(η^2-Acetonitrile)bis(η^5-cyclopentadienyl)molybdenum(II): The First Structurally Characterized Complex containing an η^2-Nitrile Ligand†

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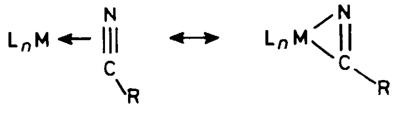
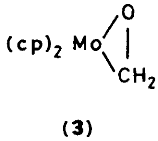
An *X*-ray diffraction study of Mo(cp)$_2$(MeCN) (cp = η^5-C$_5$H$_5$) has confirmed that acetonitrile is bound in an η^2 fashion. This is the first definitively characterized example of η^2-nitrile bonding to a transition metal.

The possibility of the existence of η^2 or 'sidebound' nitriles (**1**) or (**2**) has long been discussed with the assignments based primarily on the interpretation of i.r. spectroscopic evidence.[1,2] Some of these interpretations have involved rather small changes in the value of ν(CN), and therefore make certain structural assignments dubious at best.[1]



(**1**) (**2**)

In order unambiguously to establish the existence of this bonding mode for transition metal–nitrile complexes we have undertaken an *X*-ray crystallographic study of the complex we considered most likely to be correctly formulated as having an η^2-RCN moiety, namely Mo(cp)$_2$(MeCN)[2a] (cp = η^5-C$_5$H$_5$) whose tungsten analogue has been recently described.[2b] This choice was based on the fact that for both compounds the i.r. spectra had a band attributed to ν(CN) several hundred wavenumbers, *e.g.*, 1 725 cm^{-1} in W(cp)$_2$(MeCN), below that of σ^1-acetonitrile, *ca.* 2 000 cm^{-1}. This observation would be in accord with nitrile bonding of type (**1**) and/or (**2**), and directly analogous to the continuum used to describe the bonding of olefins and acetylenes to transition metal centres.[3] Additionally, the (cp)$_2$Mo moiety has been shown to act like a metallocarbene,[4] while Floriani and co-workers[5] have demonstrated its interaction with carbon–heteroatom π-bonding systems to produce η^2-bonded compounds such as (**3**), by reaction of *in situ* generated molybdocene with paraformaldehyde.



(**3**)

An *X*-ray structural study was made on the deep red crystals obtained, after numerous recrystallizations, of the product of the sodium amalgam reduction of Mo(cp)$_2$Cl$_2$ in acetonitrile. The analysis has confirmed the η^2-bonded structure. The unit cell contains two crystallographically independent molecules with essentially the same structure. A diagram of one molecule is given in the Figure; bond lengths and angles for both molecules are given in Table 1. The structure comprises a normal bent (cp)$_2$Mo unit in which the Cp–Mo–Cp (Cp = the centroid of the cp ring) angle is 141.6°, with the bent MeCN unit bound so that the CCN plane is approximately perpendicular to the plane containing the metal and the two ring centroids, see Table 1(*c*). The geometry of the nitrile fragment, in which the 'C≡N' bond length is slightly increased over that expected for a normal triple bond,[6] and the methyl group is bent 'outwards' so that the C–C–N angle is reduced from 180 to 138°, is analogous to that found in many η^2-bonded acetylenes. This suggests that the metalla-azacyclopropenyl canonical form (**2**) is a significant contributor to the overall electronic structure. The only other structural information[7] is that on Pt(PPh$_3$)$_2$(η^2-CF$_3$CN).[8] Hyperfine splitting in e.s.r. spectra of *trans*-[Cr(NCR)$_2$(PMe$_2$CH$_2$CH$_2$PMe$_2$)$_2$]$^{2+}$ (R = Me or Et) has been attributed to interaction of CH$_3$ groups of MeCN and CH$_2$ groups of EtCN with a 17-electron chromium(I) atom in a minor constituent where the nitrile is η^2-bonded.[9]

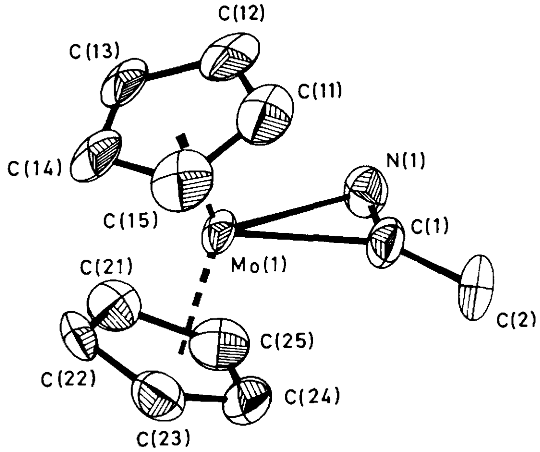


Figure. The molecular structure of (η^2-acetonitrile)bis(η^5-cyclopentadienyl)molybdenum(II)

Experimental

The complex Mo(cp)$_2$(η^2-MeCN) was prepared by the reduction of Mo(cp)$_2$Cl$_2$ (0.5 g, 1.7 mmol) in MeCN (50 cm^3) with an excess of Na/Hg amalgam.[2a] The solution was stirred for 1 h during which time the colour changed from yellow to deep red. The resultant solution was separated from the amalgam and filtered. After concentration and cooling at

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† *Supplementary data available* (No. SUP 56597, 4 pp.): H-atom co-ordinates, least-squares planes, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii–xx. Structure factors are available from the editorial office.

Table 1. Selected bond lengths, bond angles, and interplanar angles for Mo(cp)$_2$(MeCN)

(*a*) Bond lengths (Å)

Molecule (A)		Molecule (B)	
N(1)–Mo(1)	2.219(7)	N(1)–Mo(1)	2.216(7)
C(1)–Mo(1)	2.124(8)	C(1)–Mo(1)	2.110(8)
C(11)–Mo(1)	2.284(9)	C(11)–Mo(1)	2.261(8)
C(12)–Mo(1)	2.340(9)	C(12)–Mo(1)	2.275(9)
C(13)–Mo(1)	2.282(9)	C(13)–Mo(1)	2.300(9)
C(14)–Mo(1)	2.258(8)	C(14)–Mo(1)	2.331(10)
C(15)–Mo(1)	2.251(9)	C(15)–Mo(1)	2.311(9)
C(21)–Mo(1)	2.303(9)	C(21)–Mo(1)	2.282(9)
C(22)–Mo(1)	2.270(9)	C(22)–Mo(1)	2.259(9)
C(23)–Mo(1)	2.275(10)	C(23)–Mo(1)	2.282(9)
C(24)–Mo(1)	2.297(10)	C(24)–Mo(1)	2.325(10)
C(25)–Mo(1)	2.318(9)	C(25)–Mo(1)	2.308(9)
Cp(1)–Mo(1)	1.952(9)	Cp(1)–Mo(1)	1.959(9)
Cp(2)–Mo(1)	1.957(9)	Cp(2)–Mo(1)	1.957(9)
C(1)–N(1)	1.200(10)	C(1)–N(1)	1.211(10)
C(2)–C(1)	1.491(11)	C(2)–C(1)	1.508(12)
C(12)–C(11)	1.403(13)	C(12)–C(11)	1.399(12)
C(15)–C(11)	1.394(13)	C(15)–C(11)	1.426(12)
C(13)–C(12)	1.382(11)	C(13)–C(12)	1.399(13)
C(14)–C(13)	1.367(13)	C(14)–C(13)	1.407(14)
C(15)–C(14)	1.409(13)	C(15)–C(14)	1.392(11)
C(22)–C(21)	1.395(11)	C(22)–C(21)	1.411(11)
C(25)–C(21)	1.383(11)	C(25)–C(21)	1.391(11)
C(23)–C(22)	1.426(11)	C(23)–C(22)	1.411(11)
C(24)–C(23)	1.420(12)	C(24)–C(23)	1.396(11)
C(25)–C(24)	1.394(14)	C(25)–C(24)	1.391(12)

(*b*) Bond angles (°)

Molecule (A)		Molecule (B)	
C(1)–Mo(1)–N(1)	32.0(2)	C(1)–Mo(1)–N(1)	32.4(2)
Cp(1)–Mo(1)–Cp(2)	142.3(3)	Cp(1)–Mo(1)–Cp(2)	140.9(3)
C(2)–C(1)–Mo(1)	142.6(6)	C(2)–C(1)–Mo(1)	144.9(5)
C(2)–C(1)–N(1)	139.0(7)	C(2)–C(1)–N(1)	136.5(6)
C(15)–C(11)–C(12)	109.5(9)	C(15)–C(11)–C(12)	107.9(8)
C(13)–C(12)–C(11)	106.1(10)	C(13)–C(12)–C(11)	107.1(9)
C(14)–C(13)–C(12)	109.9(9)	C(14)–C(13)–C(12)	109.6(8)
C(15)–C(14)–C(13)	108.5(9)	C(15)–C(14)–C(13)	107.1(9)
C(14)–C(15)–C(11)	106.0(9)	C(14)–C(15)–C(11)	108.2(9)
C(25)–C(21)–C(22)	108.0(9)	C(25)–C(21)–C(22)	106.2(8)
C(23)–C(22)–C(21)	108.8(7)	C(23)–C(22)–C(21)	108.6(7)
C(24)–C(23)–C(22)	105.8(9)	C(24)–C(23)–C(22)	107.5(8)
C(25)–C(24)–C(23)	108.4(8)	C(25)–C(24)–C(23)	107.6(8)
C(24)–C(25)–C(21)	109.0(9)	C(24)–C(25)–C(21)	110.1(8)

(*c*) Interplanar angles (°)

Planes: I, Mo(1),Cp(1),Cp(2); II, Mo(1),N(1),C(1); III, N(1),C(1),C(2) (calculated using XANADU program *)

	Molecule (A)	Molecule (B)
I–II	89.97	92.13
I–III	89.79	92.17
II–III	1.72	0.35

* XANADU, P. Roberts and G. M. Sheldrick, University of Cambridge, 1976.

Table 2. Fractional atomic co-ordinates (× 10^4) for Mo(cp)$_2$(MeCN)

Atom	*x*	*y*	*z*
Mo(1a)	1 622(1)	1 495(0.5)	113(0.5)
N(1a)	488(6)	1 913(4)	−559(2)
C(1a)	1 423(7)	2 288(5)	−587(2)
C(2a)	2 059(9)	2 935(6)	−945(3)
C(11a)	1 352(9)	2 939(5)	448(3)
C(12a)	305(8)	2 465(5)	552(3)
C(13a)	601(9)	1 737(5)	878(3)
C(14a)	1 773(8)	1 766(6)	991(3)
C(15a)	2 273(9)	2 514(7)	717(3)
C(21a)	1 608(8)	−90(5)	92(3)
C(22a)	2 583(7)	207(5)	379(3)
C(23a)	3 338(8)	708(5)	33(3)
C(24a)	2 784(10)	695(6)	−470(3)
C(25a)	1 737(9)	206(5)	−426(3)
Mo(1b)	4 140(1)	3 818(0.5)	2 414(0.5)
N(1b)	3 213(6)	4 063(4)	3 173(2)
C(1b)	4 193(7)	4 385(5)	3 183(2)
C(2b)	4 932(8)	4 909(6)	3 576(3)
C(11b)	4 198(8)	4 364(5)	1 576(2)
C(12b)	4 796(9)	4 992(6)	1 897(3)
C(13b)	3 975(11)	5 368(5)	2 247(3)
C(14b)	2 864(10)	4 983(6)	2 149(3)
C(15b)	2 994(7)	4 370(5)	1 729(3)
C(21b)	3 878(7)	2 281(5)	2 271(3)
C(22b)	4 822(8)	2 593(5)	1 957(3)
C(23b)	5 732(7)	2 889(5)	2 296(3)
C(24b)	5 361(9)	2 744(5)	2 816(3)
C(25b)	4 235(9)	2 376(5)	2 795(3)

−20 °C for *ca.* 12 h dark red prisms were isolated (Found: C, 49.2; H, 5.1; N, 5.6. Calc. for $C_{12}H_{13}MoN$: C, 49.4; H, 5.4; N, 5.8%). I.r.: ν(CN) 1 750 cm^{-1}. N.m.r.: ^{1}H, δ 4.41 (cp), 2.66 (Me).

Crystals were mounted in thin-walled glass capillaries and sealed for the crystallographic analysis. Following a preliminary photographic examination, cell dimensions and intensity data were obtained using a CAD4 diffractometer with graphite-monochromated Cu-K_α radiation (λ = 1.541 78 Å) and following previously detailed procedures.[10]

Crystal Data.—$C_{12}H_{13}MoN$, M = 267.18, orthorhombic, a = 11.404(2), b = 14.534(1), c = 25.245(1) Å, U = 418.3 Å^3, space group *Pbca*, Z = 16, D_c = 1.70 g cm^{-3}, $F(000)$ = 2 144, μ(Cu-K_α) = 100.93 cm^{-1}; of the 4 620 intensity data measured, 3 958 were unique and 2 445 were observed [$I > 2.0\sigma(I)$].

The intensity data were corrected for absorption using azimuthal scan profiles. The structure was solved and refined *via* standard procedures using SHELX 76.[11] Non-hydrogen atoms were refined anisotropically; hydrogen atoms of the methyl groups were located in difference maps and freely refined with individual isotropic thermal parameters, whilst those on the cp rings were included in calculated positions (AFIX 85).[11] Final R and R' values were 0.033 and 0.038 respectively, with weights calculated according to $w = 1/[\sigma^2(F_o) + 0.0005\ F_o^{\ 2}]$ giving acceptable agreement analysis. The final atomic co-ordinates are given in Table 2. All calculations were made using a VAX 11/750 computer; scattering factor data were taken from the usual source.[12]

Acknowledgements

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