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Preliminary communication

Synthesis of molybdenum complexes containing η^3-bonded *trans*-butadienyl ligands: crystal structure of [Mo(2,2′-bipyridine)(CO)$_2$-(η^3-CH$_2$=C(CONHMe)=C=CH$_2$)(O$_2$CC$_3$F$_7$)]

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Abstract

Reaction of $Ph_4P[Mo(2,2'\text{-bipyridine})Cl(CO)_3]$ with 1,4-dichlorobut-2-yne in the presence of primary or secondary aliphatic amines gives high yields of neutral molybdenum complexes containing 2-substituted η^3-bonded *trans*-butadienyl ligands. The crystal structure of the perfluorocarboxylate derivative $[Mo(2,2'\text{-bipyridine})(CO)_2(\eta^3\text{-}CH_2C(CONHMe)C{=}CH_2)(O_2CC_3F_7)]$ has been determined.

We showed recently that reaction of $Ph_4P[Mo(bipy)Cl(CO)_3]$ (bipy = 2,2′-bipyridine) with $ClCH_2{\equiv}CCH_2Cl$ in wet methanol gave high yields of $[Mo(bipy)Cl(CO)_2(\eta^3\text{-}CH_2{=}C(CO_2Me){=}C{=}CH_2)]$ (**1**), which contains an η^3-bonded *trans*-butadienyl ligand [1]. A single crystal X-ray diffraction study of this product revealed unusual features within the metal-η^3-butadienyl fragment. Thus the Mo–C separations at 2.32(4), 2.22(3) and 2.22(3) Å are abnormally short compared to those in neutral Mo-η^3-allyl complexes [2], and the uncoordinated $C{=}CH_2$ bond length at 1.45(5) Å appeared anomolously long [3] even after allowance for the large uncertainty in this distance. As very few metal-η^3-butadienyl complexes have been prepared and characterised crystallographically [4], we wished to explore what seemed to be a facile, general route to a range of 2-substituted derivatives, and confirm via X-ray crystallography the anomalous structural features described above.

Treatment of $Ph_4P[Mo(bipy)Cl(CO)_3]$ in a mixture of dry, deoxygenated methanol and tetrahydrofuran at low temperature with an excess of amine RR′NH (R = Me, Et, n-Pr, $CH_2CH{=}CH_2$ or $CH_2C{\equiv}CH$, R′ = H; R = R′ = Me, Et or n-Pr) followed by 1,4-dichlorobut-2-yne yielded products of general formula $[Mo(bipy)Cl(CO)_2(\eta^3\text{-}CH_2C(CONRR')C{=}CH_2)]$ in 60–80% yields. Reaction of $[Mo(bipy)Cl(CO)_2(\eta^3\text{-}CH_2C(CONHMe)C{=}CH_2)]$ with sodium heptafluorobutyrate

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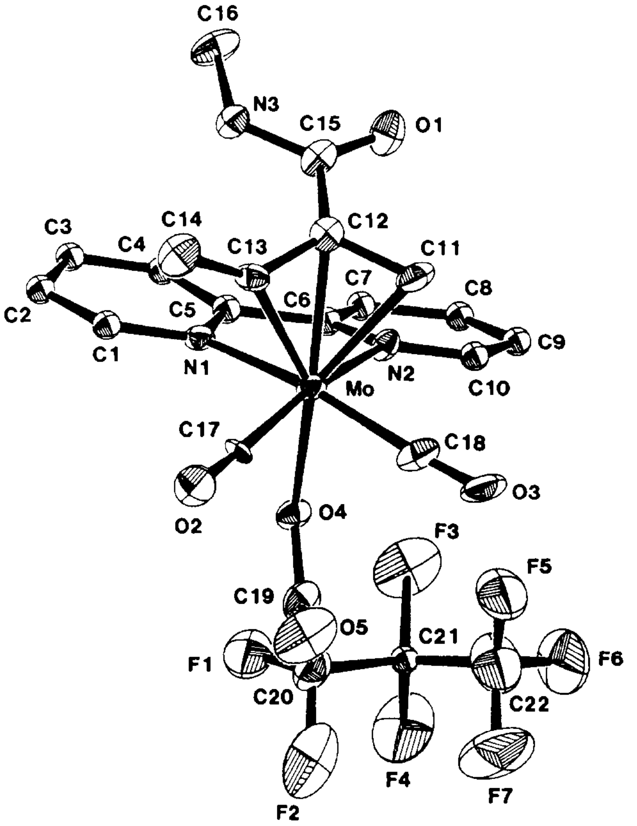

Fig. 1. Structure of 2. Pertinent distances (Å) and angles (°); Mo–C(11), 2.314(13); Mo–C(12), 2.235(10); Mo–C(13), 2.200(10); C(13)–C(14), 1.335(18); C(12)–C(15), 1.487(16); C(11)–C(12)–C(13), 112.5(1.0); C(12)–C(13)–(C14), 141.7(1.3).

in acetone in the presence of silver tetrafluoroborate yielded the carboxylate analogue [Mo(bipy)($O_2CC_3F_7$)$(CO)_2$(η^3-$CH_2C(CONHMe)C{=}CH_2$] (2), which was readily soluble in polar organic solvents and formed crystals from CH_2Cl_2/hexane suitable for X-ray crystallography *. Figure 1 shows an ORTEP view of this molecule and the atom numbering scheme used. The molybdenum coordination sphere can be described as pseudooctahedral, with normal bond distances between the metal atom and the donor atoms of the 2,2′-bipyridine, carbonyls and monodentate carboxylate ligands. The bond lengths and angles associated with the metal-bonded η^3-$CH_2C(CONHMe)C{=}CH_2$ moiety agree well, with one exception,

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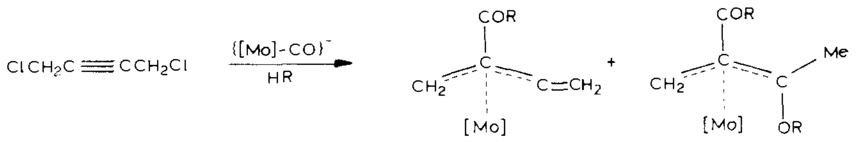
* *Crystal data*: $C_{22}H_{16}F_7O_5N_3Mo$, $M = 631.3$, triclinic, a 7.440(3), b 9.727(3), c 17.748(6) Å, α 100.57(3), β 94.84(2), γ 103.89(2)°, $U = 1214.67$ Å^3, D_c 1.73 g cm^{-3}, $Z = 2$, $F(000) = 628$, λ(Mo-K_α) 0.7107 Å, μ(Mo-K_α) 5.49 cm^{-1}, space group $P\bar{1}$ from the successful structure determination. For 2 2337 reflections with $I > 3\sigma(I)$ were used for refinement calculations, and, as we were unable to apply an absorption correction to data from this crystal, 72 reflections for which F_{obs} and F_{calc} differed by a factor of more than 3σ were omitted from the final cycles. The Mo, F, O and P atoms were refined anisotropically, and the remaining atoms isotropically. The anomolous dispersion correction factors for non-hydrogen atoms were taken from the literature. The final R value was 0.064.



(1)

[Mo] = Mo(bipy)(CO)$_2$Cl

R = OMe, OEt, NHMe, NHEt, NHPr, NHCH$_2$CH=CH$_2$, NHCH$_2$C≡CH, NMe$_2$, NEt$_2$ or NPr$_2$

R = OMe or OEt only

with dimensions for the η^3-CH$_2$C(CO$_2$Me)C=CH$_2$ ligand. Thus only carbon atoms C(11), C(12) and C(13) are bonded to molybdenum, with metal–carbon distances of 2.314(13), 2.235(10) and 2.200(10) Å, respectively, and the CONHMe substituents in **2** and **1** show similar conformations with respect to the Mo(bipy)(CO)$_2$ plane. However, in **2** the C–C separation in the non-coordinated C=CH$_2$ entity is at 1.335(18) Å, very similar to the C–C(terminal) separation of 1.344 ± 0.001 Å in free butadiene [3], and considerably shorter than the analogous distance in the η^3-CH$_2$C(CO$_2$Me)C=CH$_2$ ligand in **1**. The ^{1}H and ^{13}C NMR data recorded at ambient temperature for solutions of **2** * in CD$_2$Cl$_2$ were in accord with the solid-state structure, and provided no evidence of any facile rearrangement of the type noted for some other [Mo(η^3-allyl)(CO)$_2$(L$_2$)A] (L$_2$ = neutral bidentate, A = halide or carboxylate) complexes [5].

Thus we have been able to extend the reaction sequence reported earlier [1] for primary alcohols (R = Me or Et in eq. 1) to include a range of simple and functionalised primary and secondary amines. However, we found no evidence for the double additition of amines leading to a η^3-CH$_2$(CONRR')CMe(NR') or related ligand-containing metal complex. In view of the synthetic utility demonstrated for allylcarbonylmolybdenum complexes [6], and the evident steric control exerted by the bipyridine ligand in **1** and **2** on the butadienyl ligand, the reactivity of these derivatives is of considerable interest.

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* Selected spectroscopic data for **2**: ^{1}H NMR(CD$_2$Cl$_2$): δ(ppm) 7.5–8.9(m, 8H, aromatics), 6.31(d, 1H, J 2.2, =CH$_2$), 5.79(d, 1H, J 2.2 =CH$_2$), 5.31(q, 1H, J 5.0, NH), 3.96(2, 1H, *syn*-H), 1.99(d, 3H, J 5.0, NMe) 1.96(s, 1H, *anti*-H); ^{13}C-{^{1}H} NMR: δ(ppm) 222.7 (CO), 219.9 (O$_2$CC$_3$F$_7$), 152.7, 152.3, 140.1, 139.8, 126.6, 126.3(aromatics), 176.4(*C*ONHMe), 121.9(*C*=CH$_2$), 120.0(C–*C*–C), 106.1(C=*C*H$_2$), 41.5(CH$_2$), 26.0(NMe), IR (cm^{-1}): 3440w ν(NH), 1976s ν(CO), 1898s ν(CO) 1699m ν(CO$_2$)$_{asym}$,