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MOLECULAR STRUCTURE OF TWO DICYCLOPENTADIENYLMOLYBDENUM DERIVATIVES CONTAINING A FOUR-MEMBERED RING $[Mo(\eta^5\text{-}C_5H_5)_2(2\text{-}NHNC_5H_4)][PF_6]$ AND $[Mo(\eta^5\text{-}C_5H_5)_2(2\text{-}ONC_5H_4)][PF_6]$

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Summary

The structure of the new compound $[Mo(\eta^5\text{-}C_5H_5)_2(2\text{-}NHNC_5H_4)][PF_6]$ (**1**) has been determined. The crystals are orthorhombic, space group $Pca2_1$ with a 20.807(1), b 8.0030(8), c 10.056(3) Å, V 1674.5 Å^3, $Z = 4$. The structure of $[Mo(\eta^5\text{-}C_5H_5)_2(2\text{-}ONC_5H_4)][PF_6]$ (**2**) has also been determined. The crystals are orthorhombic, space group $Pnma$ with a 12.727(3), b 10.174(2), c 12.918(1) Å, V 1672.8 Å^3, $Z = 4$. The structures were solved by Patterson and difference electron density syntheses and refined by least-squares to R of 0.028 for 1287 reflections for **1** and 0.059 for 1178 reflections for **2**.

Although not isostructural the two cationic complexes have equivalent geometries with the normal bent bismetallocene structure. For **1** the Mo–N bond lengths are 2.160(8) and 2.142(9) Å, with a N–Mo–N bond angle of 59.8(3)°, whereas for **2** Mo–O is 2.142(10), Mo–N is 2.138(11) Å, the N–Mo–O angle is 61.2(4)°. These parameters are discussed and compared with the corresponding data for similar biscyclopentadienyl complexes of molybdenum(IV). Extended Hückel molecular orbital calculations have been carried out to throw light on the nature of the bonding between the metal and the bidentate ligand.

Introduction

Orthosubstituted pyridine derivatives are known to act as bidentate ligands and many complexes have been isolated and structurally characterized. However, in the majority of these compounds the ligand bridges two metal atoms, leading to the

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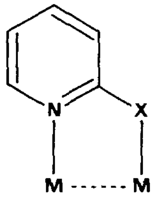
generally unstrained structural unit (**1**) [1]. Only a few complexes are known [2–4] in which this kind of ligand chelates to one metal atom to form a strained, four-membered ring system (**2**) [5,6].



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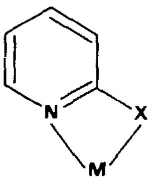

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As part of our continuing study of di-π-cyclopentadienylmolybdenum complexes we have investigated the reactions of 2-aminopyridine with several Cp_2Mo^{IV} derivatives ($Cp = \eta^5$-C_5H_5) and prepared the new complex $[MoCp_2(2\text{-}NHpy)][PF_6]$ (**1**). Single crystal X-ray structure determinations have confirmed the presence of a four-membered metallocyclic ring in this complex and in the related $[MoCp_2(2\text{-}Opy)][PF_6]$ (**2**) [4]. To provide understanding of details of the bonding in these strained chelate systems we have carried out some EHMO calculations.

Results and discussion

Synthesis and spectroscopy

The reaction of either $[MoCp_2X_2]$ ($X = Cl$, Br, I) in the presence of $Tl[PF_6]$ or $[MoCp_2H_3][PF_6]$ with an excess of 2-aminopyridine in acetone afforded an yellow solution from which orange crystals were isolated after work-up. Their IR spectrum exhibits one band at 3410 cm^{-1}, assigned to N–H stretching, suggesting the loss of a proton from the ligand in the coordination process [7]. Bands characteristic of the cyclopentadienyl ligand (3140 cm^{-1}) and the PF_6 anion were also observed. The bands at 1600 cm^{-1} (pyridine ring) and 1280 cm^{-1} ($\nu(C\text{–}N_{sub})$) in the free 2-aminopyridine were shifted to 1612 and 1298 cm^{-1}, respectively.

The ^1H NMR spectrum shows peaks corresponding to two non-equivalent cyclopentadienyl ring protons and to protons of the ligand (shifted to higher field relative to the free ligand), and a broad peak assigned to the N–H proton.

Crystallography

The two complexes are surprisingly, not isostructural, although they have equivalent geometries. Diagrams of the aminopyridine and the hydroxypyridine complexes are shown in Figs. 1 and 2, respectively. Final atomic positional parameters are listed in Tables 1 and 2. Bond lengths and angles for the complexes are given in Tables 3 and 4. The cations have the normal bent bismetallocene structures, with Cp–Mo–Cp angles of 134.8(4) (**1**) and 134.1(3)° (**2**). The highly distorted tetrahedral coordination is completed by bonds to the 2 N or 1 N, 1 O atoms of the chelating pyridyl ligands. The N–Mo–N or N–Mo–O angles at 59.8(3) and 61.2(4)° are particularly small, and prompted us to re-examine the previously debated question as to whether there is any correlation between the Cp–M–Cp and L–M–L angles [8,9].

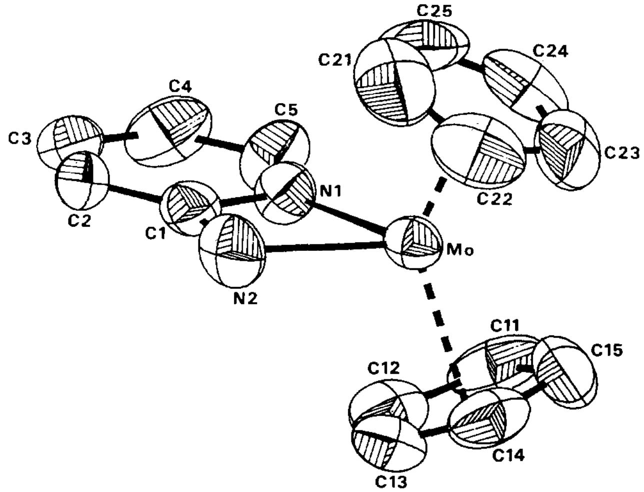


Fig. 1. Molecular structure of [$MoCp_2(2\text{-}NHNC_5H_4)$][$PF_6$] with 30% thermal ellipsoids.

Since the original debate a number of additional relevant structures have been determined, and the molecular orbital picture of bonding in Cp_2M derivatives has been extensively discussed by Lauher and Hoffmann [10]. The EHMO treatment used by those authors indicated that for the d^2 $Cp_2Mo^{IV}L_2$ system a L–Mo–L angle of 78° is preferred, compared with angles of 85 and 110° for d^1 and d^0 systems. Clearly, the d^2 Mo^{IV} centre is most suited for bonding with a restricted chelating ligand, but even so the L–Mo–L angles found in our complexes still indicate considerable strain. On the other hand the Cp–Mo–Cp angles are very typical of Cp_2MoL_2 complexes, and do not appear to show any correlation with the

(*Continued on p. 59*)

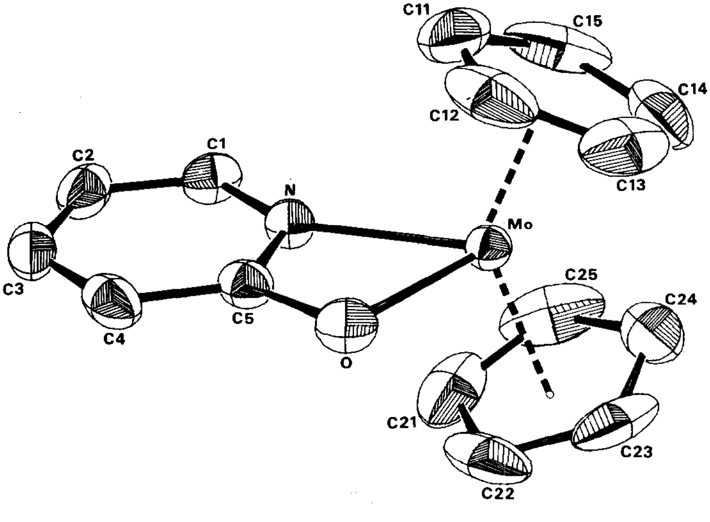


Fig. 2. Molecular structure of [$MoCp_2(2\text{-}ONC_5H_4)$][$PF_6$] with 30% thermal ellipsoids.

TABLE 1

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) FOR $[MoCp_2(2\text{-}NHNC_5H_4)][PF_6]$

Atom	*x*	*y*	*z*
Mo	1449(.5)	−1881(1)	10000
N(1)	674(3)	−91(7)	10121(8)
N(2)	1400(4)	−174(10)	11637(7)
C(1)	886(4)	694(10)	11248(8)
C(2)	566(5)	2064(10)	11734(8)
C(3)	24(5)	2573(10)	11108(10)
C(4)	−193(4)	1726(10)	9973(16)
C(5)	140(4)	406(10)	9491(9)
C(11)	735(5)	−4003(10)	9778(12)
C(12)	678(4)	−3405(12)	11097(11)
C(13)	1219(5)	−3744(12)	11771(9)
C(14)	1657(5)	−4476(12)	10998(11)
C(15)	1357(5)	−4752(13)	9704(9)
C(21)	2245(7)	−21(16)	9378(13)
C(22)	2514(5)	−1565(15)	9429(11)
C(23)	2143(5)	−2435(13)	8351(12)
C(24)	1702(5)	−1360(16)	7849(9)
C(25)	1758(7)	77(15)	8458(14)
P	1424(1)	−6389(3)	15480(2)
F(1)	1334(3)	−8243(7)	15138(16)
F(2)	2004(3)	−6842(10)	16442(7)
F(3)	837(2)	−5870(8)	14565(5)
F(4)	956(3)	−6510(12)	16693(6)
F(5)	1911(3)	−6209(10)	14292(7)
F(6)	1532(4)	−4513(8)	15846(9)

TABLE 2

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) FOR $[MoCp_2(2\text{-}ONC_5H_4)][PF_6]$

Atom	*x*	*y*	*z*
Mo	2302(1)	2500	1110(1)
N	2837(8)	2500	2679(7)
O	1162(6)	2500	2330(7)
C(1)	1878(11)	2500	3068(10)
C(2)	1691(14)	2500	4131(11)
C(3)	2567(14)	2500	4764(10)
C(4)	3573(13)	2500	4328(11)
C(5)	3683(11)	2500	3289(11)
C(11)	1738(10)	4664(8)	1153(9)
C(12)	2838(10)	4664(8)	1338(9)
C(13)	3342(10)	4147(8)	445(9)
C(14)	2553(10)	3827(8)	−290(9)
C(15)	1562(10)	4146(8)	147(9)
P	56(3)	2500	7354(2)
F(1)	148(10)	2500	6188(8)
F(2)	59(8)	1040(9)	7366(12)
F(3)	−1172(7)	2500	7330(8)
F(4)	−48(10)	2500	8530(7)
F(5)	1288(6)	2500	7382(8)

TABLE 3

BOND LENGTHS (Å) AND ANGLES (deg.) FOR [MoCp$_2$(2-NHNC$_5$H$_4$)][PF$_6$]

N(1)–Mo	2.160(8)	N(2)–Mo	2.142(9)
C(11)–Mo	2.267(10)	C(12)–Mo	2.298(10)
C(13)–Mo	2.371(10)	C(14)–Mo	2.346(11)
C(15)–Mo	2.325(12)	C(22)–Mo	2.304(12)
C(21)–Mo	2.314(11)	C(24)–Mo	2.265(11)
C(23)–Mo	2.242(11)		
C(25)–Mo	2.296(12)		
C(1)–N(1)	1.368(11)	C(5)–N(1)	1.341(11)
C(1)–N(2)	1.333(12)	C(2)–C(1)	1.373(12)
C(3)–C(2)	1.354(14)	C(4)–C(3)	1.402(17)
C(5)–C(4)	1.353(14)	C(12)–C(11)	1.415(16)
C(15)–C(11)	1.429(14)	C(13)–C(12)	1.342(14)
C(14)–C(13)	1.333(15)	C(15)–C(14)	1.460(15)
C(22)–C(21)	1.357(17)	C(25)–C(21)	1.375(19)
C(23)–C(22)	1.503(16)	C(24)–C(23)	1.356(15)
C(25)–C(24)	1.308(17)	F(1)–P	1.535(9)
F(2)–P	1.589(8)	F(3)–P	1.584(7)
F(4)–P	1.563(8)	F(5)–P	1.572(8)
F(6)–P	1.562(9)		
N(1)–Mo–N(2)	59.8(3)	C(4)–C(3)–C(2)	120.1(8)
Mo–N(1)–C(1)	96.4(5)	C(3)–C(2)–C(1)	118.6(8)
Mo–N(1)–C(5)	142.1(6)	C(2)–C(1)–N(1)	120.3(8)
C(1)–N(1)–C(5)	121.5(7)	C(2)–C(1)–N(2)	134.5(8)
N(1)–C(5)–C(4)	119.1(9)	N(2)–C(1)–N(1)	105.2(7)
C(5)–C(4)–C(3)	120.3(8)	C(1)–N(2)–Mo	98.4(5)
C(11)–C(12)–C(13)	109.5(8)	C(21)–C(22)–C(23)	100.5(10)
C(12)–C(13)–C(14)	111.6(9)	C(22)–C(23)–C(24)	108.8(9)
C(13)–C(14)–C(15)	107.1(9)	C(23)–C(24)–C(25)	108.8(11)
C(14)–C(15)–C(11)	106.5(9)	C(24)–C(25)–C(21)	109.4(12)
C(15)–C(11)–C(12)	105.5(8)	C(25)–C(21)–C(22)	112.4(11)

TABLE 4

BOND LENGTHS (Å) AND ANGLES (deg.) FOR [MoCp$_2$(2-ONC$_5$H$_4$)][PF$_6$]

N–Mo	2.138(11)	O–Mo	2.142(10)
C(11)–Mo	2.316(9)	C(12)–Mo	2.324(12)
C(13)–Mo	2.301(11)	C(14)–Mo	2.279(11)
C(15)–Mo	2.289(12)	C(1)–N	1.320(16)
C(5)–N	1.335(16)	C(1)–O	1.318(16)
C(2)–C(1)	1.394(19)	C(3)–C(2)	1.383(21)
C(4)–C(3)	1.398(20)	C(5)–C(4)	1.349(19)
C(12)–C(11)	1.420	C(15)–C(11)	1.420
C(13)–C(12)	1.420	C(14)–C(13)	1.420
C(15)–C(14)	1.420	F(1)–P	1.511(12)
F(2)–P	1.485(10)	F(3)–P	1.563(11)
F(4)–P	1.525(11)	F(5)–P	1.569(10)
O–Mo–N	61.2(4)	C(1)–N–Mo	93.8(9)
C(5)–N–Mo	144.7(9)	C(5)–N–C(1)	121.4(12)
C(1)–O–Mo	93.7(8)	C(2)–C(1)–N	122.2(14)
O–C(1)–N	111.3(12)	C(3)–C(2)–C(1)	116.4(15)
C(2)–C(1)–O	126.5(14)	C(5)–C(4)–C(3)	119.8(14)
C(4)–C(3)–C(2)	119.9(14)	C(15)–C(11)–C(12)	108.0
C(4)–C(5)–N	120.2(14)	C(14)–C(13)–C(12)	108.0
C(13)–C(12)–C(11)	108.0	C(14)–C(15)–C(11)	108.0
C(15)–C(14)–C(13)	108.0		

TABLE 5

STRUCTURAL DATA FOR $MoCp_2$ DERIVATIVES CONTAINING LIGANDS WITH OXYGEN OR NITROGEN DONOR ATOMS

	Mo–O (Å)	Mo–N (Å)	L–Mo–L′ (°)	Mo–Cp (Å)	Cp–MoCp (°)	$R(<7)$	Ref.
$[MoCp_2(OH)(NH_2CH_3)][PF_6]$	2.050(5)	2.188(6)	72.2(2)	1.94			
				1.96	133.1	0.049	8
$[MoCp_2NH(CH_3)CH_2COO]Cl.CH_3OH$	2.10(2)	2.23(2)	73.4(6)	1.991			
				1.962	133.9	0.072	11
$[MoCp_2NH_2CH(CH_2S)COO]_2HCl$		2.256(7)	77.0(2)	1.981			
				1.980	133.7	0.038	11
$[MoCp_2(NH_3)HNC(CH_3)(C_2H_5)][PF_6]_2$		2.216(6)		1.980			
		2.192(5)	79.1(2)	1.980	134.0	0.055	12
$[MoCp_2NHC_4H_8COO][PF_6]$	2.108(4)	2.255(5)	75.6(2)	1.991			
				1.986	135.6	0.044	13
$[MoCp_2NH_2C_5H_{12}COO][PF_6]$	2.078(7)	2.215(8)	76.2(3)	1.970			
				1.971	133.6	0.061	13
$[Cp_2MoO_2PO_2MoCp_2][PF_6]$	2.137(4)			1.976			
	2.116(3)		68.0(1)	1.976	134.3		
	2.122(3)			1.973			
	2.129(3)		67.6(1)	1.981	131.0	0.041	14
$[MoCp_2(S_2O_3)]$	2.134(4)		72.3(1)	1.980			
				1.985	133.2	0.023	9
$[MoCp_2N_2C_3H_3C(CH_3)_2O][PF_6]$	2.026(2)	2.123(3)	75.4(1)	1.993			
				1.996	128.8	0.046	15
$[MoCp_2(N_2C_3H_3)_2]$		2.166(3)		1.980			
		2.157(3)	83.3(1)	1.983	133.2	0.029	15
$[MoCp_2(SO_4)]$	2.113(3)		66.1(2)	1.964	1.34.1	0.029	16
$[MoCp_2(O_2CC_6H_5)_2]$	2.113(4)			1.97			
	2.102(4)		72.3(2)	1.975	133.3	0.035	17
$[MoCp_2(2\text{-}NHNC_5H_4)][PF_6]$		2.160(8)		1.958			This
		2.142(9)	59.8(3)	1.992	134.8	0.028	work
$[MoCp_2(2\text{-}ONC_5H_4)[PF_6]$	2.142(10)	2.139(11)	61.2(4)	1.959	134.1	0.059	This work

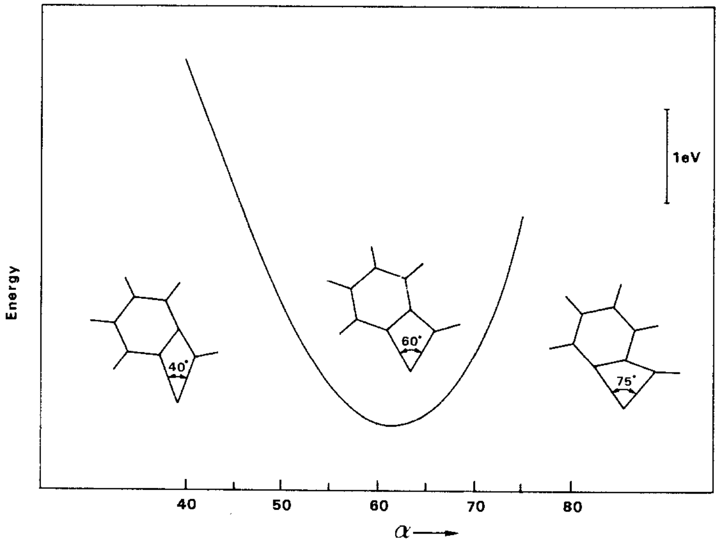
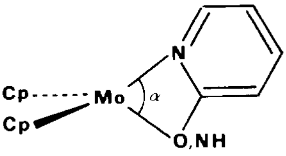


Fig. 3. Energy change with α, the N–Mo–N angle, for the complex $[MoCp_2(2\text{-}NHNC_5H_4)]^+$.

strongly reduced L–Mo–L angles. This is illustrated by the data collected in Table 5, which also shows the spread of the Mo–Cp and Mo–O,N distances.

The Mo–O and Mo–N distances in both complexes lie close to those previously found, although the Mo–O distance in the hydroxypyridine complex is clearly at the long end of its range and all the Mo–N distances are at the short end of their range. Surprisingly perhaps, there is no significant difference between the Mo–O and Mo–N distances in the hydroxypyridine compound. These results indicate that the strain in the chelate does not seem to affect bond lengths to any great degree. However, the effect on bond angles is quite significant, with deformations not only at the metal and coordinating atoms but also at the pyridine α-carbon positions.

In an attempt to determine how the strain is accommodated at the various centres, we carried out some Extended Hückel molecular orbital calculations on both complexes. The model used is shown in **3**, in which the chelate ring defines the *xz* plane. (Details are given in the Appendix.) The bonding between the Cp_2Mo fragment and the ligands is assumed to be essentially the same as described earlier [9] for Cp_2MoL_2 complexes where L is a σ donor. All atomic distances were held fixed and, under these circumstances, any change in α implies a change in all other angles. We adopted this model in view of the previously mentioned observation that the strain does not seem to have much effect on distances, and also because Extended Hückel calculations, whilst giving reliable energy differences for angular variations, are not so reliable for mapping changes in bond lengths.



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The results obtained for the aminopyridine complex are illustrated in Fig. 3, which shows the variation of energy with α.

The results for the hydroxypyridine are very similar. The curve shows a clear minimum at a value for α of $\sim 63°$, very close to the experimental angle (the geometry shown is schematic).

In addition, the curve is fairly symmetrical, especially at values of α not too distant from the minimum, indicating comparable strain energy variations for the combinations Mo–O, N–C, Mo–N–C (dominant for values of α greater than 60°, and O,N–Mo–N (dominant for values of α less than 60°).

Experimental

Crystallography

All X-ray measurements were made using an Enraf–Nonius CAD 4 diffractometer and graphite monochromatised Mo-K_α radiation ($\bar{\lambda}$ 0.71069 Å). Cell dimensions and orientation matrices were obtained by least-squares refinement of setting angles for 25 automatically centred reflections. Intensity data were recorded using the

TABLE 6

CRYSTALLOGRAPHY DATA AND ENRAF–NONIUS CAD4 DATA COLLECTION PARAMETERS

	$[MoCp_2(2\text{-}NHNC_5H_4)][PF_6]$	$[MoCp_2(2\text{-}ONC_5H_4)][PF_6]$
Formula	$C_{15}H_{15}N_2PF_6Mo$	$C_{15}H_{14}NOPF_6Mo$
M	464.2	465.18
Space group	$Pca2_1$	$Pnma$
a (Å)	20.807(1)	12.727(3)
b (Å)	8.0030(8)	10.174(2)
c (Å)	10.056(3)	12.918(1)
V (Å^3)	1674.5	1672.8
Z	4	4
d_{calc} (g cm^{-3})	1.841	1.847
μ(Mo-K_α) (cm^{-1})	8.35	8.38
Scan speed (° s^{-1})	1.3–10.2	1.2–6.8
Data collected	$+h, +k, +l$	$+h, +k, +l$
No. of unique data	1568	1556
No. of data $\|F\| < 3\sigma(F)$	1287	1178
No. Variables	285	128
R	0.028	0.059
R_w	0.027	0.070
Largest shift/error value on final cycle	0.45	0.063
Largest peak in final difference Fourier (e Å^3)	0.57	0.71

$R = \Sigma(|F_0| - |F_c|)/\Sigma|F_0|$. $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2}$.

ω–2θ scan mode with $1.5 < \theta < 25$ and $\omega = 0.8 \pm 0.35\tan\theta$ in both cases. The structures were solved via the heavy atom method and refined by least-squares.

For complex **1**, all non-hydrogen atoms were freely refined anisotropically and hydrogens, which were located on difference maps, isotropically. In the refinement unit weights gave satisfactory agreement analyses.

Intensity data for complex **2** were corrected for absorption empirically [19] (minimum and maximum transmission factors of 0.894 and 0.999, respectively). The Cp ring was refined as a rigid group with fixed C–C and C–H distances and H atoms were assigned a single group U_{iso} value. H atoms on chelate ligand were inserted in idealised positions but allowed individual, refined U_{iso} values. Data were further corrected for absorption using DIFABS [20], after isotropic refinement. C atoms were then refined anisotropically and a weighting scheme $w = 0.5402/[\sigma^2|F_0| + 0.0001F_0^2]$ was used to give satisfactory agreement analyses.

Details of the data collection and refinement are given in Table 6. Data for atomic scattering factors and anomalous scattering terms were taken from the literature [21]. Drawings were made with SNOOPI [22] (**1**) and ORTEP [23] (**2**).

Tables of anisotropic thermal parameters and structure factors are given in the supplementary material.

Synthesis

All the reactions were carried out under dry nitrogen. $[MoCp_2X_2]$ (X = Cl, Br, I), $[MoCp_2H_3][PF_6]$ and $[MoCp_2(ONC_5H_4)][PF_6]$ were prepared as described previously [24,25,4] and 2-aminopyridine (Merck) was used without further purification.

^1H NMR spectra were obtained in a Bruker CXP300 spectrometer (chemical shifts in τ values downfield from tetramethylsilane used as internal reference). Infrared spectra were recorded on a Perkin–Elmer 457 using KBr pellets and calibrated against polystyrene. Conductivities were measured at 25 °C using a Radiometer CDM3 Conductivity Meter, calibrated with standard KCl solution.

C, H, and N analysis were made in Centro de Química Estrutural using a Perkin–Elmer Instrument.

Preparation of $[MoCp_2(2\text{-}NHNC_5H_4)][PF_6]$

A mixture of either $[MoCp_2X_2]$ (X = Cl, Br, I) (1 mmol) and $Tl[PF_6]$ (0.40 g, 1.2 mol) or $[MoCp_2H_3][PF_6]$ (0.37 g, 1 mmol) and an excess of 2-aminopyridine (0.20 g, 2.13 mmol) was refluxed in acetone for 28 h. The resulting yellow solution was evaporated under vacuum and the residue chromatographed on an alumina column. Elution with acetone gave an yellow solution from which an orange product was obtained after evaporating to dryness.

The residue was recrystallized from acetone/water to give large orange crystals of $[MoCp_2(2\text{-NHpy})][PF_6]$. Yield ca. 60%. Analysis. Found: C, 39.10; H, 3.37; N, 6.02. $C_{15}H_{15}N_2MoPF_6$ calc: C, 38.79; H, 3.23; N, 6.03%. Infrared (selected bands). 3430, 1612, 1298 cm^{-1}. ^1H NMR (acetone, 20 °C): Cp protons 4.17 τ (s); pyridine protons 2.50 τ (d,H(6)), 2.63 τ (t,H(4)), 3.72 τ (t,H(5)), 4.06 τ (d,H(3)); N–H proton 4.53 τ (s), broad. Conductivity: 110 ohm^{-1} cm^2 mol^{-1} (1×10^{-3} *M* solution in nitromethane). Melting point: 250 °C (dec.).

Appendix

The Extended Hückel calculations were made by use of the ICON8 program [26] with the Wolfsberg–Helmholz modification [27]. The basis set for the molybdenum atom consisted of 5*s*, 5*p*, and 4*d* orbitals. The *s* and *p* orbitals were described by single Slater-type wave functions and *d* orbitals were taken as contracted linear combinations of two Slater-type wave functions. The geometry for the model $[Mo(\eta^5\text{-}C_5H_5)_2(NHpy)]^+$ was taken from the X-ray determined structure. The cyclopentadienyl rings were assumed to be eclipsed and the following values were used for the distances: Mo–Cp 1.975, C–C 1.40, Mo–N 2.15, C–H 1.08, N–H 1.08, and C–C or C–N (pyridine ring) 1.365 Å. The parameters used for the calculations were the standard ones for C, H, N and O [26], and those reported in Table 7 for molybdenum.

TABLE 7

ORBITAL EXPONENTS AND PARAMETERS USED FOR THE EXTENDED HÜCKEL MOLECULAR ORBITAL CALCULATIONS

Orbital	$-H_{ii}$ (eV)	ξ_1	ξ_2	C_1	C_2	Ref.
Mo 5*s*	8.77	1.960				28
Mo 5*p*	5.60	1.900				28
Mo 4*d*	11.06	4.54	1.90	0.5899	0.5899	28, 29

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