	200	29.8 (30.5)	2.4 (2.4)	3.9 (3.7)	254
(4d)	$[W(\eta\text{-}C_5H_5)_2(aquin)][PF_6]$	Mauve	215	37.3 (37.9)	2.8 (2.8)	5.0 (4.65)	87
(4e)	$[Ti(\eta\text{-}C_5H_5)_2(Haquin)][PF_6]$	Purplish brown	190	48.5 (48.8)	4.2 (3.9)	5.8 (6.0)	104
(5a)	$[Mo(\eta\text{-}C_5H_5)_2(Hhpim)][PF_6]$	Red	155	42.8 (42.9)	3.7 (3.6)	4.9 (5.3)	88
(5b)	$[W(\eta\text{-}C_5H_5)_2(Hhpim)][PF_6]$	Orange-brown	180	36.75 (36.8)	3.1 (3.1)	5.1 (4.5)	80
(6a)	$[Mo(\eta\text{-}C_5H_5)_2(Hhpb)][PF_6]$	Brown	210	47.2 (47.6)	3.3 (3.3)	4.6 (4.8)	74
(6b)	$[Mo(\eta\text{-}C_5H_5)_2(hpb)]$	Brown	250	61.3 (63.6)	4.3 (4.2)	6.2 (6.45)	7
(6c)	$[W(\eta\text{-}C_5H_5)_2(Hhpb)][PF_6]$	Brown	210	41.3 (41.3)	3.2 (2.9)	4.85 (4.2)	97
(6d)	$[W(\eta\text{-}C_5H_5)_2(hpb)]$	Brown-orange	250	52.2 (52.9)	3.5 (3.5)	5.9 (5.4)	4
(7)	$[Ti(\eta\text{-}C_5H_5)_2(phen)][PF_6]_2$	Green		41.1 (40.8)	3.0 (2.8)	5.6 (4.3)	186
(8)	$[Ti(\eta\text{-}C_5H_5)_2(bipy)][PF_6]_2$	Green		39.2 (38.5)	3.1 (2.9)	4.7 (4.5)	193

[a] Calculated values are given in parentheses. [b] For 10^{-3} mol dm^{-3} solutions in nitromethane.

The electronic spectra are of the type usually found for bent sandwich complexes [3] and are very similar to those recently reported for analogous complexes with other nitrogen-donor ligands.[4] It was also observed that the deprotonation of the dicationic complexes leads to the appearance of a new charge-transfer band in the visible region

The i.r. spectra in KBr pellets show bands characteristic of a η-cyclopentadienyl ring, of the anion PF_6^- (in the case of the cationic complexes), and those of the other ligands. For ligands Hpyim, Hpym, and Hpyb it is observed that the N–H stretching frequency appears at 3 415 cm^{-1} in the spectra of complexes (1a), (1c), and (1e), at 3 350 cm^{-1} in complexes (2a), (2c), and (2e), and at 3 360 cm^{-1} in complex (3e). This band was not observed for complexes (3a) and (3c) being presumably under a broad band at 2 900 cm^{-1}. It is not possible to make a meaningful comparison between the N–H stretching frequencies in the co-ordinated and in the free ligands. In fact, in KBr pellets this band for the free ligands is broad and appears at 3 300 (Hpyim), 3 020 (Hpym), and 3 050 cm^{-1} (Hpyb) due to intermolecular hydrogen bonding; in dilute $CHCl_3$ solutions the same band appears at 3 460 cm^{-1} for all the three ligands. However, the complexes are not soluble in $CHCl_3$ being only soluble in solvents such as $(CH_3)_2CO$ and CH_3CN in which a strong interaction between solute and solvent is to be expected. The usual shifts of the *o*-substituted pyridinic ligand upon co-ordination [5] were also observed. Deprotonation causes the disappearance of the N–H stretching as well as small shifts in other bands.

In the ^{1}H n.m.r. spectra the chemical shifts of the protons of the ligands generally move towards lower fields upon co-ordination. On deprotonation a general shift to higher field is observed.

Acid-ionisation constants of the co-ordinated ligands were determined by potentiometric titration in acetone–water (1 : 1) solution; the calculated pK_a values are given in Table 2. The titanium(III) compounds were too unstable to oxidation in solution for such studies to be undertaken. Attempts to calculate the acid-ionization constants of the hydrogen bonded to the *sp*^{3} nitrogen in the free ligands using this method were unsuccessful due to the very high value of the constants. In agreement with published data (with the possible exception of Hhpim), the acidity of the ligands generally increased upon co-ordination. This has been taken to show that the electronic shift which occurs as a consequence of metal–nitrogen, and to some extent metal–oxygen, bond formation can be transmitted through the aromatic ring, decreasing the electron availability at the imino-nitrogen and thus facilitating the deprotonation reaction.[6]

TABLE 2

Acid-ionisation constants for $[M(\eta\text{-}C_5H_5)_2(HL\text{–}L')][PF_6]_n \rightleftharpoons [M(\eta\text{-}C_5H_5)_2(L\text{–}L')][PF_6]_{n-1} + H^+$ ($n = 1$ or 2)

Complex	pK_a *	Complex	pK_a *
$[Mo(\eta\text{-}C_5H_5)_2(Hpyim)][PF_6]_2$	*ca.* 10	$[W(\eta\text{-}C_5H_5)_2(Hpyim)][PF_6]_2$	9.12 ± 0.03
$[Mo(\eta\text{-}C_5H_5)_2(Hpym)][PF_6]_2$	5.20 ± 0.03	$[W(\eta\text{-}C_5H_5)_2(Hpym)][PF_6]_2$	4.68 ± 0.03
$[Mo(\eta\text{-}C_5H_5)_2(Hpyb)][PF_6]_2$	3.98 ± 0.03	$[W(\eta\text{-}C_5H_5)_2(Hpyb)][PF_6]_2$	3.53 ± 0.03
$[Mo(\eta\text{-}C_5H_5)_2(Haquin)][PF_6]_2$	4.08 ± 0.03	$[W(\eta\text{-}C_5H_5)_2(Haquin)][PF_6]_2$	3.14 ± 0.03
$[Mo(\eta\text{-}C_5H_5)_2(Hhpim)][PF_6]$	>11	$[W(\eta\text{-}C_5H_5)_2(Hhpim)][PF_6]$	>11
$[Mo(\eta\text{-}C_5H_5)_2(Hhpb)][PF_6]$	8.40 ± 0.03	$[W(\eta\text{-}C_5H_5)_2(Hhpb)][PF_6]$	8.03 ± 0.03

* $0.03 = \tau_m t$ where τ_m is the mean standard deviation and t is the Student parameter for 95% probability and between six and eight degrees of freedom. Calculations were made using the method of ref. 13.

The relative acidities of the various co-ordinated ligands, as measured by the pK_a values, follow the extent of delocalisation of the π-electron density of the ligands and reflect the electron-withdrawing and -donating properties of the nitrogen and oxygen donor atoms respectively. As expected, the increase in acidity upon co-ordination is maximal for ligands Hpym and Haquin and negligible for Hhpim.

It has been suggested that the increase in acidity of the imino-hydrogen of the imidazole or imidazoline nucleus is a function of the metal–nitrogen bond strength,[5] but this claim has recently been disputed.[7] On these grounds our observation of a consistently higher acidity for the tungsten complexes seems to indicate the following order for the bond strengths: W–N > Mo–N. Thermochemical studies now initiated may provide the necessary evidence to establish this point.

EXPERIMENTAL

All preparations and further manipulations were carried out under dinitrogen unless otherwise stated. Tetrahydrofuran and diethyl ether were dried over sodium and acetonitrile was dried over calcium hydride. 8-Aminoquinoline (Fluka), 2,2′-bipyridyl (B.D.H.), 1,10-phenanthroline (Fluka), and 2-(2′-pyridyl)benzimidazole (Aldrich) were commercial products and were used without further purification.

2-(2′-Pyridyl)imidazoline was prepared by condensing α-picolinic acid (pyridine-2-carboxylic acid) with ethylenediamine. 2-(2′-Hydroxyphenyl)-imidazoline and -benzimidazole were obtained by condensing salicylamide with ethylenediamine and 1,2-phenylenediamine, respectively. 2-(2′-Pyridyl)imidazole was prepared from pyridine-2-carbaldehyde, glyoxal, and ammonia. The experimental details have been reported.[8,9]

The compounds $[M(\eta\text{-}C_5H_5)_2Br_2]$ (M = Mo or W), $[\{Ti(\eta\text{-}C_5H_5)_2Cl\}_2]$, $[Ti(\eta\text{-}C_5H_5)_2(phen)][PF_6]$, and $[Ti(\eta\text{-}C_5H_5)_2(bipy)][PF_6]$ were prepared as described in the literature.[10-12]

Proton n.m.r. spectra were determined on a JEOL JNM 100 PFT instrument. Infrared spectra were recorded on a Perkin-Elmer 457 instrument as KBr pellets or in chloroform solution and were calibrated with polystyrene. Conductivity measurements were made at 25 °C using a Radiometer CDM3 conductivity meter calibrated with standard KCl solution. Electronic spectra were measured in solution in a Cary 17 instrument.

Ionisation constants were determined by potentiometric titration of 10^{-3} mol dm^{-3} solutions, of the metal complexes in acetone–water (1 : 1) with a 0.100N solution of K[OH] in water at 20 °C using a Radiometer GK 2301 C combined electrode connected to a Radiometer 4 pH meter. Potential values were converted into pH values by comparison with a titration of 0.100N HCl in the same mixed solvent with the same solution of K[OH]. Calculations were based partly on the method of Silva,[13] according to an adaptation of Irving and Stacey [14] of Bjerrum's method and using 8—10 experimental points.

Analyses for C, H, and N were carried out in this laboratory and at the Inorganic Chemistry Laboratory, Oxford. The conditions used for the preparation of the complexes are shown in Table 3; typical methods of synthesis are described below.

Method 1.—*Bis*(η-*cyclopentadienyl*)[2-(2′-*pyridyl*)*imidazoline*]*molybdenum bis*(*hexafluorophosphate*), (1a). The compound $[Mo(\eta\text{-}C_5H_5)_2Br_2]$ (0.4 g, *ca.* 1 mmol) and 2-(2′-pyridyl)imidazoline (200 mg, *ca.* 1.5 mmol) were heated for 1 h at 110 °C so that the ligand acted also as the solvent. The dark sticky mixture obtained was extracted with water giving a red solution from which a red precipitate was obtained by addition of $[NH_4][PF_6]$. The product was recrystallised from acetone–water as red crystals.

Method 2.—*Bis*(η-*cyclopentadienyl*)[2-(2′-*pyridyl*)*imidazolinato*]*molybdenum hexafluorophosphate*, (1b). A saturated solution (10 cm^3) of Na[OH] was added to a red solution of $[M(\eta\text{-}C_5H_5)_2(Hpyim)][PF_6]_2$ (0.2 mmol) in acetone (10 cm^3) and the mixture was shaken for a few minutes. The orange organic phase was separated from the aqueous phase and pumped to dryness under vacuum. The residue was extracted with acetone, and addition of ethanol followed by evaporation of the acetone yielded an orange precipitate, which was recrystallised twice from acetone–ethanol as orange crystals.

Method 3.—*Bis*(η-*cyclopentadienyl*)[2-(2′-*pyridyl*)*imidazole*]*molybdenum bis*(*hexafluorophosphate*), (2a), *and bis*(η-*cyclopentadienyl*)[2-(2′-*pyridyl*)*imidazolato*]*molybdenum hexafluorophosphate*, (2b). The compound $[Mo(\eta\text{-}C_5H_5)_2Br_2]$ (0.4 g, *ca.* 1 mmol) and 2-(2′-pyridyl)imidazole (0.3 g, *ca.* 2 mmol) were heated for 4 h at 140 °C so that the ligand acted also as the solvent. The dark orange mixture was extracted with water and the solution was treated as in method 1. Orange crystals were obtained after recrystallisation from acetone-ethanol. These were divided into two parts (a) and (b).

Aqueous HCl (1 : 1) (3 cm^3) was added to a solution of (a) in acetone. The pink solution obtained was pumped under vacuum, to eliminate the excess of HCl, excess of Tl[PF$_6$] was added, and the mixture stirred for 2 h at room temperature to precipitate all the chloride as TlCl. The solution was then filtered and, upon reducing the volume of the filtrate under vacuum, pink crystals precipitated. These were recrystallised from acetone–water as reddish orange crystals which were identified as [Mo(η-C$_5$H$_5$)$_2$(Hpym)][PF$_6$]$_2$. Crystals (b) were treated as described in method 2, giving dark yellow crystals identified as [Mo(η-C$_5$H$_5$)$_2$(pym)][PF$_6$].

TABLE 3

Experimental conditions for the preparation of the complexes

Compound	Method	Reactants	Solvent	Conditions	Yield (%)
(1a)	1	[Mo(η-C$_5$H$_5$)$_2$Br$_2$],Hpyim		1 h, 110 °C	80
(1b)	2	(1a), Na[OH]	(CH$_3$)$_2$CO	5 min, r.t.	*ca.* 100
(1c)	1	[W(η-C$_5$H$_5$)$_2$Br$_2$],Hpyim		1 h, 110 °C	70
(1d)	2	(1c), Na[OH]	(CH$_3$)$_2$CO	5 min, r.t.	*ca.* 100
(1e)	6	[{Ti(η-C$_5$H$_5$)$_2$Cl}$_2$],Hpyim	thf	30 min, r.t.	70
(1f)	5	(1b), MeI	(CH$_3$)$_2$CO	10 h, reflux	60
(2a)	3	[Mo(η-C$_5$H$_5$)$_2$Br$_2$],Hpym		4 h, 140 °C	60
(2b)	3	[Mo(η-C$_5$H$_5$)$_2$Br$_2$],Hpym,Na[OH]		4 h, 140 °C	80
(2c)	3	[W(η-C$_5$H$_5$)$_2$Br$_2$],Hpym,HCl		4 h, 140 °C	60
(2d)	3	[W(η-C$_5$H$_5$)$_2$Br$_2$],Hpym,Na[OH]		4 h, 140 °C	80
(2e)	6	[{Ti(η-C$_5$H$_5$)$_2$Cl}$_2$], Hpym	thf	30 min, r.t.	70
(2f)	5	(2b), MeI	(CH$_3$)$_2$CO	10 h, reflux	60
(2g)	5	(2d), MeI	(CH$_3$)$_2$CO	10 h, reflux	80
(3a)	1	[Mo(η-C$_5$H$_5$)$_2$Br$_2$], Hpyb		6 h, 210 °C	80
(3b)	2	(3a), Na[OH]	(CH$_3$)$_2$CO	5 min, r.t.	*ca.* 100
(3c)	1	[W(η-C$_5$H$_5$)$_2$Br$_2$],Hpyb		12 h, 210 °C	60
(3d)	2	(3c), Na[OH]	(CH$_3$)$_2$CO	5 min, r.t.	*ca.* 100
(3e)	6	[{Ti(η-C$_5$H$_5$)$_2$Cl}$_2$],Hpyb	thf	30 min, r.t.	70
(3f)	5	(3b), MeI	(CH$_3$)$_2$CO	10 h, reflux	60
(4a)	1	[Mo(η-C$_5$H$_5$)$_2$],Haquin		1 h, 110 °C	70
(4b)	2	(4a), Na[OH]	(CH$_3$)$_2$CO	5 min, r.t.	*ca.* 100
(4c)	3	[W(η-C$_5$H$_5$)$_2$Br$_2$],Haquin		1 h, 110 °C	5
(4d)	3	[W(η-C$_5$H$_5$)$_2$Br$_2$],Haquin		1 h, 110 °C	70
(4e)	6	[{Ti(η-C$_5$H$_5$)$_2$Cl}$_2$],Haquin	thf	30 min, r.t.	70
(5a)	4	[Mo(η-C$_5$H$_5$)$_2$Br$_2$],H$_2$hpim,NEt$_3$	EtOH	3 h, reflux	70
(5b)	4	[W(η-C$_5$H$_5$)$_2$Br$_2$],H$_2$hpim,NEt$_3$	EtOH	3 h, reflux	70
(6a)	4	[Mo(η-C$_5$H$_5$)$_2$Br$_2$],H$_2$hpb,NEt$_3$	EtOH	2.5 h, reflux	60
(6b)	2	(6a), Na[OH]	(CH$_3$)$_2$CO	5 min, r.t.	*ca.* 100
(6c)	4	[W(η-C$_5$H$_5$)$_2$Br$_2$],H$_2$hpb,NEt$_3$	EtOH	2.5 h, reflux	60
(6d)	2	(6c), Na[OH]	(CH$_3$)$_2$CO	5 min, r.t.	*ca.* 100
(7)	7	[Ti(η-C$_5$H$_5$)$_2$(phen)][PF$_6$],[NO][PF$_6$]	CH$_3$CN	5 min, r.t.	90
(8)	7	[Ti(η-C$_5$H$_5$)$_2$(bipy)][PF$_6$],[NO][PF$_6$]	CH$_3$CN	1 min, r.t.	90

r.t. = Room temperature.

Method 4.—*Bis*(η-*cyclopentadienyl*)[2-(2′-*hydroxyphenyl*)-*benzimidazolato*]*molybdenum hexafluorophosphate*, (6a). The compound [Mo(η-C$_5$H$_5$)$_2$Br$_2$] (*ca.* 1 mmol) and 2-(2′-hydroxyphenyl)benzimidazole (300 mg, *ca.* 1.5 mmol) were refluxed in ethanol (10 cm^3) in the presence of triethylamine (2 cm^3) during 2.5 h. The reaction mixture was filtered, the volume of the filtrate reduced under vacuum, and addition of water and [NH$_4$][PF$_6$] gave a dark solid. This was dissolved in acetone and chromatographed on an alumina column using acetone as the solvent. A dark yellow band was collected; this was filtered, the filtrate concentrated under vacuum, and diethyl ether added to give brown crystals.

Method 5.—*Methylation reactions to give* (1f), (2f), (2g), *and* (3f). A solution of the deprotonated species (1b), (2b), (2d), or (3b) (0.3 mmol) in acetone (30 cm^3) was refluxed in the presence of CH$_3$I (2 cm^3) for 10 h. The excess of CH$_3$I was evaporated under vacuum, and excess of Tl[PF$_6$] was added to the reaction mixture (the precipitate then dissolved). After 2 h the mixture was filtered, the volume was reduced under vacuum, and addition of diethyl ether precipitated a solid. This was recrystallised from either acetone–diethyl ether or acetone–ethanol. In the latter case pink crystals precipitated on removing the acetone under vacuum.

Method 6.—*Bis*(η-*cyclopentadienyl*)[2-(2′-*pyridyl*)*imidazoline*]*titanium*(III) *hexafluorophosphate*, (1c). 2-(2′-Pyridyl)-imidazoline (0.3 g, *ca.* 2 mmol) was added to a solution of [{Ti(η-C$_5$H$_5$)$_2$Cl}$_2$] (0.4 g, *ca.* 1 mmol) in dry thf (30 cm^3) and the mixture was stirred at room temperature for 30 min. The mixture was then filtered and the solid extracted with water giving a dark blue solution. Upon addition of [NH$_4$][PF$_6$] a grey solid precipitated which was recrystallised from acetone–ethanol as purple crystals.

Method 7.—*Bis*(η-*cyclopentadienyl*)(1,10-*phenanthroline*)-*titanium*(IV) *bis*(*hexafluorophosphate*), (7). Solid [NO][PF$_6$] in excess was added to a solution of [Ti(η-C$_5$H$_5$)$_2$(phen)][PF$_6$] (200 mg, *ca.* 0.4 mmol) in dry acetonitrile (5 cm^3). The solution immediately became olive green and stirring was continued for 5 min. The solution was filtered, the filtrate concentrated under vacuum, and addition of diethyl ether precipitated green crystals.

[9/091 *Received*, 19*th January*, **1979**]

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