The Reaction of MoMe(CO)$_3$(η-C$_5$H$_5$) with LiEt$_3$BH, Formation of an Anionic η^2-Acetaldehyde–Molybdenum Complex via Formyl Alkyl and Hydrido Acyl Molybdenum Intermediates

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The reaction of MoMe(CO)$_3$(η-C$_5$H$_5$) with LiEt$_3$BH results in initial formation of the anionic formyl Mo(CHO)Me(CO)$_2$(η-C$_5$H$_5$)$^-$ (3) which undergoes subsequent successive rearrangements to the hydrido acyl Mo[C(O)Me]H(CO)$_2$(η-C$_5$H$_5$)$^-$ (4) and the η^2-acetaldehyde complex Mo(η^2-MeCHO)(CO)$_2$(η-C$_5$H$_5$)$^-$ (2).

Activation of carbonyl ligands by hydride donors is a subject of attention owing to its relevance to CO reduction. We report such an activation for a molybdenum alkyl complex and the subsequent isomerisation of the primary product.
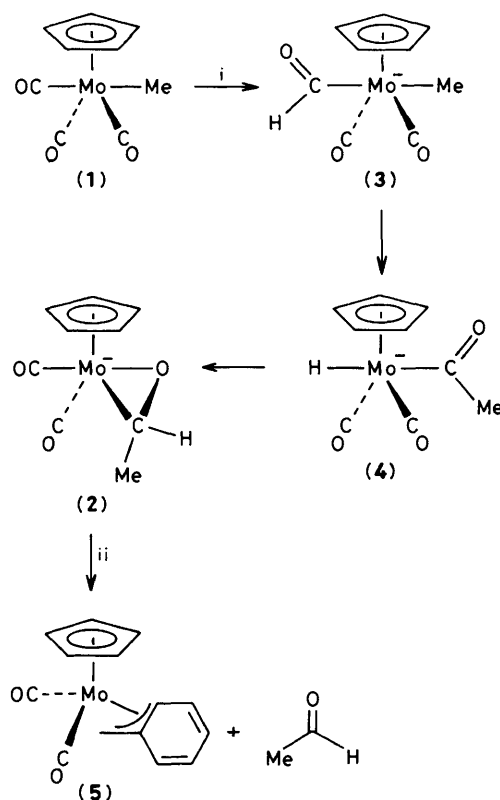
Treatment of a tetrahydrofuran (THF) solution of MoMe(CO)$_3$(η-C$_5$H$_5$) (1) with a slight excess of LiEt$_3$BH at −78 °C and warming to ambient temperature results in apparently quantitative conversion to species spectroscopically characterised as the η^2-acetaldehyde complex Mo(η^2-MeCHO)(CO)$_2$(η-C$_5$H$_5$)$^-$ (2) and small quantities of the anion Mo(CO)$_3$(η-C$_5$H$_5$)$^-$. Monitoring by variable temperature i.r. and ^{1}H and ^{13}C n.m.r. spectroscopy [using both (1) and its ^{13}CO enriched analogue] allows the successive observation of two spectroscopically characterised reaction intermediates Mo(CHO)Me(CO)$_2$(η-C$_5$H$_5$)$^-$ (3) and Mo[C(O)Me]H(CO)$_2$(η-C$_5$H$_5$)$^-$ (4) prior to formation of (2).†

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† Compound (3): ν_{CO}(THF), 1922m and 1833s cm^{-1}; ^{1}H n.m.r. δ(THF), 14.30 (br. s, 1H, CHO) and 5.00 (s, 5H, C$_5$H$_5$); ^{2}H n.m.r δ(THF) [for Mo(CHO)(C{^{2}H}$_3$)(CO)$_2$(η-C$_5$H$_5$)$^-$], −0.3 p.p.m. (s, Me); ^{13}C n.m.r. δ(THF), 287.7 (br. s, CHO), 229.8 (2CO), 94.4 (C$_5$H$_5$), and −19.6 p.p.m. (Me). Compound (4): ν_{CO}(THF), 1906m and 1816s cm^{-1}; ^{1}H n.m.r. δ(THF), 4.90 (s, 5H, C$_5$H$_5$), 2.25 (s, 3H, COMe), and −5.15 (s, 1H, MoH); ^{13}C n.m.r. δ(THF), 306.9 (COMe), 237.9 (2CO), 92.1 (C$_5$H$_5$), and 51.8 p.p.m. (CO*Me*). Compound (2): ν_{CO}(THF), 1870s and 1766s cm^{-1}; ^{1}H n.m.r. δ(THF), 5.06 (s, 5H, C$_5$H$_5$); ^{2}H n.m.r. δ(THF) [for Mo(η^2-MeC{^{2}H}O)(CO)$_2$(η-C$_5$H$_5$)$^-$], 3.5 and [for Mo[η^2-(C{^{2}H}$_3$)CHO] (CO)$_2$(η-C$_5$H$_5$)$^-$] 1.6 p.p.m.; ^{13}C n.m.r. δ(THF), 255.5 (CO), 254.4 (CO), 56.2 (Me*C*HO, $^1J_{CH}$ 156 Hz), and 92.5 p.p.m. (C$_5$H$_5$).

Mixing of (1) and LiEt$_3$BH at −78 °C and warming to −60 °C causes formation of the anionic formyl (3). Assignment of the formyl structure is supported by the characteristic high frequency shifts of the formyl hydrogen (^{1}H n.m.r., δ 14.3) and carbon (^{13}C n.m.r., δ 287.7 p.p.m.).[1] The position of the methyl signal in the ^{1}H n.m.r. spectrum is not unambiguously assignable owing to coincidence with a multiplicity of ethyl boron resonances, but separate experiments monitoring the ^{2}H n.m.r. spectrum for the reaction of Mo(C{^{2}H}$_3$)(CO)$_3$(η-C$_5$H$_5$) with LiEt$_3$BH unambiguously identifies the methyl signal (^{2}H n.m.r., δ −0.3 p.p.m.). Observation of a single carbonyl resonance at δ 229.8 p.p.m. (2CO) in the ^{13}C n.m.r. spectrum suggests the *trans* dicarbonyl depicted and this is reinforced by band intensities characteristic of a *trans* dicarbonyl in the i.r. spectrum.[2] The n.m.r. spectra suggest the presence of very small amounts of the *cis* substituted isomer of (3).

Raising the temperature further to *ca.* −20 °C causes isomerisation of (3) to the hydrido acyl (4). Pure solutions of (4) cannot be obtained since it itself isomerises slowly at these temperatures to the ultimate product (2). Complex (4) displays a typically low frequency signal (δ −5.15) due to the hydrido ligand in the ^{1}H n.m.r. spectrum and a high frequency ^{13}C n.m.r. signal (δ 306.9 p.p.m.) indicative of the acyl carbon.[3] Only the *trans* isomer (4) depicted has been detected. The methyl signal (^{13}C n.m.r., δ 51.8 p.p.m.) of the acyl is in a position very similar to those of related acyl complexes.[4]

Warming the solution further to ambient temperature causes conversion of (4) to the η^2-acetaldehyde complex (2); small quantities of Mo(CO)$_3$(η-C$_5$H$_5$)$^-$ were also identifiable

Scheme 1. *Reagents:* i, LiEt₃BH; ii, PhCH₂Br

in both i.r. and n.m.r. spectra of the final reaction mixture. Small quantities of formate and ethoxide were identified by comparison of $^1J_{CH}$ coupling constants and chemical shifts in the ^{13}C n.m.r. spectra with authentic samples run under similar conditions. We have not yet isolated (2) as a solid.

It is not possible to characterise (2) in the ^1H n.m.r. spectrum owing to solvent and ethyl boron interference but deuteriated analogues may be characterised by ^2H n.m.r. spectroscopy, these are $Mo(\eta^2\text{-MeC}\{^2H\}O)(CO)_2(\eta\text{-}C_5H_5)^-$, from $MoMe(CO)_3(\eta\text{-}C_5H_5) + LiEt_3B\{^2H\}$, and $Mo[\eta^2\text{-}(C\{^2H_3\})CHO](CO)_2(\eta\text{-}C_5H_5)^-$, from $Mo(C\{^2H_3\})(CO)_3(\eta\text{-}C_5H_5) + LiEt_3BH$. In the proton coupled ^{13}C n.m.r. spectrum a doublet (^{13}C n.m.r., δ 56.2 p.p.m., $^1J_{CH}$ 156 Hz) is assigned to the aldehyde carbon, this is virtually coincident with a much weaker triplet assigned to the CH_2 of ethoxide. A signal attributable to the methyl group has yet to be located owing to a probable coincidence with solvent or boron ethyl resonances.

Spectroscopic data on other η^2-acetaldehyde complexes for comparison is sparse, however, signals at δ 5.26 and 81.3 p.p.m. are assigned to the aldehyde H and C in the ^1H and ^{13}C n.m.r. spectra of complex (6).[5] Some η^2-acetaldehyde complexes have been characterised crystallographically[5,6] and are depicted as metallaoxiranes, in the absence of crystallographic data for (2) we do the same.
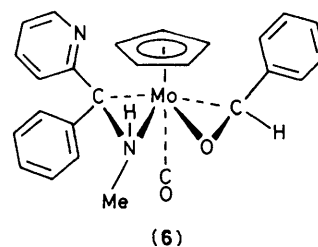
Chemical evidence for the presence of an aldehyde ligand in (2) comes from its reactivity, which is nucleophilic. As an interesting example, treatment of the reaction mixture containing (2) with PhCH₂Br results in nucleophilic replacement of Br⁻, evolution of acetaldehyde [g.l.c. and g.c.-mass spectrometry (m.s.)], and co-ordination of one double bond of the C_6 ring during formation of the known η^3-benzyl complex (5),[7] isolatable in yields in excess of 60% based on (1). A similar reaction sequence employing $Mo(C\{^2H\}_3)(CO)_3(\eta\text{-}C_5H_5)$ as starting material leads to formation of $C\{^2H\}_3CHO$ (g.c.-m.s.). It is likely that formation of (5) proceeds *via* $Mo(\eta^1\text{-}CH_2Ph)(CO)_2(MeCHO)(\eta\text{-}C_5H_5)$. Acetaldehyde is evolved by displacement from the metal by a double bond of the benzyl group.

Significant points of the reaction sequence (1) → (2) are (i) attack of H⁻ upon a neutral metal species to give an anionic formyl complex, well documented in other systems;[1] (ii) isomerisation of the resulting formyl species to an hydrido acyl species, probably through a facile methyl to carbonyl migration; (iii) formation of an aldehyde ligand from an hydrido acyl complex. We note the converse reaction of some metal complexes which with aldehydes lead to hydrido acyl species.[8] These reactions appear irreversible. Protonation of the anionic iron acyl $Fe(COR)(CO)_4^-$ results in formation of free aldehyde[9] and it has been suggested that this occurs by decomposition of the hydrido acyl $FeH(COR)(CO)_4$, perhaps *via* a transient aldehyde complex.

The evolution of aldehyde from the anion (2) by treatment with PhCH₂Br is an apparently unique reaction.

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References

1 J. A. Gladysz, *Adv. Organomet. Chem.,* 1982, **20**, 1.
2 A. R. Manning, *J. Chem. Soc. A,* 1967, 1824.
3 B. E. Mann and B. F. Taylor, '^{13}C N.m.r. Data for Organometallic Compounds,' Academic Press, London, 1981.
4 L. J. Todd, J. R. Wilkinson, J. P. Hickey, D. L. Beach, and K. W. Barnett, *J. Organomet. Chem.,* 1978, **154**, 151.
5 H. Brunner, J. Wachter, I. Bernal, and M. W. Creswick, *Angew. Chem., Int. Ed. Engl.,* 1979, **18**, 861.
6 M. W. Creswick and I. Bernal, *Inorg. Chim. Acta,* 1983, **71**, 41; W. R. Roper, G. E. Taylor, J. M. Waters, and L. J. Wright, *J. Organomet. Chem.,* 1979, **182**, C46; K. L. Brown, G. R. Clark, C. E. L. Headford, K. Marsden, and W. R. Roper, *J. Am. Chem. Soc.,* 1979, **101**, 503.
7 R. B. King and A. Fronzaglia, *J. Am. Chem. Soc.,* 1966, **88**, 709.
8 T. B. Rauchfuss, *J. Am. Chem. Soc.,* 1979, **101**, 1045.
9 J. P. Collman, *Acc. Chem. Res.,* 1975, **8**, 342.