NITRILE COMPLEXES OF DICYCLOPENTADIENYL-MOLYBDENUM AND -TUNGSTEN: PREPARATION AND REACTIVITY.
THE STRUCTURE OF DI-η^5-CYCLOPENTADIENYLIODOACETONITRILE-MOLYBDENUM(IV) HEXAFLUOROPHOSPHATE, [Mo(η^5-C$_5$H$_5$)$_2$I(NCCH$_3$)][PF$_6$]

M.J. CALHORDA, M.A.A.F. de C.T. CARRONDO, A.R. DIAS*, A.M.T. DOMINGOS *,
M.T.L.S. DUARTE, M.H. GARCIA, and C.C. ROMÃO

Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, 1096 Lisboa Codex (Portugal)

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Summary

New complexes of the type [MCp$_2$X(NCR)][PF$_6$] (M = Mo, W; X = SR, halides; R = Me, Et, Ph) have been prepared from [MCp$_2$X$_2$] and TlPF$_6$, NOPF$_6$ or [FeCp$_2$][PF$_6$], in nitrile solvents. Some reactions of these cations with nucleophiles [L] have been studied. With L = PR$_3$ or CO, the complexes [MCp$_2$(SR)L]$^+$ (R = Me, Ph) are formed. [MoCp$_2$(SPh)(NCMe)]$^+$ reacts with NaBH$_4$ to give [MoCp$_2$(SPh)H] and with acetone to give [MoCp$_2$\{S(Ph)C(Me)$_2$O\}]$^+$. The W complexes [WCp$_2$X(NCR)]$^+$ add NHR$'_2$ to give amidine complexes [WCp$_2$X\{HN= C(R)NR$'_2$\}]$^+$ (X = SPh, Br). The mode of coordination of the nitriles to the [MoCp$_2$Cl]$^+$ fragment has been studied by EHMO calculations.

The molecular structure of [MoCp$_2$I(NCMe)][PF$_6$] has been determined. The crystals are triclinic, space group $P\bar{1}$, a 7.7989(6), b 10.3044(8), c 10.5565(5) Å, α 96.218(4), β 94.466(4), γ 102.697(5)°, V 818.21 Å^3, $Z = 2$. The cation has the usual bent bis-metallocene structure, and within this family of complexes is the first reported example of a complex containing a Mo–I bond.

Introduction

Our studies on the chemistry of cationic complexes of the type [MoCp$_2$XL]$^+$ (M = Mo, W; Cp = η^5-C$_5$H$_5$; X = Cl, Br, I, H; L = neutral ligand) have led to new

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* Laboratório Nacional de Engenharia Tecnológica e Industrial.

synthetic routes to such complexes, involving either (a) reaction of $[MCp_2H_3]^+$ with L, (b) halide abstraction from the dihalides $[MCp_2X_2]$ by $TlPF_6$ in the presence of an excess of L [1,2] or (c) electrochemical oxidation of $[MCp_2X_2]$ (X = halide, SR) complexes in nitrile solvents [3]. We have now further explored this last route by employing $[FeCp_2][PF_6]$ and $NO[PF_6]$ as oxidising agents. A wide range of $[MCp_2X(NCR)]^+$ cations has been prepared and some of their reactions are reported. An X-ray diffraction has been carried out on the complex [Mo-$Cp_2I(NCCH_3)][PF_6]$, and the bonding in this type of complex is discussed. Some of the results have been previously communicated [4], and a full study of the photo-chemical generation and reactions of the nitrile complexes has been published [5].

Chemical studies

Preparation of the nitrile complexes [MCp₂X(NCR)][PF₆]

Addition of a $[FeCp_2][PF_6]$ solution in NCMe to a suspension of $[MoCp_2(SMe)_2]$ (**1**) in the same solvent at room temperature (r.t.) gives, after work-up, the complex $[MoCp_2(SR)(NCMe)][PF_6]$ (**2a**) in ca. 70% yield. Similar reactions afforded complexes **2a–d**.

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(**2a**, M = Mo; R = Me; **2b**, M = Mo; R = ^{i}Pr;

2c, M = Mo; R = Ph; **2d**, M = W; R = Ph)

This formulation is supported by the analytical and conductivity data (Table 1) and also by the IR and ^{1}H NMR spectra (Table 2), as discussed below.

Treatment of a suspension of $[MCp_2X_2]$ (**3**) (M = Mo, W; X = Cl, Br, I) with one equivalent of $NO[PF_6]$ in dry nitrile yielded a mixture of two complexes **4** and **5** (eq. 1).

$$[MCp_2X_2] + NO[PF_6] \xrightarrow{\text{NCR}} [MCp_2X_2][PF_6] + [MCp_2X(NCR)][PF_6] \qquad (1)$$
$$\text{(3)} \qquad\qquad\qquad\qquad \text{(4)} \qquad\qquad \text{(5)}$$

The isolated yield of the nitrile complexes **5** depends on the nature of X, increasing in the order Cl < Br < I for both Mo and W (see Table 3). Longer reaction times favour formation of **5** at the expense of the known cations **4** [6]. This procedure gave complexes **5a, b, c, d, e** and **h**.

TABLE 1

COLOURS AND ANALYTICAL DATA FOR COMPLEXES 2–6

Compound	Colour	Analysis (Found (calc) (%))		
		C	H	N
[Mo(Cp)$_2$(SMe)(NCMe)][PF$_6$] (2a)	Dark-red	35.3	3.6	3.3
		(34.0)	(3.5)	(3.0)
[Mo(Cp)$_2$(S^{i}Pr)(NCMe)][PF$_6$] (2b)	Dark-red	36.5	4.0	2.4
		(37.0)	(4.1)	(2.9)
[Mo(Cp)$_2$(SPh)(NCMe)][PF$_6$] (2c)	Dark-red	41.0	3.4	2.8
		(41.5)	(3.5)	(2.7)
[W(Cp)$_2$(SPh)(NCMe)][PF$_6$] (2d)	Dark-red	35.9	3.1	2.1
		(35.4)	(3.0)	(2.3)
[Mo(Cp)$_2$Cl(NCMe)][PF$_6$] (5a)	Brown	31.9	2.9	3.2
		(32.2)	(2.9)	(3.1)
[Mo(Cp)$_2$Br(NCMe)][PF$_6$] (5b)	Dark-blue	30.1	3.2	2.9
		(29.8)	(2.7)	(2.9)
[Mo(Cp)$_2$I(NCMe)][PF$_6$] (5c)	Green	26.3	2.5	2.5
		(26.7)	(2.4)	(2.6)
[W(Cp)$_2$Cl(NCMe)][PF$_6$] (5d)	Brown	26.5	2.5	2.7
		(26.9)	(2.3)	(2.6)
[W(Cp)$_2$I(NCMe)][PF$_6$] (5e)	Blue-grey	23.0	2.1	2.2
		(23.4)	(2.0)	(2.5)
[Mo(Cp)$_2$I(NCPh)][PF$_6$] (5f)	Green	34.4	3.1	2.5
		(34.0)	(2.5)	(2.3)
[W(Cp)$_2$I(NCPh)][PF$_6$] (5g)	Dark-blue	30.0	2.3	1.8
		(29.6)	(2.2)	(2.0)
[Mo(Cp)$_2$Br(NCEt)][PF$_6$] (5h)	Dark-blue	30.5	2.9	3.4
		(30.9)	(3.0)	(2.8)
[W(Cp)$_2$I(NCEt)][PF$_6$] (5i)	Green	24.8	2.5	2.2
		(24.4)	(2.4)	(2.2)
[Mo(Cp)$_2$I(NCEt)][PF$_6$] (5j)	Dark-green	28.3	2.6	2.9
		(28.2)	(2.7)	(2.5)
[Mo(Cp)$_2$(NCPh)$_2$][PF$_6$]$_2$ (6)	Red	39.8	3.2	3.8
		(39.9)	(2.8)	(3.9)

When a 1/2 ratio of **3** to NO[PF$_6$] was used, high yields of **5c** and **5i** were obtained. In benzonitrile under these conditions the salt [MoCp$_2$(NCPh)$_2$][PF$_6$]$_2$ (**6**) was also isolated in 30% yield. However, neither the Mo-acetonitrile, nor the W-benzonitrile analogues of **6** could be prepared by this route, but the latter was obtained from photochemical reaction [5].

Alternatively, the nitrile cations **5** can be prepared by halide abstraction by Tl$^+$ (eq. 2) (see [7]) using a short reflux time (ca. 15 min), and this method gave

$$[MCp_2X_2] + Tl[PF_6] \xrightarrow{\text{NCR}} [MCp_2X(NCR)][PF_6] + TlX \qquad (2)$$

complexes **5b**, **5c** and **5j**. Use of excess Tl[PF$_6$] does not readily give **6** or its analogues; suggesting that the abstraction of the first halide ion is much easier than the second one.
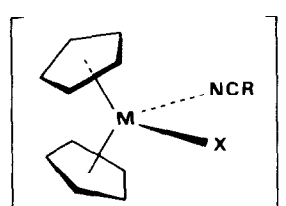
TABLE 2

^{1}H NMR SPECTRA OF COMPLEXES 2–6

Compound	τ (ppm), multiplicity, relative integrals, assignment
2a [a]	4.42 (s,10,η^5-C$_5$H$_5$), 8.22 (s,3,S-CH$_3$), 8.02 (s,3,NCCH$_3$)
2b [a]	4.40 (s,10,η^5-C$_5$H$_5$), 7.65 (m,1,SCH(CH$_3$)$_2$), 8.02 (s,3;NCCH$_3$), 8.85 (d,6,SCH(CH$_3$)$_2$)
2c [a]	3.40 (m,5,SC$_6$H$_5$), 4.50 (s,10,η^5-C$_5$H$_5$), 7.53 (s,3,NCCH$_3$)
2d [a]	2.91 (m,5,SC$_6$H$_5$), 4.41 (s,10,η^5-C$_5$H$_5$), 8.04 (s,3,NCCH$_3$)
5a [b]	3.96 (s,10,η^5-C$_5$H$_5$), 7.34 (s,3,NCCH$_3$)
5b [a]	4.20 (s,10,η^5-C$_5$H$_5$), 7.58 (s,3,NCCH$_3$)
5c [b]	3.93 (s,10,η^5-C$_5$H$_5$), 7.33 (s,3,NCCH$_3$)
5d [b]	4.03 (s,10,η^5-C$_5$H$_5$), 7.03 (s,3,NCCH$_3$)
5e [b]	3.99 (s,10,η^5-C$_5$H$_5$), 6.99 (s,3,NCCH$_3$)
5f [b]	2.24 (m,5,NCC$_6$H$_5$), 3.87 (s,10,η^5-C$_5$H$_5$)
5g [b]	2.14 (m,5,NCC$_6$H$_5$), 3.86 (s,10,η^5-C$_5$H$_5$)
5h	3.95 (s,5,η^5-C$_5$H$_5$), 7.02 (q,2,NCCH$_2$CH$_3$), 8.69 (t,3,NCCH$_2$CH$_3$)
5i [b]	3.98 (s,10,η^5-C$_5$H$_5$), 6.67 (q,2,NCCH$_2$CH$_3$), 8.65 (t,3,NCCH$_2$CH$_3$)
5j [b]	3.95 (s,10,η^5-C$_5$H$_5$), 7.02 (q,2,NCCH$_2$CH$_3$), 8.69 (t,3,NCCH$_2$CH$_3$)
6	2.20 (m,10,NCC$_6$H$_5$), 3.41 (s,10,η^5-C$_5$H$_5$)

[a] In NCMe-d_3 as solvent and TMS as internal reference. [b] In Me$_2$CO-d_6 as solvent and TMS as internal reference.

Complexes **5** have the following general structural formulation:

	M	X	R
5a	Mc	Cl	Me
5b	Mo	Br	Me
5c	Mo	I	Me
5d	W	Cl	Me
5e	W	I	Me
5f	Mc	I	Ph
5g	W	I	Ph
5h	Mo	Br	Et
5i	W	I	Et
5j	Mo	I	Et

as shown by the data listed in Tables 1 and 2.

Typical IR bands confirm the presence of both the MCp$_2$($\sim$ 3100 cm^{-1}) fragment and the PF$_6^-$ cation (840 and 560 cm^{-1}) in all the complexes. The ionic formulation is suggested by the observed conductivity values (75–95 ohm^{-1} cm mol^{-1} for monocations and 188 ohm^{-1} cm mol^{-1} for the dication **6**) [8]. Of

TABLE 3

YIELDS OF [MCp$_2$X(NCMe)]$^+$ IN REACTIONS OF [MCp$_2$X$_2$] WITH [NO][PF$_6$] IN 1/1 RATIO

M	X	Yield (%)
Mo	Cl	15
Mo	Br	48
Mo	I	70
W	Cl	5
W	I	80

particular interest in connection with the bonding and possibly the reactivity of the coordinated nitrile is the value of the C–N stretching vibrations in the IR. As usual the acetonitrile complexes show two bands around 2300 cm^{-1}; the higher frequency band (ca. 2310 cm^{-1}), which has a slightly lower intensity, was assigned to a combination band of $\delta_{sym}(CH_3)$ and $\nu(C-C)$ [9], the lower frequency band being assigned to $\nu(C-N)$. Indeed, the spectra of [MoCp$_2$I(NCCD$_3$)][PF$_6$] and [MoCp$_2$I(NCEt)][PF$_6$], where such a combination band is absent, show only the lower frequency band (2290 cm^{-1}).

In all these compounds there is a positive shift of $\nu(C-N)$ relative to that for the free ligand, independent of the nature of X, of ca. 30 cm^{-1} for M = Mo, and slightly lower for the W complexes (ca. 20 cm^{-1}). This is a typical situation for "end-on" coordinated nitriles bound to weakly back-donating metal centers (see below under discussion of MO calculations).

The structure of di-η^5-cyclopentadienyliodoacetonitrilemolybdenum(IV) hexafluorophosphate (5c)

Final atomic coordinates for the non-hydrogen atoms are given in Table 4 and the bond lengths and angles in Table 5. The structure, with the atom numbering, is shown in Fig. 1.

The crystal structure of **5c** consists of discrete [MoCp$_2$I(NCCH$_3$)]$^+$ cations and PF$_6^-$ anions. The metal atom is coordinated to two η^5-cyclopentadienyl rings, to an iodide, and to the nitrogen atom of the acetonitrile ligand. The coordination geometry about the central Mo atom is a distorted tetrahedron, with the angle between the ring normals of 133.8(3)° and an I–Mo–N angle of 81.2(2)°.

TABLE 4

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) FOR [MoCp$_2$I(NCMe)][PF$_6$]

Atom	x	y	z
Mo	1268(1)	2339	8034
I	−1164(1)	2433(1)	9880
N(1)	89(6)	3848(4)	7375(4)
C(1)	−541(8)	4649(5)	7022(5)
C(111)	−1336(10)	5700(7)	6564(7)
C(10)	1724(11)	760(7)	6430(7)
C(11)	1116(12)	20(7)	7422(7)
C(12)	−575(13)	192(7)	7568(8)
C(13)	−1052(10)	1019(7)	6706(8)
C(14)	445(11)	1384(7)	5976(6)
C(15)	3069(15)	3634(27)	9766(12)
C(16)	3330(13)	4315(12)	8755(17)
C(17)	3996(13)	3612(13)	7901(10)
C(18)	4205(10)	2435(12)	8262(12)
C(19)	3567(20)	2421(17)	9515(20)
P	5529(2)	2416(2)	3794(2)
F(1)	5810(13)	3975(6)	4034(12)
F(2)	5179(10)	901(6)	3620(15)
F(3)	5763(21)	2525(16)	5299(7)
F(4)	7564(7)	2497(10)	3804(12)
F(5)	3547(8)	2234(8)	3823(14)
F(6)	5278(27)	2409(20)	2375(7)

TABLE 5

BOND LENGTHS (Å) AND BOND ANGLES (°) FOR [MoCp$_2$I(NCMe)][PF$_6$]

I–Mo	2.832(4)	N(1)–Mo	2.124(6)
Cp(1)–Mo	1.986(8)	Cp(2)–Mo	1.965(10)
C(10)–Mo	2.323(8)	C(11)–Mo	2.381(8)
C(12)–Mo	2.337(9)	C(13)–Mo	2.280(8)
C(14)–Mo	2.267(8)	C(15)–Mo	2.312(11)
C(16)–Mo	2.312(11)	C(17)–Mo	2.264(9)
C(18)–Mo	2.264(9)	C(19)–Mo	2.266(9)
C(1)–N(1)	1.130(7)	C(111)–C(1)	1.476(9)
C(11)–C(10)	1.413(11)	C(14)–C(10)	1.383(11)
C(12)–C(11)	1.387(13)	C(13)–C(12)	1.396(13)
C(14)–C(13)	1.452(13)	C(16)–C(15)	1.344(23)
C(19)–C(15)	1.393(27)	C(17)–C(16)	1.305(19)
C(18)–C(17)	1.348(17)	C(19)–C(18)	1.450(24)
F(1)–P	1.563(8)	F(2)–P	1.513(8)
F(3)–P	1.574(9)	F(4)–P	1.570(7)
F(5)–P	1.518(8)	F(6)–P	1.495(8)
N(1)–Mo–I	81.2(1)		
Mo–N(1)–C(1)	179.8(1)		
N(1)–C(1)–C(111)	179.3(6)		
C(10)–C(11)–C(12)	106.5(8)	C(15)–C(16)–C(17)	108.4(15)
C(11)–C(12)–C(13)	110.5(8)	C(16)–C(17)–C(18)	113.2(13)
C(12)–C(13)–C(14)	106.3(8)	C(17)–C(18)–C(19)	104.2(12)
C(13)–C(14)–C(10)	106.8(7)	C(18)–C(19)–C(15)	105.3(11)
C(14)–C(10)–C(11)	109.9(8)	C(19)–C(15)–C(16)	108.9(13)

The structural parameters about the Mo atom exhibit normal values, as can be seen by the comparison in Table 6 with values observed for similar MoCp$_2$LL′ compounds. The Mo–N bond length 2.124(6) Å is similar to the corresponding distance observed in compound **d** (Table 6) but is shorter than that for the other compounds.

The Mo–I distance of 2.832(4) is 0.33 Å longer than the Mo–Cl distance in [MoCp$_2$Cl(C$_2$H$_5$)] [10], in good agreement with the difference in covalent radii of chlorine (0.99 Å) and iodine (1.33 Å). To our knowledge this is the first reported Mo–I bond length in this particular type of compound. The I–Mo–N angle lies within the 76–82° range reported for similar d^2 compounds [10].

The molybdenum atom is 1.986(8) and 1.965(10) Å from the best least-squares planes of the cyclopentadienyl rings. For the Cp(1) ring the Mo–C$_{Cp}$ distances range from 2.267(8) to 2.381(8), with a mean value of 2.318 Å and the C–C values range from 1.383(11) to 1.452(13) with a mean value of 1.406 Å. In the Cp(2) ring, the Mo–C$_{Cp}$ distances range from 2.264(9) to 2.312(11), with a mean value of 2.284 Å, and the C–C values range from 1.305(19) to 1.450(24) with a mean value of 1.368 Å. A projection on to the Mo,I,N plane shows that the Cp rings adopt an almost staggered conformation.

As is usually observed in ions having near spherical symmetry, the fluorine atoms have large temperature factors, indicating considerable disorder in the PF$_6$ anion.

Reactions of the complexes [MoCp$_2$X(NCR)][PF$_6$]

The thiolato complexes **2a, c** and **d** in solution in NCMe react readily with
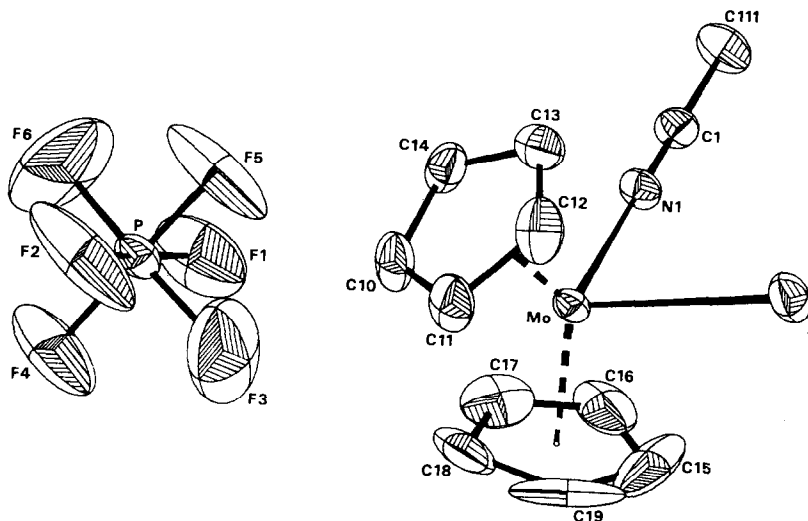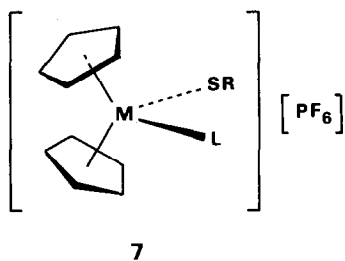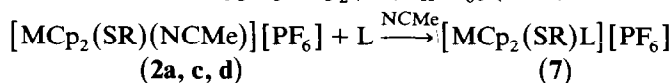
Fig. 1. Molecular structure of [MoCp$_2$I(NCCH$_3$)][PF$_6$] with 30% probability thermal ellipsoids.

neutral donors, L, with displacement of the coordinated nitrile to give new cationic derivatives of the type [MCp$_2$(SR)L][PF$_6$] (7a–h).

$$[\text{MCp}_2(\text{SR})(\text{NCMe})][\text{PF}_6] + \text{L} \xrightarrow{\text{NCMe}} [\text{MCp}_2(\text{SR})\text{L}][\text{PF}_6]$$
$$(2\text{a, c, d}) \qquad\qquad\qquad\qquad (7)$$

	M	R	L
7a	Mo	Ph	PPh$_3$
7b	Mo	Ph	P(OPh)$_3$
7c	Mo	Ph	CO
7d	Mo	Ph	NH$_3$
7e	Mo	Me	dppe *
7f	W	Ph	PPh$_3$
7g	W	Ph	P(OPh)$_3$
7h	W	Ph	CO

All the compounds 7 are soluble in polar organic solvents (Me$_2$CO, NCMe, NO$_2$Me) and can be handled in air for short periods without noticeable decomposition. They were fully characterized by elemental analysis (Table 7), conductivity (molar conductivity 75–85 ohm^{-1} cm mol^{-1}), and IR and ^{1}H NMR spectroscopy (Table 7).

Similar substitution reactions can be expected for the complexes 5a–h. For instance, 5c reacts in refluxing acetone with PPh$_3$ to give the known [Mo-Cp$_2$I(PPh$_3$)][PF$_6$] in quantitative yield.

A neutral hydride [MoCp$_2$(SPh)H] (8) resulted from the reaction of 2c with NaBH$_4$. It shows the Mo–H stretching vibration (ν(Mo–H) 1845 cm^{-1}) in the IR, and in the ^{1}H NMR the expected high field singlet (17.9τ).

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* dppe = 1,2-bis(diphenyl)phosphinoethane.

TABLE 6

COMPARISON OF STRUCTURAL PARAMETERS WITH THOSE FOR SIMILAR [MoCp$_2$LL′] COMPLEXES

[MoCp$_2$LL′]	Mo–N (Å)	Mo–I (Å)	L–Mo–L′ (°)	Mo–Cp (Å) [a]	Cp–Mo–Cp′ (°) [b]	Ref.
[MoCp$_2$I(NCCH$_3$)][PF$_6$] (5c)	2.124(6)	2.832(4)	81.2(2)	1.973	133.8	This work
[MoCp$_2$(N$_2$C$_3$H$_3$)$_2$] (a)	2.166(3) 2.157(3)		83.3(1)	1.982	133.2	13
[MoCp$_2$(OH)(NH$_2$CH$_3$)][PF$_6$] (b)	2.188(6)		72.2(2)	1.95	133.1	10
[MoCp$_2$(NH$_3$)HNC(CH$_3$)(C$_2$H$_5$)][PF$_6$]$_2$ (c)	2.216(6) 2.192(5)		79.1(2)	1.980	134	18
[MoCp$_2$(N$_2$C$_3$H$_3$C(CH$_3$)$_2$O][PF$_6$] (d)	2.123(3)		75.4(1)	1.995	128.8	13

[a] Average ring normal. [b] Angle between the ring normals.

TABLE 7

COLOURS AND ANALYTICAL DATA FOR COMPLEXES 7–11

Compound	Colour	Analysis (Found (calc) (%))		
		C	H	N
$[Mo(Cp)_2(SPh)(PPh_3)][PF_6]$ (7a)	Dark-red	55.2 (55.0)	4.1 (4.1)	
$[Mo(Cp)_2(SPh)\{P(OPh)_3\}][PF_6]$ (7b)	Orange	51.6 (51.6)	3.6 (3.8)	
$[Mo(Cp)_2(SPh)(CO)][PF_6]$ (7c)	Red	40.5 (40.2)	3.1 (3.0)	
$[Mo(Cp)_2(SPh)(NH_3)][PF_6]$ (7d)	Dark-red	39.2 (38.6)	3.9 (3.6)	2.7 (2.8)
$[Mo(Cp)_2(SMe)dppe][PF_6]$ (7e)	Red	53.5 (53.4)	4.7 (4.6)	
$[W(Cp)_2(SPh)(PPh_3)][PF_6]$ (7f)	Dark-red	48.7 (49.2)	3.8 (3.6)	
$[W(Cp_2)_2(SPh)\{P(OPh)_3\}][PF_6]$ (7g)	Orange	46.2 (46.5)	3.5 (3.4)	
$[W(Cp)_2(SPh)(CO)][PF_6]$ (7h)	Dark-red	34.8 (34.3)	3.0 (2.5)	
$[Mo(Cp)_2(SPh)H]$ (8)	Yellow	^{a}		
$[Mo(Cp)_2(S(Ph)C(Me)_2O)][PF_6]$ (9)	Dark-red	42.7 (42.3)	3.5 (3.9)	
$[Mo(Cp)_2(NO)(NCMe)][PF_6]$ (10)	Dark-brown	32.4 (32.6)	3.0 (3.0)	5.4 (6.3)
$[Mo(Cp)_2Br(NCMe)][PF_6]_2$ (11)	Red	23.7 (22.6)	2.7 (2.1)	2.0 (2.2)

^{a} A satisfactory analysis could not be obtained for this compound, but the spectroscopic data are conclusive (see [15]).

This simple substitution does not always occur. Thus reaction of 2c with pyridine and 1,10-phenantroline (phen) gave the known complexes $[MoCp_2(SPh)_2]$ [11] and $[MoCp_2phen][PF_6]$ [2], respectively, as the only isolable products. On the other hand, 2c failed to react in refluxing NCMe with either cycloocta-1,5-diene or 1,3-butadiene.

Dissolution of 2c in refluxing acetone gives a red complex, 9, to which the following structure is assigned.

9
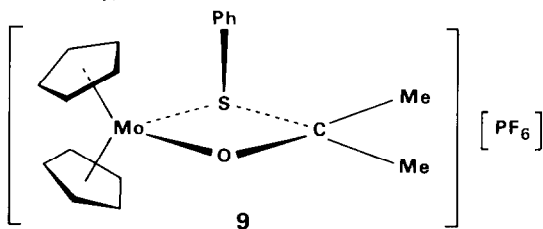
The ^1H NMR spectrum of 9 shows the expected peaks for the Ph and Cp protons and a further singlet at 7.55 τ assignable to the methyl groups, integrating as 5/10/6. The presence of only one signal for the two methyl groups can be explained on the basis of a rapid inversion at the sulphur atom, a process known to occur in analogous complexes [12]. A similar intramolecular attack on acetone has been reported [1], and the structure of the product confirmed by an X-ray study [13].
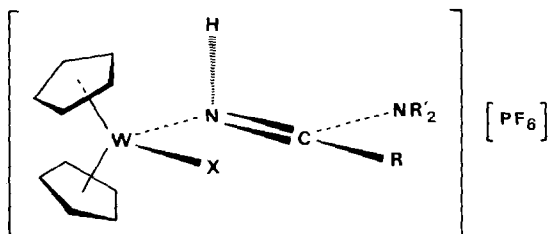
TABLE 8

^{1}H NMR AND IR SPECTRAL DATA FOR COMPLEXES 7–11

Compound	τ (ppm), multiplicity, relative integral, assignment	IR $\bar{\nu}$(cm^{-1})
7a	2.70 (m,15,P(C$_6$H$_5$)$_3$), 3.16 (m,5,SC$_6$H$_5$), 4.42 (d[J(^{31}P–H) 2 Hz],10,η^5-C$_5$H$_5$)	
7b ^{a}	3.09 (m,5,SC$_6$H$_5$), 3.27 (m,15,P(OC$_6$H$_5$)$_3$), 4.81 (s,10,η^5-C$_5$H$_5$)	
7c	2.85 (m,5,SC$_6$H$_5$), 3.70 (s,10,η^5-C$_5$H$_5$)	2040 (C≡O)
7d	2.88 (m,5,SC$_6$H$_5$), 4.22 (s,10,η^5-C$_5$H$_5$), 6.77 (br,3,NH_3)	3360, 3320, 3230 (N–H)
7e	2.95 (m,20,P(C$_6$H$_5$)$_2$), 5.19 (d[J(^{31}P–H)2 Hz], 10,η^5-C$_5$H$_5$) 7.54 (m,4,PCH_2CH_2P), 8.52 (s,3,SCH_3)	
7f	2.34 (m,15,P(C$_6$H$_5$)$_3$), 2.95 (m,5,SC$_6$H$_5$) 4.42 (d,[J(^{31}P–H) 1.8 Hz],10,η^5-C$_5$H$_5$)	
7g	2.68 (m,15,P(OC$_6$H$_5$)$_3$), 4.07 (d[J(^{31}P–H) 2.0 Hz],10,η^5-C$_5$H$_5$)	
7h	2.9 (m,5,SC$_6$H$_5$), 3.75 (s,10,η^5-C$_5$H$_5$)	2040 (C≡O)
8	3.16 (m,5,SC$_6$H$_5$), 5.05 (s,10,η^5-C$_5$H$_5$) 17.86 (s,1,MoH)	1845 (Mo–H)
9	3.40 (m,5,SC$_6$H$_5$), 4.57 (s,10,η^5-C$_5$H$_5$) 7.55 (S,6,sC(CH_3)$_2$O)	
10	3.57 (s,10,η^5-C$_5$H$_5$), 7.37 (s,3,NCCH_3)	1650 (N=O), 2320, 2290 (C≡N)
11		2320, 2290 (C≡N)

^{a} In NCMe-d_3 as solvent and TMS as internal standard; all other spectra in Me$_2$CO-d_6 and same standard.

Reaction of **2c** with gaseous NO in refluxing NCMe led to displacement of the SPh ligand and formation of the salt [MoCp$_2$(NO)(NCMe)][PF$_6$] (**10**). The cation in this complex has been previously reported by Legzdins and Nurse [14] as its BF$_4$ salt, and was formed by I$^-$ abstraction from [MoCp$_2$(NO)I] with Ag$^+$ in NCMe.

Suspensions of **5b** and **5c** in dry CH$_2$Cl$_2$ react with an excess of NO[PF$_6$]. The blue colour of **5b** turns to red, but the product **11** could not be purified by recrystallisation owing to rapid decomposition. Its IR spectrum is virtually identical to that of the starting material, its conductivity is compatible with a 2/1 electrolyte, and the elemental analysis is close to that expected for the dicationic species [MoCp$_2$Br(NCMe)][PF$_6$]$_2$ (**11**). The turquoise product from **5c** and NO[PF$_6$] is even less stable, and no reliable data could be obtained. When **2c** is treated with gaseous NH$_3$ in NCMe, nitrile replacement takes place and **7d** is formed. Similarly, when [MoCp$_2$Br$_2$] is treated in NCMe with one equivalent of Tl[PF$_6$], and NH$_3$ is bubbled in the solution, [MoCp$_2$Br(NH$_3$)][PF$_6$] is formed [15]. However, when the tungsten analogue **2d** in NCMe is treated with gaseous NH$_3$, addition to the nitrile takes place, the product being formulated as the amidine complex [WCp$_2$(SPh)-{HN=C(Me)NH$_2$}][PF$_6$] (**12a**). Furthermore, when [WCp$_2$Br(NCR)][PF$_6$] (R = Me, Ph) formed "in situ" by reaction of an equimolar suspension of [WCp$_2$Br$_2$] and Tl[PF$_6$] in NCMe or NCPh are treated with either gaseous NH$_3$ or NHMe$_2$, addition products are isolated, and can be formulated as [WCp$_2$Br{HN=C(R)-NR'$_2$}][PF$_6$] (**12b**, R = Me, R' = H; **12c**, R = Me, R' = Me; **12d**, R = Ph, R' = H; **12e**, R = Ph, R' = Me). The basis of the structural assignment for the amidine complexes **12a–e** is discussed below.

12

The cationic formulation is supported by the analytical data (Table 9), the presence of the PF_6^- anion (IR) and, in the case of **12b** the molar conductivity in NO_2Me solution (100 ohm^{-1} cm mol^{-1}).

Figure 2 shows the IR spectra of complexes **12b** and **12c**, along with the spectrum of **12b** recovered from its solution in Me_2CO-d_6/H_2O-d_2 (**12b′**). The new N–D stretching bands shown by **12b′** in the region 2650–2450 cm^{-1} indicate that the NH_2 group of the amidine ligand is free and undergoes H/D exchange. (In contrast, no such exchange is observed under the same conditions for the complex $[WCp_2Br(NH_3)][PF_6]$.) On the other hand, the =N–H group remains unaffected in Me_2CO-d_6/H_2O-d_2, the =N–H stretching vibration appearing in the same position in **12b** and **12b′** as in **12c**.

Kharitonov et al. [16] have reported that for the amidine complex $[Pt(NH_3)_2$-$\{NH=C(C_3H_7)NH_2\}]Cl_2$, there is a decrease in the C=N stretching vibration upon deuteration of the free NH_2 group. Similar results have been obtained with complexes **12a** and **12d**. These assignments are supported by ^1H NMR data (Table 10); the spectra of **12a**, **12b** and **12d** show three broad resonances for the three N-bonded protons, and upon addition of D_2O, two of these disappear rather quickly, implying fast H/D exchange. They were assigned to the free NH_2 protons, with the remaining peak assigned to the =NH proton.

The magnetic inequivalence of the two NH_2 protons can be explained in terms of restricted rotation around the C–NH_2 bond; the double bond character of such bond has been estimated at 35% in the above-mentioned Pt-amidine complex [17]. These observations are paralleled in the spectra of complexes **12c** and **12e**, where the =N–H proton does not exchange in the presence of D_2O and two N–CH_3 resonances are observed.

TABLE 9. COLOURS AND ANALYTICAL DATA FOR COMPLEXES 12

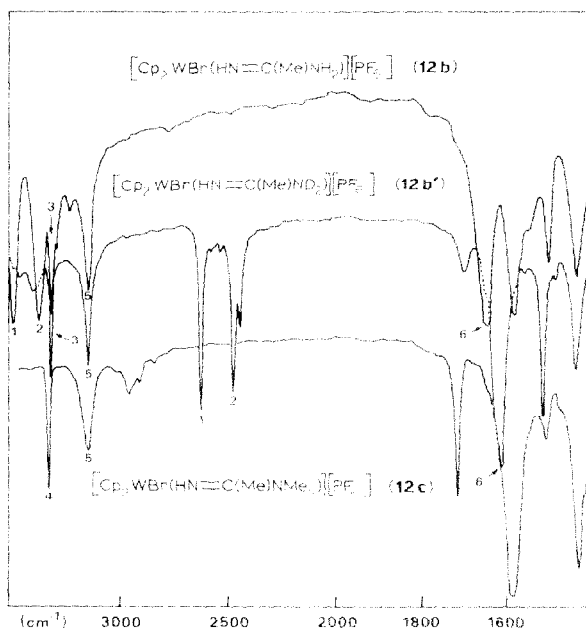| Compound	Colour	Analysis (Found (calc) (%))			Conductivity (ohm^{-1} cm mol^{-1})
		C	H	N	
$[W(Cp)_2(SPh)(HN=C(Me)NH_2)][PF_6]$ (**12a**)	Red-brown	34.4 (34.5)	3.5 (3.4)	4.5 (4.5)	83
$[W(Cp)_2Br(HN=C(Me)NH_2)][PF_6]$ (**12b**)	Purple	24.0 (24.1)	2.8 (2.7)	4.8 (4.7)	100
$[W(Cp)_2Br(HN=C(Me)NMe_2)][PF_6]$ (**12c**)	Purple	26.7 (26.9)	3.1 (3.2)	4.5 (4.5)	
$[W(Cp)_2Br(HN=C(Ph)NH_2)][PF_6]$ (**12d**)	Violet	31.5 (30.9)	3.4 (3.0)	4.1 (4.2)	
$[W(Cp)_2Br(HN=C(Ph)NMe_2)][PF_6]$ (**12e**)	Violet	33.6 (33.2)	3.4 (3.2)	3.9 (4.1)	

Fig. 2. Infrared spectra of **12b**, **12b′**, and **12c**. Assignments: 1 and 2: uncoordinated NH_2; 1′ and 2′ uncoordinated ND_2; 3 and 4: Coordinated =NH (unchanged in **12b′**); 5: C_5H_5 in WCp_2; 6: C=N stretch; 6′: C=N stretch slightly displaced upon deuteration of NH_2 (see [16]).
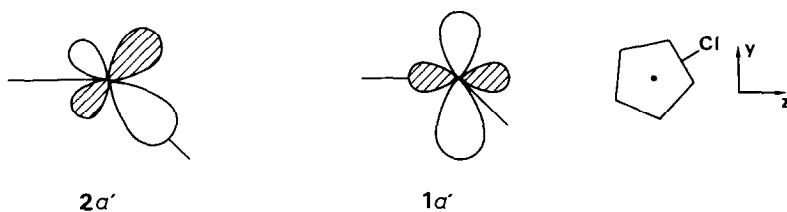
Molecular orbital calculations

The frontier orbitals of the $MoCp_2Cl^+$ fragment may be derived from those of $MoCp_2$ after interaction with a chloride and have been described [19]. They are essentially the two lower energy frontier orbitals of the MCp_2 fragment, $1a_1$ and b_2 [20], which have rehybridized after the lowering of the symmetry and point towards the vacant position, **13**.

TABLE 10

^{1}H NMR SPECTRA FOR COMPLEXES **12** (All spectra in Me_2CO-d_6, with solvent peak as reference; all NH resonances are solvent-sensitive)

Compound	τ (ppm), multiplicity, relative integrals, assignment
12a [a]	1.57 [b] (s, br,1,NH_2), 2.82 (m,5,SC_6H_5), 3.34 (s br,1,=NH), 4.37 (s,10,η^5-C_5H_5) 4.59 [b] (br,1,NH_2), 7.68 (s,3,CH_3)
12b	2.07 (s, br,1, NH_2), 3.77 (s, br,1,=NH), 4.07 (s, br, 1, NH_2) 4.20 (s,10,η^5-C_5H_5), 7.67 (s,3,CH_3)
12c	4.16 (s,10,η^5-C_5H_5), 4.22 [c] (v br,1,=NH), 6.73 (s,3,N(CH_3)$_2$) 6.93 (s,3,N(CH_3)$_2$), 7.69 (s,3,CH_3)
12d	1.63 [b] (s br,1,NH_2) 2.34 (m,5,C_6H_5), 3.19 (s br,1,=NH) 3.67 [b] (s br,1,NH_2), 4.06 (s,10,η^5-C_5H_5)
12e	2.28 (m,5,C_6H_5), 3.78 [d] (s br,1,=NH) 4.45 (s,10,η^5-C_5H_5) 6.78 (s,3,N(CH_3)$_2$), 7.11 (s,3,N(CH_3)$_2$)

[a] Recorded at -30°C to give sharper N–H resonances. [b] Disappears on addition of D_2O. [c] Almost invisible at r.t. owing to broadening. [d] Sharpens at -30°C (3.95τ), and further at -70°C (4.07τ).

13

Orbital $2a'$ is empty and can receive electrons from the nitrile ligand. $1a'$ is apparently suited for backdonation to empty π^* orbitals of the ligand.

The molecular orbital diagram showing the interaction between $MoCp_2Cl^+$ and NCMe is represented in Fig. 3. The HOMO of the NCMe ligand is a σ type orbital, essentially located on the N atom. It interacts strongly with $2a'$, the resulting bonding molecular orbital being slightly destabilized by admixture of a low energy filled orbital of the nitrile in an antibonding fashion.

The nitrile ligand has two sets of orthogonal orbitals, which are essentially the π and π^* orbitals of the C=N group. Both π and π^* have the right symmetry to interact with $1a'$, **14**.

14
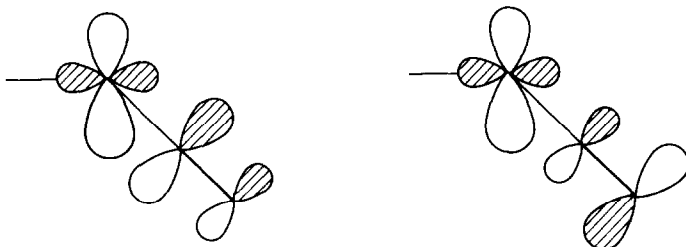
As usual, the π orbital is more localized in the more electronegative atom, N, and the π^* orbital on the less electronegative C. We have then a three orbital interaction, similar to that observed between a metal centre and carbonyl π and π^* orbitals [21]. The main difference between CO and NCMe is that the latter binds to the metal through the more electronegative atom. This means that the metal–π overlap is larger than the metal–π^* overlap (the overlap integrals are respectively 0.064 and 0.046), as the nitrogen atom contributes more to π^*. Backdonation to a nitrile appears therefore to be impossible owing to these competing interactions.

These results are in accordance with those from ab initio calculations by Howell et al. [22] on nitrile ligands and their interaction with metal centres; the authors concluded that NCMe is a weak π-donor, and associate this characteristic with its kinetic lability in many complexes. The same holds for $MoCp_2Cl(NCMe)^+$. From the molecular orbital diagram it can be seen that the overall interaction of $1a'$ with π and π^* is destabilizing (repulsion between two filled levels, $1a'$ and π), although small since the overlap integrals are small. The bond between $MoCpCl^+$ and the nitrile is thus a single bond, resulting from electron donation from a σ level of the nitrile to an empty orbital on the metal fragment. π-Interactions are negligible.

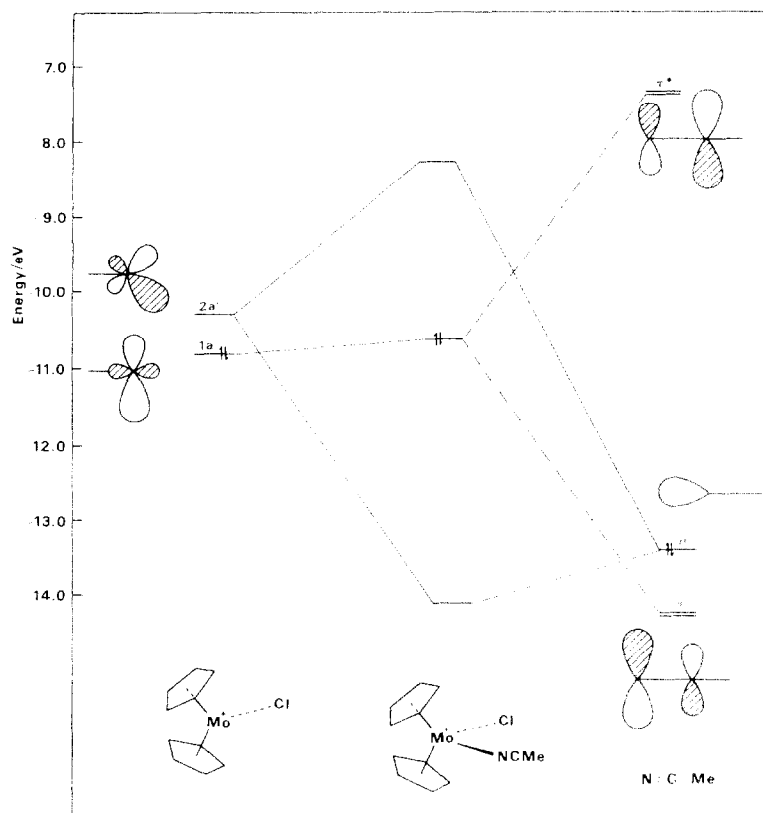This bonding model can be related to the structural features of the coordinated nitrile (Table 11).

Fig. 3. Molecular orbital diagram for the interaction between $MoCp_2Cl^+$ and $NCCH_3$.

The σ donor orbital, which is depopulated by the bond formation, is mainly a nitrogen lone pair, but also weakly bonding between either N–C or C–C. We would expect only small changes in these bond lengths, as is indeed the case. Small deviations from this behaviour are due to the low symmetry of the complex. Many other levels are able to mix, thus disturbing this simplified picture.
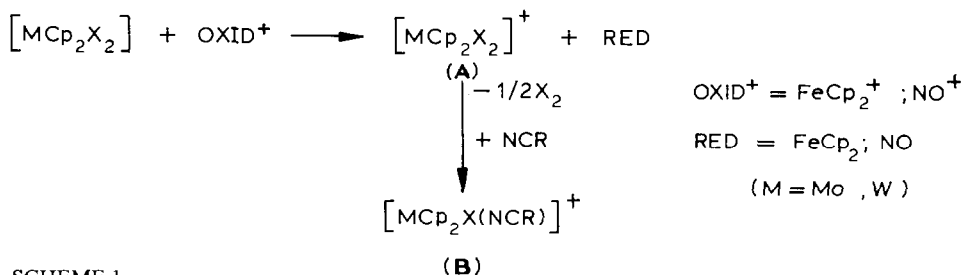
Discussion

Previous electrochemical studies have shown that the oxidation of $[MCp_2X_2]$ (M = Mo, W; X = Cl, Br, I, SR) in NCMe leads ultimately to the solvolysis

TABLE 11

COMPARISON BETWEEN FREE AND COORDINATED $NCCH_3$

		Free $NCCH_3$	Coordinated $NCCH_3$
Distances (Å)	N–C	1.157	1.13
	C–C	1.458	1.467
Overlap	N–C	1.73	1.74
Population	C–C	0.84	0.85

products $[MCp_2(NCMe)X]^+$ through reductive elimination of X_2 from the intermediate $[MCp_2X_2]^+$ cations [3]. A similar reaction might be expected with suitable chemical oxidants such as $[FeCp_2][PF_6]$ or $[NO][PF_6]$. This was indeed shown to be the case, and in the light of the above-mentioned electrochemical results the following mechanism is proposed (see Scheme 1).

$$\left[MCp_2X_2\right] + OXID^+ \longrightarrow \left[MCp_2X_2\right]^+ + RED$$

$$\textbf{(A)}$$

$$\downarrow -1/2X_2 \qquad\qquad OXID^+ = FeCp_2^+ \ ; NO^+$$

$$\downarrow +NCR \qquad\qquad RED = FeCp_2 \ ; NO$$

$$\qquad\qquad\qquad (M = Mo \ , W)$$

$$\left[MCp_2X(NCR)\right]^+$$

SCHEME 1 $\qquad\qquad \textbf{(B)}$

Both of the products **A** and **B** can be isolated from the reaction mixtures. The fact that the yield of **B** increases in the order Cl < Br < I reflects the expected order for the ease of loss of $X^\cdot$ from species **A**. Indeed, $[MCp_2I_2]^+$ was shown to have a relatively short half-life time in NCMe [3].

Although the instability of the products prevented a more thorough study, it was shown that NO^+ can bring about the oxidation of **B** to the dication $[MCp_2X(NCR)]^{2+}$. The product of the reductive elimination of X from such a species in nitrile solvent should be the dication $[MCp_2(NCR)_2]^{2+}$, and this was found to be the case with benzonitrile.

The lability of the nitrile ligands in the cations $[MCp_2X(NCR)]^+$ is known and has been object of a separate study [5]. The MO calculations performed on these complexes provide a theoretical explanation of this lability, since π interactions are negligible, so that ready displacement of the nitrile by neutral donors can be explained on the basis of a dissociative mechanism involving a 16 e intermediate to which the donor L adds.

In this regard it is of interest to note the differing behaviour of the $[MCp_2X(NCR)]^+$ cations towards amines. For M = Mo nitrile substitution occurs, whereas with M = W addition takes place with formation of the amidine complexes $[WCp_2X\{HN=C(R)NR'_2\}]^+$. This is a well-known reaction [9], and we believe that it involves direct nucleophilic attack of the amine on the coordinated nitrile. The difference in the mode of reaction may be due either to a higher lability of the NCR ligand in the Mo complexes, with NH_3 attack on the metal being favoured over addition at the C≡N carbon, or to amidine displacement by excess NH_3. Some support for the former explanation comes from the fact that the ketimine complex $[MoCp_2(NH_3)(NH=CMe_3)][PF_6]_2$ is inert towards an excess of NH_3 [23].

Experimental

All experiments were carried out under N_2 by use of standard Schlenk tube techniques. NCMe was dried over CaH_2 and distilled. Acetone was dried by distillation and stored over 4Å molecular sieves. IR spectra were measured on a Perkin–Elmer 457 spectrophotometer with KBr pellets. ^1H NMR spectra were

recorded on a JEOL JNM-100 PFT spectrometer. Microanalyses were performed in our laboratories.

[MCp_2X_2] (M = Mo, W; X = Cl, Br, I, SR) were prepared from the parent dihydrides [MCp_2H_2][24] as described previously [6,11].

Reactions of [$MCp_2(SR)_2$] with [$FeCp_2$][PF_6]

Preparation of [$MoCp_2(SCH_3)(NCMe)$][PF_6] (2a). To a suspension of [$MoCp_2(SCH_3)_2$] (1 mmol) in 30 ml of NCMe a solution of [$FeCp_2$][PF_6] (1 mmol) in the same solvent was added with stirring. The mixture was filtered and the filtrate evaporated to dryness. The residue was washed with dry Et_2O and then recrystallized from acetone/ethanol. Yield 70%.

Complexes **2b, c, d** were prepared in the same way in yields of ca. 70–80%.

Reactions of [MCp_2X_2] with [NO][PF_6]

Method 1 (In 1/1 M/NO^+ stoichiometry). Solid [NO][PF_6] (1 mmol) was added to a suspension of [$MoCp_2Br_2$] (1 mmol) in NCMe (25 ml). The purple-blue solution was filtered and concentrated. Careful addition of Et_2O caused precipitation of violet crystals of [$MoCp_2Br_2$][PF_6] in ca. 60% yield. Upon further addition of Et_2O to the mother liquor deep-blue crystals of [$MoCp_2Br(NCMe)$][PF_6] (**5b**) separated. They were recrystallized from NCMe/Et_2O. Yield ca. 40%.

Similar procedures gave compounds **5a, c, d, e, h**.

Method 2 (in 1/2 M/NO^+ stoichiometry). The reactions were performed as in method 1, but with 1 mmol of [NO][PF_6] and 0.5 mmol of [$M(Cp)_2X_2$]. After evaporation of the nitrile solvent the products were separated by fractional crystallization induced by addition of Et_2O, and purified by recrystallization from the same solvents.

Complexes **5c, f, g, i** and **6** (30% yield) were also prepared in this way.

Reactions of [MCp_2X_2] with TlPF_6 in NCR solvents

Preparation of [$MoCp_2I(NCMe)$][PF_6] (**5c**). A suspension of [$MoCp_2I_2$] (1 mmol) and Tl[PF_6] (1 mmol) in NCMe (30 ml) was refluxed for 30 h. The green solution was filtered, and concentrated, and upon addition of Et_2O green crystals separated. These were recrystallized from NCMe/Et_2O. Yield 80%.

Complexes **5b** and **j** were prepared similarly.

Reactions of [$MCp_2(SR)(NCMe)$][PF_6] with donor ligands L

Preparation of [$MoCp_2(SPh)(PPh_3)$][PF_6] (7a). Triphenylphosphine (0.6 mmol) was added to a solution of [$MoCp_2(SPh)(NCMe)$][PF_6] (0.6 mmol) in 50 ml of NCMe and the mixture refluxed for 30 min. The solvent was evaporated off under vacuum and the residue washed with Et_2O then recrystallized from Me_2CO/EtOH to give orange-red crystals. Yield 80%.

Complexes **7b, e, f,** and **g** were prepared similarly. Complexes **7c, d,** and **h** were prepared bubbling CO or NH_3 through refluxing solutions of the [$MCp_2(SR)$-$(NCMe)$][PF_6] complexes. The products were recrystallized from Me_2CO/EtOH. The reaction of **5c** with PPh_3 similarly gave [$MoCp_2I(PPh_3)$][PF_6] in quantitative yield.

Preparation of [$MoCp_2H(SPh)$] (8). A solution of [$MoCp_2(SPh)(NCMe)$][PF_6] (0.5 mmol) in 30 ml of NCMe was treated under reflux (4 h) with $NaBH_4$ (1 mmol).

The mixture was filtered and the solvent evaporated under vacuum. The residue was taken up in Me_2CO and the solution concentrated to a yellow product. This was recrystallized from $Me_2CO/EtOH$. Yield: 60%.

Preparation of [MoCp$_2$S(Ph)C(Me)$_2$O][PF$_6$] *(9)*. A solution of [MoCp$_2$-(SPh)(NCMe)][PF$_6$] (0.5 mmol) in 20 ml of Me_2CO was refluxed for 2 h. The resulting red solution was filtered and evaporated and the residue recrystallized from $Me_2CO/EtOH$. Yield 70%.

Preparation of [MoCp$_2$(NO)(NCMe)][PF$_6$] *(10)*. NO was bubbled for 2 h through a refluxing solution of [MoCp$_2$(SPh)(NCMe)][PF$_6$] (0.8 mmol) in NCMe (40 ml). The mixture was then filtered and the brown solution concentrated. Addition of EtOH gave a dark-brown microcrystalline precipitate, which was recrystallized from $Me_2CO/EtOH$. Yield 50%.

Reactions of [MCp$_2$X(NCMe)][PF$_6$] with [NO][PF$_6$]

When a suspension of [MoCp$_2$Br(NCMe)][PF$_6$] (1 mmol) in dry CH_2Cl_2 (20 ml) was treated with solid [NO][PF$_6$] (2.4 mmol) the solid turned red. The solid was filtered off and thoroughly washed with Et_2O. Yield 60%.

The analogous reaction with [MoCp$_2$I(NCMe)][PF$_6$] gave a turquoise-blue solid which could not be purified owing to extensive decomposition of its solutions.

Reactions of [WCp$_2$X(NCR)][PF$_6$] with amines

Preparation of [WCp$_2$(SPh){NH=C(Me)NH$_2$}][PF$_6$] *(12a)*. Gaseous NH_3 was bubbled for 2 h through a refluxing solution of [WCp$_2$(SPh)(NCMe)][PF$_6$] (1 mmol) in 40 ml of NCMe. The solution was filtered then taken to dryness. The residue was taken up in Me_2CO, and the solution was filtered. Addition of EtOH followed by concentration gave dark-red crystals, which were recrystallized from $Me_2CO/EtOH/Et_2O$. Yield 60%.

Preparation of [WCp$_2$Br{HN=C(Me)NH$_2$}][PF$_6$] *(12b)*. Gaseous NH_3 was bubbled for 30 min through a suspension of [WCp$_2$Br$_2$] (1 mmol) and Tl[PF$_6$] (1 mmol) in 50 ml of NCMe at 55°C. The mixture was then evaporated and the residue extracted with Me_2CO. Upon concentration of the extract and addition of EtOH, purple blue crystals separated, and these were recrystallized from the same solvents. Yield 50%.

Complexes **12c, d**, and **e** were prepared similarly in the appropriate nitrile by use of either gaseous NH_3 or $NHMe_2$.

X-Ray crystal structure of [MoCp$_2$I(NCMe)][PF$_6$] (5c)

Crystal data. $C_{12}H_{13}F_6IMoNP$; $M = 539.05$, triclinic, $P\bar{1}$, a 7.7989(6), b 10.3044(8), c 10.5565(5) Å, α 96.218(4), β 94.466(4), γ 102.697(5)°, V 818.21 Å^3, $Z = 2$, D_c 2.19 g cm^{-3}, λ(Mo-K_α) 0.71069 Å, μ 26.18 cm^{-1}, $F(000) = 512$.

Data collection. Data were collected at room temperature on a Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo-K_α radiation. Unit-cell parameters were refined from 2θ values of 73 reflections ($27.0° < 2\theta < 56.0°$), the intensities were measured in a ω–2θ scan mode (collection range $\pm h$, $\pm k$, l with $2.0° < 2\theta < 60.0°$). There was no significant intensity variation for three standard reflections.

Of 4726 unique reflections, 4183 with $F > 3\sigma(F)$ were used in the structure analysis.

Structure solution and refinement. The structure was solved by Patterson and Fourier methods and refined by full matrix least-squares using the SHELX system of programs [25]. After refinement with isotropic thermal parameters for all the non-hydrogen atoms an absorption correction was made by use of the DIFABS [26] program was applied. Further refinements were made with anisotropic thermal parameters for all the non-hydrogen atoms, to give $R = 0.057$ and $R_w = 0.066$ with a maximum shift/esd of 0.60.

The anisotropic thermal parameters for C(15),C(16) and C(19) atoms are rather large, suggesting that the Cp may be disordered. Attempts were made to refine a disordered model assuming two different arrangements for this Cp ring but with no success.

A weighting scheme with $w^{-1} = \sigma^2(F) + 0.0001(F)^2$ was used. Four strong low-angle reflections affected by extinction were omitted from the data. Hydrogen atoms were not observed and so were not included in the refinement. The largest peaks on the final difference Fourier map were located near the Mo and I atom. The maximum residual electron density 1.97 e Å^{-3} was 0.88 Å from the I atom. Scattering factors were taken from ref. 27.

Anisotropic thermal parameters for the non-hydrogen atoms and lists of observed and calculated structure factors are available from the authors.

Appendix

All the calculations were made by the Extended Hückel Method [28] with the Wolfsberg–Helmholz modification [29].

The basis set for the molybdenum atom consisted of $4d,5s$, and $5p$ orbitals. Only $3s$ and $3p$ orbitals were considered for the chlorine atom. The s and p orbitals were described by single Slater-type wave-functions and the d orbitals as contracted linear combinations of two Slater-type wave functions. The orbital exponents and parameters are listed in Table 12.

TABLE 12

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

Orbital	Slater exponent	$-H_{ii}$ (eV) [a]
H 1s	1.300	13.60 [b]
C 2s	1.625	21.40 [c]
C 2p	1.625	11.40 [c]
N 2s	1.950	26.00 [c]
N 2p	1.950	13.40 [c]
Cl 3s	2.033	30.00 [d]
Cl 3p	2.033	15.00 [d]
Mo 5s	1.96	8.77 [e]
Mo 5p	1.90	5.60 [e]
Mo 4d	[f]	11.60 [e,g]

[a] 1 eV = 96.4845 kJ mol^{-1}. [b] [28]. [c] R. Hoffmann, J. Chem. Phys., 40 (1964) 2745. [d] M. Elian and R. Hoffmann, Inorg. Chem., 14 (1975) 1058. [e] M. Kamata, K. Hirotsu, T. Higuchi, K. Tatsumi, R. Hoffmann, T. Yoshida and S. Otsuka, J. Am. Chem. Soc., 103 (1981) 5772. [f] $\xi_1 = 5.54$, $\xi_2 = 1.90$, $c_1 = 0.5899$, $c_2 = 0.5899$. [g] J.W. Richardson, W.C. Nieuwpoort, R.R. Powell and W.E. Edgell, J. Chem. Phys., 36 (1962) 1057.

The $MoCp_2Cl(NCMe)^+$ cation was modelled on the geometry of the iodide derivative, with eclipsed cyclopentadienyl rings and the following bond lengths (pm) and angles (°): Mo–Cl 247.0 [10], Mo–N 212.4, N–C 113.0, C–C (nitrile) 146.7, C–C (ring) 140, Mo–Cp 197.3, C–H 108, Cp–Mo–Cp 133.8, Cl–Mo–N 81.2.

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