Surprises in enolate binding at high valent molybdenum

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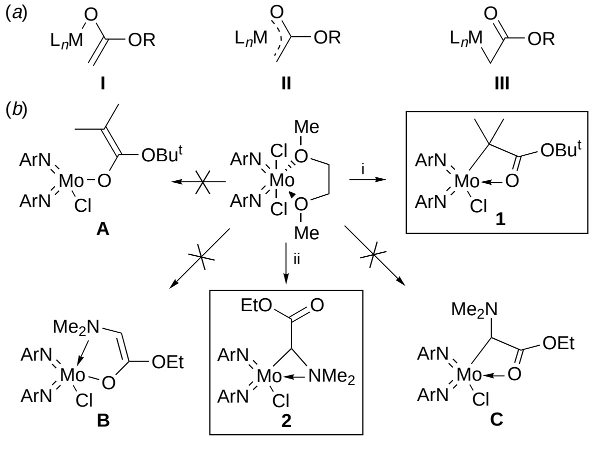
Treatment of [Mo(NAr)$_2$Cl$_2$(DME)] (Ar = 2,6-diisopropylphenyl; DME = 1,2-dimethoxyethane) with LiOC(OBu^t)CMe$_2$ at low temperature affords the unexpected carbon-bound molybdenum(VI) enolate complex [Mo(NAr)$_2$Cl{η^2-C(Me$_2$)CO$_2$Bu^t}] 1; the novel α-aminoenolate derivative [Mo(NAr)$_2$Cl{η^2-CH(NMe$_2$)CO$_2$Et}] 2 is obtained under analogous conditions using LiNPr$^i_2$/Me$_2$NCH$_2$CO$_2$Et; the structures of 1 and 2 confirm the carbophilic nature of the [Mo(NAr)$_2$] core.

Transition metal enolate chemistry nowadays features prominently in organic synthetic methodology. The enolate ligand, an intermediate between an allyl and an acetate unit, has two different binding modes. Depending on the oxophilicity/carbophilicity of the metal centre, the enolato functionality can bind either *via* the 'CH$_2$' unit or *via* its oxygen atom [Scheme 1(*a*)], giving rise to different reactivity in further transformations. In general, the oxygen binding mode **I** predominates for early transition metals, whereas M–C bonding **III** is favoured by the softer late transition metals. A number of oxygen bound enolate complexes of early transition metals have been isolated and structurally characterised.[1–4] For molybdenum, only low valent molybdenum enolate complexes as in [MoCp(CO)$_3$R] (R = enolate ligand) have been made and these are exclusively carbon bound.[5–9]

With a view to exploiting the isolobal relationship between the Cp$_2$M^{IV} and the (RN)$_2$M^{VI} cores,[10,11] we became interested in establishing whether or not the relatively 'hard' high valent molybdenum centre would promote a switch from a carbon-bound to an oxygen-bound enolate binding mode, since oxygen-bound enolate complexes of early transition metal[12,13] and rare earth metallocenes[14,15] are implicated as the active species in the polymerisation of methyl methacrylate (MMA). Here, we describe the first examples of high valent molybdenum enolate complexes and their unusual and unanticipated structures.

Complex **1** was prepared according to Scheme 1(*b*), from [Mo(NAr)$_2$Cl$_2$(DME)] and [LiOC(OBu^t)CMe$_2$][16] at −78 °C. Recrystallisation from pentane at −30 °C afforded **1** as an orange crystalline product.‡ A second recrystallisation from heptane gave X-ray quality crystals of **1** and the molecular structure is shown in Fig. 1.§ Compound **1** decomposes slowly in solution ($t_{1/2}$ *ca.* 1 week) but can be stored for weeks in the solid state at −20 °C.



Scheme 1 (*a*) Potential binding modes of the ester enolate ligand. (*b*) *Reagents and conditions*: i, LiOC(OBu^t)CMe$_2$ (1 equiv.), Et$_2$O, −78 °C → room temp.; ii, LDA, Me$_2$NCH$_2$CO$_2$Et, THF, −78 °C → room temp.

The X-ray analysis of **1** reveals the unexpected bidentate coordination of the enolate ligand *via* the carbonyl oxygen atom O(2) and the α-carbon atom C(1). The geometry at Mo, although five-coordinate, is probably best described as distorted tetrahedral with the chelating enolate ligand occupying one of the tetrahedral sites; the angles subtended at Mo by the two imido N atoms and the Cl atom range between 105.4(4) and 111.3(3)°. The Mo–N distances are typical of 'linear' imido ligands, the angles at the N atoms being 157.6(8) [N(10)] and 158.5(8)° [N(23)].[17,18] The feature of most interest is the pattern of bonding to, and within, the enolate ligand. The 'stronger' coordination is to the α-C atom [Mo–C(1) 2.208(11) Å] whereas that to the carbonyl O atom is 2.370(6) Å. The C(1)–C(2) linkage [1.50(2) Å] has lost all its double bond character, though there is not a full pyramidalisation at C(1), the sum of the C–C(1)–C angles being *ca.* 342°. There is evidence for delocalisation between the two O atoms of the ester, the C(2)–O(2) and C(2)–O(3) distances being 1.24(2) and 1.29(2) Å, respectively.

Interestingly, complex **1** unveils a fundamental difference between the isolobal Cp$_2$M^{IV} and the (ArN)$_2$M^{VI} cores. Whereas the analogous Cp$_2$M^{IV} complex [Cp$_2$Ti{OC(OMe)CMe$_2$}Cl] was found to be an O-bound enolate complex,[4] complex **1** does not bind similarly *via* the O atom as in complex **A**, but clearly establishes the carbophilic nature of the (ArN)$_2$Mo^{VI} core.

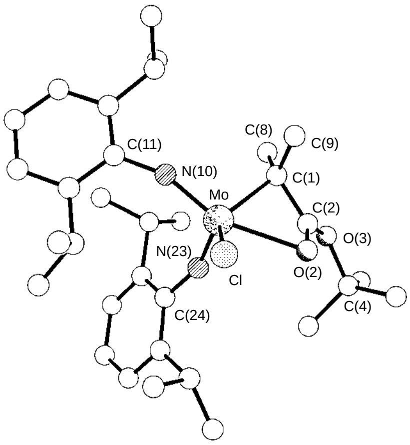


Fig. 1 Molecular structure of **1**. Selected bond lengths (Å) and angles (°); Mo–C(1) 2.208(11), Mo–C(2) 2.579(12), Mo–N(10) 1.754(9), Mo–N(23) 1.730(9), Mo–Cl 2.362(3), C(1)–C(2) 1.50(2), C(2)–O(2) 1.24(2), C(2)–O(3) 1.29(2); C(1)–Mo–O(2) 60.6(4), C(1)–Mo–Cl 128.1(3), C(1)–Mo–N(10) 101.4(4), C(1)–Mo–N(23) 105.4(5), O(2)–Mo–Cl 82.4(2), O(2)–Mo–N(10) 158.2(4), O(2)–Mo–N(23) 92.0(4), Cl–Mo–N(10) 102.6(3), Cl–Mo–N(23) 111.3(3), N(10)–Mo–N(23) 105.4(4), Mo–C(1)–C(2) 85.9(7), C(1)–C(2)–O(2) 115.1(11), C(2)–O(2)–Mo 85.1(6), C(11)–N(10)–Mo 157.6(8), C(24)–N(23)–Mo 158.5(8).

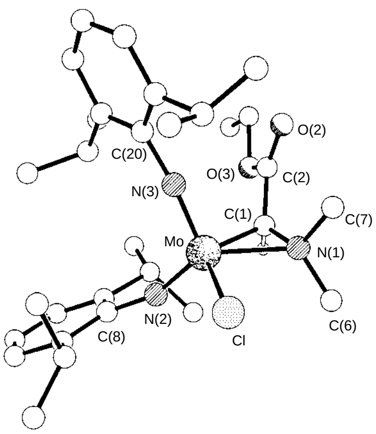


Fig. 2 Molecular structure of **2**. Selected bond lengths (Å) and angles (°): Mo–C(1) 1.149(6), Mo–N(1) 2.198(4), Mo–N(2) 1.753(4), Mo–N(3) 1.746(4), Mo–Cl 2.336(1), C(1)–N(1) 1.452(7), C(1)–C(2) 1.477(7), C(2)–O(2) 1.219(7), C(2)–O(3) 1.337(7), C(1)–Mo–N(1) 39.0(2), C(1)–Mo–N(2) 103.8(2), C(1)–Mo–N(3) 101.4(2), C(1)–Mo–Cl 124.3(2), N(1)–Mo–N(2) 125.8(2), N(1)–Mo–N(3) 112.4(2), N(1)–Mo–Cl 85.8(1), N(2)–Mo–N(3) 113.2(2), N(2)–Mo–Cl 105.9(1), N(3)–Mo–Cl 108.3(2), Mo–C(1)–N(1) 72.3(3), Mo–N(1)–C(1) 68.7(3), C(8)–N(2)–Mo 171.1(4).

Subsequently, an attempt was made to force the enolate ligand into an O-bound coordination mode, by using an α-aminoester enolate ligand [Scheme 1(*b*)]. It was anticipated that this ligand should produce a five-membered chelate, bound *via* the N and the carbonyl O donor to the metal centre as in complex **B** [Scheme 1(*b*)]. However, the strong carbophilic nature of the $(ArN)_2Mo^{VI}$ fragment again became apparent, resulting in the C-bound enolate complex **2**. Moreover, a three-membered chelate with an intramolecular coordination of the amine donor is formed. Thus, chelation of the carbonyl O to give a four-membered ring as in complex **C** is not observed [Scheme 1(*b*)]. Similar preferred arrangements have been reported previously for low valent Mo complexes.[19,20]

The preparation of complex **2** involved the *in situ* formation of the lithium enolate from LDA and $Me_2NCH_2CO_2Et$ in THF at −78 °C. Addition to $[Mo(NAr)_2Cl_2(DME)]$ at this temperature and extraction of the product with pentane at room temp. gave complex $[Mo(NAr)_2\{CH(NMe_2)CO_2Et\}Cl]$ **2** as a dark red crystalline solid.‡ Suitable crystals for X-ray analysis were obtained from pentane, and the molecular structure is given in Fig. 2.§

The X-ray structure of **2** again reveals an unexpected coordination of the α-aminoenolate ligand, with chelation *via* the amino atom N(1) and the α-C atom C(1) [with consequent loss of double bond character for C(1)–C(2)], rather than the carbonyl O atom O(2). As in **1**, the coordination at Mo can be considered as distorted tetrahedral, the enolate occupying a single coordination site [the N–Mo–N and N–Mo–Cl angles are in the range 106.9(1)–113.2(2)°]. The Mo–N(imido) distances are again typical of 'linear' species, with angles at N of 161.0(4) and 171.1(4)° for N(2) and N(3) respectively. As in **1**, the 'strong' bond to the α-aminoenolate ligand is to the α-C atom [2.149(6) Å] whereas that to N(1) is 2.198(4) Å. This contrasts with the pattern observed for related chelation to a Mo^{II} centre where the Mo–C bond is noticeably longer than that to N.[20] In the absence of coordination to the ester carbonyl O atom there is no delocalisation between the two O atoms.

In conclusion, we have shown that enolate complexes of the bis(imido)Mo^{VI} core are readily accessible and that the metal–carbon bonded form is favoured over the oxygen-bonded arrangement, confirming the surprisingly carbophilic nature of the Mo^{VI} centres in these complexes.

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Notes and References

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‡ Satisfactory microanalyses and MS data were obtained for complexes **1** and **2**. *Selected spectroscopic data*: for **1**: IR (CsI, Nujol, cm^{-1}): 1567 [ν(C=O)]; ^1H NMR (C_6D_6, 250 MHz, 298 K), δ 6.99–6.91 (m, 6 H, *m*- and *p*-$C_6H_3Pr^i_2$-2,6), 3.92 [spt, 4 H, $^3J_{HH}$ 6.8 Hz, $CH(CH_3)_2$], 1.73 [s, 6 H, $C(CH_3)_2$], 1.34 [s, 9 H, $C(CH_3)_3$], 1.20 [d, 12 H, $^3J_{HH}$ 6.8 Hz, $CH(CH_3)_2$], 1.13 [d, 12 H, $^3J_{HH}$ 6.8 Hz, $CH(CH_3)_2$]; ^{13}C NMR (C_6D_6, 62.5 MHz, 298 K), δ 185.7 (s, O–C=O), 153.3 (s, *ipso*-$C_6H_3Pr^i_2$-2,6), 143.5 (s, *o*-$C_6H_3Pr^i_2$-2,6), 127.0 (d, *p*-$C_6H_3Pr^i_2$-2,6), 123.1 (d, *m*-$C_6H_3Pr^i_2$-2,6), 86.4 [s, Mo–$C(CH_3)_2$], 56.7 [s, $C(CH_3)_3$], 28.8, 28.0, 24.6, 24.0 (4s, 2Pr^i *Me*, Bu^t *Me*, Mo–C(*Me*)$_2$, 23.0 [d, $CH(CH_3)_2$]. For **2**: IR: 1718m [ν (C=O)]; ^1H NMR (C_6D_6, 250 MHz, 298 K), δ 7.1–6.8 (m, 6 H, Ar-H), 4.0–3.8 [4 spt., 4 H, $^3J_{HH}$ 6.8 Hz, $CH(CH_3)_2$], 3.85–3.57 (q, 2 H, $^3J_{HH}$ 7.1 Hz, OCH_2CH_3), 3.73 [s, 1 H, $(CH_3)_2NCH$], 3.12, 2.33 [2s, 6 H, $(CH_3)_2NCH$], 1.37, 1.24, 1.20, 1.14 [4d, 24 H, $^3J_{HH}$ 6.8 Hz, $CH(CH_3)_2$], 0.75 (t, 3 H, $^3J_{HH}$ 7.1 Hz, OCH_2CH_3). ^{13}C NMR (C_6D_6, 62.5 MHz, 298 K), δ 170.0 (s, C=O), 154.2, 153.0, 146.6, 140.9, 128.3, 127.6, 125.3, 122.5 (8s, ArC), 60.2 (s, OCH_2CH_3), 58.8 (s, NCH), 51.0, 42.8 [2s, $(CH_3)_2N$], 28.9, 28.5 [2s, $CH(CH_3)_2$], 24.4, 23.9, 23.4, 23.2 [4s, $CH(CH_3)_2$], 14.1 (s, OCH_2CH_3).

§ *Crystal data*: for **1**: $C_{32}H_{49}ClMoN_2O_2$, M = 625.1, monoclinic, space group $P2_1$ (no. 4), a = 9.376(2), b = 11.061(4), c = 16.496(3) Å, β = 103.18(2)°, U = 1665.8(7) Å^3, Z = 2, D_c = 1.25 g cm^{-3}, μ(Mo-Kα) = 5.0 cm^{-1}, $F(000)$ = 660. An orange plate of dimensions 0.33 × 0.32 × 0.07 mm was used. For **2**: $C_{30}H_{46}ClMoN_3O_2$, M = 612.1, monoclinic, space group $C2/c$ (no. 15), a = 22.823(1), b = 8.981(1), c = 30.877(4) Å, β = 90.34(1)°, U = 6329(1) Å^3, Z = 8, D_c = 1.29 g cm^{-3}, μ(Cu-Kα) = 43.9 cm^{-1}, $F(000)$ = 2576. An orange–red prism of dimensions 0.18 × 0.10 × 0.07 mm was used. 2661 (4325) Independent reflections were measured at 203 K on Siemens P4 diffractometers with graphite monochromated Mo-Kα and Cu-Kα (rotating anode source) radiation for **1** and **2** respectively using ω-scans. The structures were solved by direct methods and all the non-hydrogen atoms were refined anisotropically (with absorption corrected data for **2**) using full-matrix least squares based on F^2 to give R_1 = 0.057 (0.046), wR_2 = 0.097 (0.098) for 2088 (3430) independent observed reflections [$|F_o| > 4\sigma)|F_o|$), $2\theta \geqslant 47°$ (115°)] and 343 (339) parameters for **1** and **2** respectively. The absolute chirality of **1** could not be unambiguously determined. CCDC 182/776.

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