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# Di-cyclopentadienyl complexes of molybdenum and tungsten with methyl-, amino- and cyano-pyridines. Synthesis, spectral, and electrochemical studies

**R.G. Costa *, A.R. Dias and J.C. Kotz ****

*Centro de Química Estrutural, Complexo 1, Instituto Superior Técnico, Avenida Rovisco Pais,
1096 Lisboa Codex (Portugal)*

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## Abstract

New complexes of the type $[Cp_2MX(Rpy)][PF_6]$ (M = Mo; R = 2-$CH_3$, X = H; R = 3-$CH_3$ and 4-$CH_3$, X = H, Cl, Br; R = 3-$NH_2$, X = H; R = 4-$NH_2$, X = Cl, Br, OH; R = 3-CN, 4-CN, X = Cl, Br; (b) M = W: R = 3-$CH_3$, 4-$CH_3$, X = Cl, Br; R = 4-$NH_2$, 3-CN, 4-CH, X = Br) have been synthesized and characterized. When 2-aminopyridine was used as a ligand, chelated complexes were obtained, the substituted pyridine being coordinated through both nitrogen atoms. In the case of 2-cyanopyridine, the product is suggested to contain a chelating *N*-metalamide group. Cyclic voltammetry of some of these complexes showed that: (i) for closely related complexes, chloride complexes are oxidized at slightly lower potentials than bromide complexes; (ii) for complexes where only the substituent R in the pyridine ligand Rpy is varied, the potential required for oxidation increases approximately in line with the Hammett $\sigma$ parameter for R; and (iii) tungsten complexes undergo oxidation at lower potentials than molybdenum complexes.

## Introduction

A general synthetic route to complexes of the type $[Cp_2MLX]^+$ (where Cp = $\eta^5$-$C_5H_5$; M = Mo or W; X = H, Cl, Br, or I; and L = pyridine) has been previously described [1]. This method has been used to make a series of analogous complexes in which L is one of a variety of substituted pyridines, and the availability of this new set of complexes has enabled a comparative study to be made of their spectroscopic and electrochemical properties.

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* Present address: Departmento de Tecnologia de Industrias Químicas, (LNETI), Queluz de Baixo, 2745 Queluz (Portugal).

** Department of Chemistry, State University College, Oneonta, NY 13820 (U.S.A).

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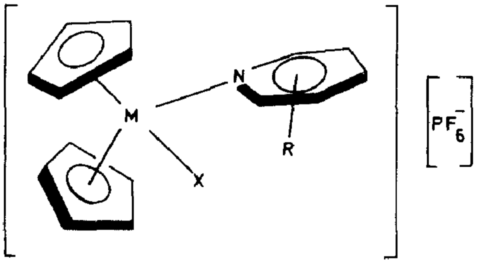
In this paper we report the synthesis and characterization of a series of complexes where the ligands L are methyl-, cyano-, or amino-pyridines; the IR and $^1$H NMR spectra and electrochemical properties of the resulting complexes are discussed.

## Results and discussion

### *Chemical properties*

We find that, dicyclopentadienyl metal dihalides, $Cp_2MX_2$, as well as complexes such as $[Cp_2MBr(SMe_2)]PF_6$ and $[Cp_2MH_3]PF_6$, usually react in acetone (in the presence of $TlPF_6$) with methyl-, cyano-, at amino-pyridines (Rpy) to yield the complexes $[Cp_2MX(Rpy)]PF_6$ (X = H, Cl, Br) (**1**). Not all such reactions proceeded in this way, however, and only about one-third of the compounds corresponding to all the possible combinations were isolated (see Table 1). We were unable to isolate the expected products in the case of (a) iodide derivatives, (b) hydrides in the case of M = W and (c) complexes of type **1** with Rpy with R in the 2-position *.



Finally, molybdenum complexes were generally easier to prepare than their tungsten analogues.

The isolated pyridine complexes **1** are all crystalline solids. The hydrides are yellow, while the chlorides and bromides vary from green to brown. All complexes were characterized by elemental analysis and conductivity measurements (Table 1) and by IR (Table 2), and $^1$H NMR spectroscopy (Table 3). The presence of water or acetone of crystallization in some complexes is indicated by the analytical and spectroscopic evidence.

Reaction of $[Cp_2MoH_3]PF_6$ with 4-aminopyridine in acetone gave a light brown crystalline solid that was formulated as $[Cp_2Mo(OH)(4\text{-}NH_2py)]PF_6$ on the basis of elemental analysis, the absence of $\nu$(Mo–H) in the infrared spectrum, and the appearance of a metal–hydride resonance in the $^1$H NMR spectrum. The infrared spectrum shows a band at 3125 cm$^{-1}$ that can be assigned to the O–H stretch.

In the 2-aminopyridine complex the metal is chelated by the ligand, and we recently described the molecular structure of the complex [2].

2-Cyanopyridine gave a purple crystalline compound **2**. On the basis of elemental analysis, the $^1$H NMR spectrum, and the infrared spectrum (which shows an

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* A possible exception is the reaction of $[Cp_2MoH_3]PF_6$ with 2-methylpyridine, which gave an unstable yellow crystalline product; although the compound was not fully characterized owing to its instability, the infrared spectrum and elemental analysis suggested that it was $[Cp_2MoH(2\text{-}Mepy)]PF_6$.

Table 1

Analytical and conductimetric data

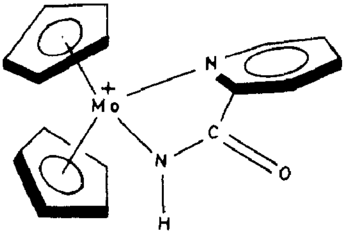
| Compound | Colour | Decomp. temperature $\theta_c$ (°C) | Analysis (Found (calc) (%)) | | | $\Lambda^b$ ($\Omega^{-1}$ cm$^2$ mol$^{-1}$) |
|---|---|---|---|---|---|---|
| | | | C | H | H | |
| $[MoCp_2H(3\text{-}CH_3py)][PF_6]$ **(1a)** | yellow | 180 | 41.3(41.3) | 3.1(3.8) | 3.5(3.0) | 95 |
| $[MoCp_2Cl(3\text{-}CH_3py)][PF_6]$ **(1b)** | green | 220 | 35.6(35.8) | 3.8(3.9) | 2.4(2.6) | 72 |
| $[MoCp_2Br(3\text{-}CH_3py)][(PF_6]\cdot CH_3COCH_3$ **(1c)** | green | 225 | 37.6(37.9) | 3.8(4.1) | 2.3(2.5) | 72 |
| $[WCp_2Cl(3\text{-}CH_3py)][PF_6]\cdot H_2O$ **(1d)** | brown | 240 | 31.7(31.7) | 3.2(3.1) | 2.0(2.3) | 71 |
| $[WCp_2Br(3\text{-}CH_3py)][PF_6]$ **(1e)** | brown | 220 | 30.3(30.4) | 2.8(2.7) | 2.6(2.1) | 65 |
| $[MoCp_2H(4\text{-}CH_3py)][PF_6]$ **(1f)** | yellow | 240 | 41.4(41.3) | 4.1(3.9) | 2.8(3.0) | 92 |
| $[MoCp_2Cl(4\text{-}CH_3py)][PF_6]$ **(1g)** | brown | 200 | 38.1(38.4) | 3.5(3.4) | 2.6(2.8) | 61 |
| $[MoCp_2Br(4\text{-}CH_3py)][PF_6]\cdot CH_3COCH_3$ **(1h)** | green | 240 | 37.7(37.9) | 3.9(3.8) | 2.5(2.3) | 61 |
| $[WCp_2Cl(4\text{-}CH_3py)][PF_6]\cdot H_2O$ **(1i)** | brown | 250 | 31.2(31.7) | 2.9(3.2) | 2.1(2.3) | 81 |
| $[WC_{p2}Br(4\text{-}CH_3py)][PF_6]$ **(1j)** | green | 270 | 30.6(30.4) | 2.6(2.7) | 1.9(2.2) | 70 |
| $[MoCP_2H(3\text{-}NH_2pu)][PF_6]$ **(1k)** | yellow | 200 | 38.5(38.6) | 3.5(3.6) | 5.9(6.0) | 92 |
| $[MoCp_2(OH)(4\text{-}NH_2py)][PF_6]$ **(1l)** | light brown | 230 | 37.2(37.3) | 3.3(3.5) | 5.7(5.8) | 71 |
| $[MoCp_2Cl(4\text{-}NH_2py)][PF_6]\cdot 1/2CH_3COCH_3$ **(1m)** | green | 200 | 37.3(37.4) | 3.7(3.6) | 5.5(5.3) | 81 |
| $[MoCp_2Br(4\text{-}NH_2py)][PF_6]\cdot 1/2CH_3COCH_3$ **(1n)** | green | 140 | 35.1(34.5) | 3.2(3.3) | 5.5(4.9) | 96 |
| $[WCp_2Br(4\text{-}NH_2py)][PF_6]\cdot 2H_2O$ **(1o)** | brown | 210 | 31.5(31.4) | 2.8(2.8) | 4.9(5.1) | 100 |
| $[MoCp_2Cl(1\text{-}CNpy)][PF_6]\cdot H_2O$ **(1p)** | brown | 180 | 35.9(36.3) | 3.1(3.0) | 4.8(5.3) | 68 |
| $[MoCp_2Br(3\text{-}CNpy)][PF_6]\cdot CH_3COCH_3$ **(1q)** | green | 190 | 37.4(37.2) | 3.1(3.3) | 4.6(4.6) | 64 |
| $[WCp_2Br(3\text{-}CNpy)][PF_6]\cdot 3H_2O$ *a* **(1r)** | brown | 150 | 27.4(27.6) | 2.7(2.9) | 2.2(4.0) | 80 |
| $[MoCp_2Cl(4\text{-}CNpy)][PF_6]$ [a] **(1s)** | brown | 180 | 37.2(37.6) | 3.3(2.8) | 4.2(5.5) | 71 |
| $[MoCp_2Br(4\text{-}CNpy)][PF_6]\cdot 1/2CH_3COCH_3$ [a] **(1t)** | green | 220 | 35.2(36.0) | 2.9(2.9) | 3.3(4.8) | 110 |
| $[WCp_2Cl(4\text{-}CNpy)][PF_6]$ [a] **(1u)** | brown | 200 | 31.1(32.1) | 2.5(2.3) | 4.4(4.2) | 71 |
| $[WCp_2Br(4\text{-}CNpy][PF_6]$ [a] **(1v)** | brown | 240 | 30.1(29.9) | 2.0(2.2) | 5.2(4.4) | 100 |

[a] The poor results for the elemental analysis may be due to the fact the compound is highly hygroscopic. [b] $1\times10^{-3}$ *M* solution in nitromethane.

Table 2
Infrared data ($\nu$ in cm$^{-1}$)

| Compound | Infrared bands (vibrational modes) |
|---|---|
| 3-methylpyridine [4,9,10] | 1600(8a),1043(1),1031(12),788(10b),713(4),631(6b),457(11) |
| $[MoCp_2H(3\text{-}CH_3py)][PF_6]$ | 1610(8a),1068(1),1018(12),805(10b),702(4),658(6b)4,490(11) |
| $[MoCp_2Cl(3\text{-}CH_3py)][PF_6]$ | 1610(8a),1070(1),1020(12),803(10b),702(4),680(6b),490(11) |
| $[MoCp_2Br(3\text{-}CH_3py)][PF_6]$ | 1610(8a),1068(1),1018(12),805(10b),708(4),655(6b),492(11) |
| $[WCp_2Cl(3\text{-}CH_3py)][PF_6]$ | 1610(8a),1060(1),1050(12),805(10b),705(4),680(6b),495(11) |
| $[WCp_2Br(3\text{-}CH_3py)][PF_6]$ | 1610(8a),1070(1),1050(12),805(10b),705(4),680(6b),495(11) |
| 4-methylpyridine [4,9,10] | 1604(8a),1225(9a),997(1),1042(12),800(10b),730(4),485(11) |
| $[MoCp_2H(4\text{-}CH_3py)][PF_6]$ | 161098a),1250,1228(9a),725(4),508(11) |
| $[MoCp_2Cl(4\text{-}CH_3py)][PF_6]$ | 1610(8a),1245,1232(9a),702(4),490(11) |
| $[MoCp_2Br(4\text{-}CH_3py)][PF_6]$ | 1622(8a),1235(9a),718(4),505(11) |
| $[WCp_2Cl(4\text{-}CH_3py)][PF_6]$ | 1630(8a),1235,1225(9a),720(4),500(11) |
| $[WCp_3Br(4\text{-}CH_3py)][PF_6]$ | 1622(8a),1235(9a),720(4),495(11) |
| 3-aminopyridine [9–11] | 3380($\nu(NH_2)_{asym}$),3310($\nu(NH_2)_{sym}$),1622$(NH_2)_{sc}$,1590(8a),<br>1575(8b),1292($\nu(C\text{–}N_{sub})$,706(11) |
| $[MoCp_2H(3\text{-}NH_2py)][PF_6]$ | 3475($\nu(NH_2)_{asym}$),3390($\nu(NH_2)_{sym}$,1630$(NH_2)_{sc}$,1600(8a),<br>1585(8b),1310($\nu(C\text{–}N_{sub})$),740(11) |
| 4-aminopyridine [10–12] | 3540$(NH_2)_{asym}$),3440$(NH_2)_{sym}$),1600(8a),842(11) |

absence of a C≡N stretch and the presence of an absorption at 3220 cm$^{-1}$ attributable to an N–H stretch), we tentatively assign to it the following structure.



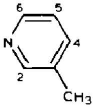
This compound would be the result of the hydrolysis of the cyano group, a reaction previous observed [3]. However, without an X-ray determination of the molecular structure, other possibilities cannot be ruled out. Such possibilities include a structure involving an $\alpha$-hydroxymetalimine group (MN=C(OH)py) instead of its tautomer, the *N*-metalimide group (MN(H)C(=O)py), or even a structure containing the metalopyridinecarboximidate group (MOC(=NH)py).

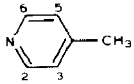
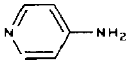
## Spectroscopic studies

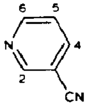
### *Infrared spectra*

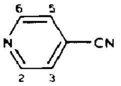
Infrared data for the cationic metal complexes are summarized in Table 2. (Assignment of vibrational modes is based on Pfeffer, et al. [4], Radecka-Paryzek [5], Marchese and West [6], Walton [7], Green and Harrison [8], Spinner [9] and Cunliffe-Jones [10].) When coordination to the metal ion takes place through the pyridine nitrogen atom, some $\nu$(CN), $\nu$(CC), and $\gamma$(CH) and ring frequencies shift to higher frequencies, while $\phi$(CC) (mode 4) [10] shifts to lower frequencies. (The decrease in frequency for this last band was noticed for other complexes containing pyridine and monosubstituted pyridines.) The frequencies $\nu_1$, $\nu_{12}$, and $\nu_{6b}$ represent

Table 3
$^1$H NMR data [a]

| Compound | H(2),H(6) | H(4) | H(5) | $-CH_3$ | Cp | M-H |
|---|---|---|---|---|---|---|
|  | 8.45(d, 2) | 7.52(m, 1) | 7.20(d, 1) | 2.21(m, 3) | | |
| $[MoCp_2H(3\text{-}CH_3py)][PF_6]$ | 8.73(t, 2) | 7.73(d, 1) | 7.27(m, 1) | 2.36(s, 3) | 5.54(s, 10) | −9.05(s, 1) |
| $[MoCp_2Cl(3\text{-}CH_3py)][PF_6]$ | 8.89(t, 2) | 7.97(d, 1) | 7.45(t, 1) | 2.38(s, 3) | 6.02(s, 10) | |
| $[MoCp_2Br(3\text{-}CH_3py)][PF_6]$ | 8.75(m, 2) | 7.77(d, 1) | 7.25(m, 1) | 2.26(s, 3) | 5.95(s, 10) | |
| $[WCp_2Cl(3\text{-}CH_3py)][PF_6]$ | 9.05(t, 2) | 7.88(d, 1) | 7.31(m, 1) | 2.24(s, 3) | 5.88(s, 10) | |
| $[WCp_2Br(3\text{-}CH_3py)][PF_6]$ | 9.24(d, 2) | 8.84(m, 1) | 7.95(m, 1) | 2.31(s, 3) | 5.90(S, 10) | |

| | H(2),H(6) | H(3),H(5) | $-CH_3$ | Cp | M-H |
|---|---|---|---|---|---|
|  | 8.06(d, 2) | 6.78(d, 2) | 1.72(s, 3) | | |
| $[MoCp_2H(4\text{-}CH_3py)][PF_6]$ | 8.60(d, 2) | 7.17(d, 2) | 2.29(s, 3) | 5.43(s, 10) | −9.05(s, 1) |
| $[MoCp_2Cl(4\text{-}CH_3py)][PF_6]$ | 8.75(d, 2) | 7.30(d, 2) | 2.40(s, 3) | 5.92(s, 10) | |
| $[MoCp_2Br(4\text{-}CH_3py)][PF_6]$ | 9.01(d, 2) | 7.24(d, 2) | 2.44(s, 3) | 5.98(s, 10) | |
| $[WCp_2Cl(4\text{-}CH_3py)][PF_6]$ | 9.12(d, 2) | 7.35(d, 2) | 2.45(s, 3) | 5.92(s, 10) | |
| $[WCp_2Br(4\text{-}CH_3py)][PF_6]$ | 9.20(d, 2) | 7.28(d, 2) | 2.49(s, 3) | 5.85(s, 10) | |
|  | 8.00(d, 2) | 6.50(d, 2) | | | |
| $[MoCp_2(OH)(4\text{-}NH_2py)][PF_6]$ | 8.25(d, 2) | 6.58(d, 2) | | 5.88(s, 10) | |
| $[MoCp_2Cl(4\text{-}NH_2py)][PF_6]$ | 8.33(d, 2) | 6.68(d, 2) | | 5.98(s, 10) | |
| $[MoCp_2Br(4\text{-}NH_2py)][PF_6]$ | 8.25(d, 2) | 6.60(d, 2) | | 5.91(s, 10) | |
| $[WCp_2Br(4\text{-}NH_2py)][PF_6]$ | 8.19(m, 2) | 6.66(m, 2) | | 5.83(s, 5) | |

| | H(2) | H(4) | H(5) | H(6) | Cp |
|---|---|---|---|---|---|
|  | 8.9(m, 2) | 8.13(m, 1) | 7.58(m, 1) | 8.9 | |
| $[MoCp_2Cl(3\text{-}CNpy)][PF_6]$ | 9.5(s, 1) | 8.65(d, 1) | 7.85(t, 1) | 9.35(s, 1) | 6.09(s, 5)<br>6.02(s, 5) |
| $[MoCp_2Br(3\text{-}CNpy)][PF_6]$ | 8.94(m, 1) | 8.22(m, 1) | 7.53(m, 1) | 8.75(m, 1) | 6.09(s, 10) |

| | H(2),H(6) | H(3),H(5) | Cp |
|---|---|---|---|
|  | 8.83(dd, 2) | 7.75(dd, 2) | |
| $[MoCp_2Cl(4\text{-}CNpy)][PF_6]$ | 9.38(d, 2) | 8.04(d, 2) | 6.13(s, 10) |
| $[MoCp_2Br(4\text{-}CNpy)][PF_6]$ | 9.94(d, 2) | 7.94(d, 2) | 6.09(s, 5)<br>5.65(s, 5) |
| $[WCp_2Br(4\text{-}CNpy)][PF_6]$ | 9.16(m, 2) | 8.21(m, 2) | 6.11(d, 10) |
| $[WCpBr(4\text{-}CNpy)][PF_6]$ | 9.76(m, 2) | 7.97(m, 2) | 6.10(s, 10) |

[a] $\delta$ in ppm (multiplet, relative intensity), $Me_2CO\text{-}d_6$; internal reference TMS.

in-plane ring deformations, while-$\nu_{10b}$, $\nu_4$, $\nu_{11}$, and $\nu_{16b}$ are assigned to out-of-plane deformations. The $\nu_{9a}$ ($\beta$-C–H) frequency for some 4-methylpyridine complexes seems to be split into two bands in agreement with observations by Pfeffer et al. [4]. The infrared spectra of the 4-methylpyridine complexes are generally simpler than that of the free ligand [9]. The $\nu$(OH) band corresponding to water of crystallization (complexes **1d**, **1i**, **1o**, **1p**, **1r**) and the $\nu$(C=O) band corresponding to acetone of crystallization (complexes **1c**, **1h**, **1m**, **1n**, **1q**, **1t**) appear as broad bands at 3420 and 1635 $cm^{-1}$, respectively.

Two N–H bands due to asymmetric and symmetric stretching frequencies appear in the spectra of complexes of the type $[Cp_2MX(n\text{-}NH_2py)]^+$ ($n = 3, 4$). When 4-aminopyridines undergo coordination there is a shift in the N–H frequencies to lower wave numbers. The relative positions of these bands are in fair agreement with Bellamy's relation, that is, $\nu_{sym} = 3455 + 0.876(\nu_{asym})$ [11,12]. Steric hindrance may account for the higher N–H frequencies for 3-aminopyridine in $[Cp_2MoH(3\text{-}NH_2py)]PF_6$.

### *$^1H$ NMR spectra*

The $^1H$ NMR spectra of all the pyridine ligands are altered significantly upon coordination (Table 3). In most complexes the signals of the pyridine ring are shifted to lower field on formation of the nitrogen–metal $\sigma$-bond. In some cases an influence of the halide ligands is also observed. Furthermore, in $[Cp_2MoH(3\text{-}NH_2py)]PF_6$, the protons of the pyridine ring are no longer deshielded by the N-metal $\sigma$-bond, and, they appear at a higher field, an effect that may be attributable to steric hindrance. More conclusive evidence for this suggestion is the nonequivalence of the cyclopentadienyl ring protons [$\delta$ 5.48 (5, s) and $\delta$ 4.23 (5, s)].

## Electrochemical studies

Relevant electrochemical data for the complexes in $CH_3CN$ (containing 0.1 *M* tetrabutylammonium hexafluorophosphate) are listed in Table 4. Data for $Cp_2MX_2$ and $[Cp_2MXpy]^+$ are included for comparison.

In each case the separation of anodic and cathodic peak potentials was larger than the theoretical value of 57 mV [13,14]. However, for scan rates between 20 and 500 mV/s, the ratio of peak currents, $i_{p,a}/i_{p,c}$, and the ratio $i_{p,a}/\nu^{1/2}$ (where $\nu$ is the scan rate) was constant, indicating a quasi-reversible process. To confirm the chemical reversibility of the process, exhaustive controlled potential electrolysis was performed on several of the complexes in Table 4. For example, oxidation of $[Cp_2WBr(4\text{-}CH_3py)][PF_6]$ at +0.85 V consumed 0.98 *F* $mol^{-1}$; the cyclic voltammogram of the resulting solution was identical with that of the unoxidized solution.

Both we [15] and Cooper and co-workers [16] have previously observed that for group 6 complexes of the type $Cp_2MoX_2$, the molybdenum complexes generally undergo oxidation at somewhat more positive potentials than analogous tungsten complexes, and the ease of oxidation as the halide ligand is varied increases in the order $Cl > Br \sim I$ *. We have also observed that cationic complexes of the type $[Cp_2MLX]^+$ generally undergo oxidation at more positive potentials than the parent

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* The reasons for the apparently anomalous oxidation order (Cl > Br > I) was suggested by Copper and coworkers (ref. 16).

Table 4
Voltammetric data [a]

| Compound | $E^{ox}_{1/2}$ (V) | $(E_{p,a} - E_{p,c})$ (mV) | $i_{p,a}/i_{p,c}$ | $\sigma$[c] |
|---|---|---|---|---|
| $[MoCp_2Cl_2]$ | +0.51 | 90 [b] | 1 | |
| $[MoCp_2Cl(4\text{-}NH_2py)][PF_6]$ | +0.90 | 90 | −1 | −0.66 |
| $[MoCp_2Cl(3\text{-}CH_3py)][PF_6]$ | +0.98 | 110 | 1 | −0.07 |
| $[MoCp_2Br_2]$ | +0.54 | 100 [b] | 1 | |
| $[MoCp_2Brpy][PF_6]$ | +0.98 | 100 [b] | 1 | |
| $[MoCp_2Br(3\text{-}CH_3py)][PF_6]$ | +0.99 | 108 | −1 | −0.07 |
| $[MoCp_2Br(3\text{-}CH_3py)][PF_6]$ | +0.99 | 108 | −1 | −0.07 |
| $[MoCp_2Cl(3\text{-}CNpy)][PF_6]$ | +1.09 | 70 | 1 | +0.68 |
| $[MoCp_2Cl(4\text{-}CNpy)][PF_6]$ | −1.12 | 120 | 1 | +0.63 |
| $[WCp_2Cl(3\text{-}CH_3py)][PF_6]$ | +0.77 | 110 | 1 | −0.07 |
| $[WCp_2Br(3\text{-}CH_3py)][PF_6]$ | +0.78 | 90 | 1 | −0.07 |
| $[WCp_2Cl(4\text{-}CH_3py)][PF_6]$ | +0.74 | 125 | 1 | −0.17 |
| $[WCp_2Br(4\text{-}CH_3py)][PF_6]$ | +0.75 | 90 | 1 | −0.17 |

[a] All electrochemical data were obtained for 0.1 *M* $Bu_4NPF_6$ solutions in acetonitrile at 22 + 2° C. Voltage relative to NaCl saturated calomel (SSCE); measured at a scan rate of 200 mV $s^{-1}$. Solute concentration was generally 1 m*M*. [b] Ref. 17. [c] Hammett's parameters for the substituents in the pyridine ligand.

$Cp_2MX_2$ complex [15,17]. These observations apply also to the complexes in Table 4. For example, $Cp_2MCl_2$ (M = Mo, W) is oxidized at a slightly lower potential than $Cp_2MBr_2$, and the same effect is observed on changing the halogen in the pyridine complexes. However, the differing effects of the halide ligands are greatly attenuated on introducing a halide ligand X in place of one of the pyridine ligands; thus the differences between the potentials for related sets of complexes (e.g., $[Cp_2WCl(4\text{-}CH_3py)]^+$ and $[Cp_2WBr(4\text{-}CH_3py)]^+$) are virtually the same within experimental error. The origin of this attenuation is not clear. One possibility is that there is a less $d_\pi$–$p_\pi$ metal-halogen interaction in cationic complexes of type **1**, an interaction that Cooper and co-workers have argued can give rise to the observed trend in potentials for the oxidation of $Cp_2MX_2$ [16].

At least one other trend in redox potentials in Table 4 is noteworthy. The potentials for the molybdenum complexes $[Cp_2MoCl(Rpy)]^+$ increas in the order R = 4-$NH_2$ < 3-$CH_3$ < 3-CN–4-CN, that is almost in line with the same sequence of values of the Hammett $\sigma$-constants for R. Thus, under these conditions, the potential required for oxidation of the complexes is determined primarily by the fact that they are cationic and secondarily by the relative inductive effects of the pyridine ligands, in keeping with the usual pattern in the electrochemistry of inorganic and organometallic compounds [17].

## Experimental

All preparations and further manipulations were carried out under dry dinitrogen by standard Schlenk techniques. All monosubstituted pyridines and solvents were reagent grade and were purified and dried by appropriate methods.

The compounds $[Cp_2MH_3][PF_6]$, $Cp_2MX_2$, and $[Cp_2MX(SMe_2)][PF_6]$ (M = Mo, W; X = H, Cl, Br, I) were prepared by methods as described elsewhere [18–20].

Electrochemical experiments were carried out with tetra-n-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. Acetonitrile was dried over $CaH_2$ and then distilled from $CaH_2$ under dinitrogen onto dry molecular sieves. For the electrochemical experiments the $CH_3CN$ was 0.1 *M* in TBAH and approximately 1 m*M* in complex.

$^1H$ NMR spectra were recorded on a JOEL JNM 100 PFT instrument. Infrared spectra were recorded on a Perkin-Elmer 457 or 683 spectrometer in KBr pellets and were calibrated with polystyrene film. Conductivity measurements were carried out at 25 °C with a Radiometer CDM 3 conductivity meter calibrated with a standard KCl solution. Elemental analyses (C, H, N) were carried out in these laboratories.

Electrochemical experiments were carried out under dry dinitrogen with a Princeton Applied Research (PAR) Model 173 potentiostat, a PAR 175 programmer, a PAR 179 coulometer, and a Houston Instrument Model 2000 recorder. A sodium chloride saturated calomel (SSCE) electrode was used as reference. Cyclic voltammograms were recorded at $22 \pm 2\,°C$ in a PAR polarographic cell; the working electrode consisted of a platinum wire, and a platinum coil was used as the auxiliary electrode. In controlled potential electrolysis experiments a platinum gauze was used as the working electrode, and the working electrode compartment was separated from the auxiliary and reference electrode compartments by medium porosity glass frits. In all electrochemistry experiments, the solutions were degassed

Table 5
Experimental conditions for the preparations of the complexes

| Compound [a] | Method | Reactants | Solvent | Conditions, [b] reaction time (h) | Yield (%) |
|---|---|---|---|---|---|
| **(1a)** | 3 | $[MoCp_2H_3][PF_6]$,3-$CH_3$py | $(CH_3)_2CO$ | 20 | 30 |
| **(1b)** | 2 | $[MoCp_2Cl_2]$,3-$CH_3$py,$TlPF_6$ | | 30 min | 30 |
| **(1c)** | 1 | $[MoCp_2Br(SMe)_2][PF_6]$ 3-$CH_3$py | $(CH_3)_2CO$ | 20 | 50 |
| **(1d)** | 2 | $WCp_2Cl_2$,3-$CH_3$py,$TlPf_6$ | | 2 | 40 |
| **(1e)** | 2 | $[WCp_2Br_2]$,3-$CH_3$py,$TlPf_6$ | | 1 | 40 |
| **(1f)** | 3 | $[MoCp_2H_3][PF_6]$,4-$CH_3$py | $(CH_3)_2CO$ | 21 | 50 |
| **(1g)** | 2 | $[MoCp_2Cl_2]$,4-$CH_3$py,$TlPF_6$ | $(CH_3)_2CO$ | 1 | 40 |
| **(1h)** | 2 | $[MoCp_2Br_2]$,4-$CH_3$py,$TlPF_6$ | $(CH_3)_2CO$ | 1 | 30 |
| **(1i)** | 2 | $[WCp_2Cl_2]$,4-$CH_3$py,$TlPF_6$ | $(CH_3)_2CO$ | 1 | 40 |
| **(1j)** | 2 | $[WCp_2Br_2]$,4-$CH_3$py,$TlPF_6$ | | 1 | 40 |
| **(1k)** | 3 | $[MoCp_3H_3PF_6]$,3-$NH_2$py | $(CH_3)_2CO$ | 21 | 60 |
| **(1l)** | 3 | $[MoCp_2H_3][PF_6]$,4-$NH_2$py | $(CH_3)_2CO$ | 17 | 30 |
| **(1m)** | 2 | $[MoCp_2Cl_2]$,4-$NH_2$py,$TlPF_6$ | $(CH_3)_2CO$ | 5 | 20 |
| **(1n)** | 2 | $[MoCp_2Br_2]$,4-$NH_2$py,$TlPF_6$ | $(CH_3)_2CO$ | 22 | 50 |
| **(1o)** | 2 | $[WCp_2Br_2]$,4-$NH_2$py,$TlPF_6$ | $(CH_3)_2CO$ | 10 | 50 |
| **(1p)** | 2 | $[MoCp_2Cl_2]$,3-CNpy,$TlPF_6$ | $(CH_3)_2CO$ | 4 | 30 |
| **(1q)** | 2 | $[MoCp_2Br_2]$,3-CNpy,$TlPF_6$ | $(CH_3)_2CO$ | 4 | 40 |
| **(1r)** | 2 | $[WCp_2Br_2]$,3-CNpy,$TlPF_6$ | $(CH_3)_2CO$ | 6 | 60 |
| **(1s)** | 2 | $[MoCp_2Cl_2]$,4-CNpy,$TlPF_6$ | $(CH_3)_2CO$ | 10 | 60 |
| **(1t)** | 2 | $[MoCp_2Br_2]$,4-CNpy,$TlPF_6$ | $(CH_3)_2CO$ | 10 | 70 |
| **(1u)** | 2 | $[WCp_2Cl_2]$,4-CNpy,$TlPF_6$ | $(CH_3)_2CO$ | 4 | 60 |
| **(1v)** | 2 | $[WCp_2Br_2]$,4-CNpy,$TlPF_6$ | $(CH_3)_2CO$ | 4 | 70 |

[a] For compounds see Table 1. [b] Reflux.

for about 10 min with $CH_3CN$-saturated dry dinitrogen, and this atmosphere was maintained over the solution during the experiment.

The compounds listed in Table 5 were prepared by one of the following methods:
*Method 1: Preparation of [$Cp_2MoBr(3$-$CH_3py)$][$PF_6$].* The complex was obtained by dissolving [$Cp_2MoBr(SMe_2)$][$PF_6$] (0.52 g, ca. 1 mmol) and an excess of 3-methylpyridine (1.5 ml) in acetone. This solution was refluxed for 20 h and then filtered. The green filtrate was concentrated and chromatographed on an acid alumina column with acetone as eluent. The solution from the green band was filtered and evaporated the residue dissolved in an acetone/water mixture. Removal of the acetone gave green crystals.

*Method 2: Preparation of [$Cp_2WCl(3$-$CH_3py)$][$PF_6$].* A solution of $Cp_2WCl_2$ (0.4 g, 1 mmol) in an excess of 3-methylpyridine (7 ml) containing $TlPF_6$ (0.4 g, 1 mmol) was refluxed for 2 h. The resulting brown solution was filtered and the solvent was removed in vacuum. The product was extracted with acetone, and brown crystals were obtained by evaporating off the acetone as ethanol was added.

*Method 3: Preparation of [$Cp_2MoH(3$-$CH_3py)$][$PF_6$].* This compound was prepared by the reaction of [$Cp_2MoH_3$][$PF_6$] (0.46 g, 1.2 mmol) with an excess of 3-methylpyridine (4 ml) in acetone. The mixture was refluxed for 20 h, after which the yellow solution was concentrated and chromatographed on an acid alumina column with acetone as eluent. The solution from the yellow band was filtered and evaporated. The residue was taken up in an acetone/water mixture and the acetone then removed to give yellow crystals.

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