Reactions of Hydride Reagents with Alkylmolybdenum Carbonyl Complexes. Reaction of $LiBHEt_3$ with $[MoMe(CO)_3(\eta\text{-}C_5H_5)]$, Formation of an Anionic Acetaldehyde Complex, and a Stoicheiometric Cycle for the Synthesis of Acetaldehyde

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The molybdenum alkyl complex $[MoMe(CO)_3(\eta\text{-}C_5H_5)]$ (**1**) reacts with $LiBHEt_3$ in tetrahydrofuran (thf) solution at ambient temperature to give the anionic acetaldehyde complex $[Mo(\eta^2\text{-}MeCHO)(CO)_2(\eta\text{-}C_5H_5)]^-$ (**2**) as the predominant organomolybdenum product together with very small quantities of the anion $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$. Monitoring experiments using low-temperature i.r. and n.m.r. spectroscopy allows the spectroscopic identification of the formyl $[MoMe(CHO)(CO)_2(\eta\text{-}C_5H_5)]^-$ (**3**) as the primary product at −66 °C. Slow warming of the reaction mixture results in the spectroscopic observation of the successive rearrangements of (**3**) into the hydrido-acyl $[MoH(COMe)(CO)_2(\eta\text{-}C_5H_5)]^-$ (**6**) and finally of (**6**) into the ultimate product (**2**). Treatment of a solution of (**2**) with $PhCH_2Br$ at ambient temperature results in formation of predominantly the η^3-benzyl $[Mo(CO)_2(\eta^3\text{-}CH_2Ph)(\eta\text{-}C_5H_5)]$ and the evolution of acetaldehyde. In a related reaction (**2**) reacts with MeI and PPh_3 to form acetaldehyde and *trans*-$[MoMe(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$. Complex (**2**) reacts with MeI under a CO atmosphere to regenerate (**1**) with the evolution of acetaldehyde, thus completing a stoicheiometric cycle for the synthesis of acetaldehyde. Possible mechanisms for the above reactions are discussed.

In recent years studies of the reactions of hydride sources with transition-metal carbonyl complexes have attracted attention owing to their relevance to CO reduction.[1] The formation of neutral or anionic formyl complexes as a consequence of attack at co-ordinated carbonyl is well established; they often subsequently rearrange to other species.[2]

In a preliminary communication[3] we discussed the reactions of $[Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5H_5)]$ and related species with $LiBHEt_3$. With the aim of understanding some aspects of this reaction we examined the reaction of $[MoMe(CO)_3(\eta\text{-}C_5H_5)]$ (**1**) with hydride donors. This paper is an account of that work, some aspects of which formed the subject of a preliminary communication.[4]

Results and Discussion

Some reactions of (**1**) with anionic nucleophiles other than hydride have been mentioned in the literature and are worth noting at this point. Treatment of (**1**) with CN^- in methanol at reflux results in the cyano-anion $[Mo(CN)(COMe)(CO)_2(\eta\text{-}C_5H_5)]^-$, a consequence of migration of methyl to carbonyl and attack by CN^-, probably at the metal.[5] Several reactions of (**1**) with transition-metal nucleophiles have been observed. Reactions with $[Mn(CO)_5]^-$, $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$, and $[W(CO)_3(\eta\text{-}C_5H_5)]^-$ lead to displacement of $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ and formation of respectively $[MnMe(CO)_5]$, $[FeMe(CO)_2(\eta\text{-}C_5H_5)]$, and $[WMe(CO)_3(\eta\text{-}C_5H_5)]$.[6] We investigated the reaction of I^- with (**1**) having already established[7] that I^- reacts with the more complex $[Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5H_5)]$. However, the i.r. spectrum of a solution of (**1**) and excess LiI in methanol or tetrahydrofuran (thf) at reflux remains unchanged even after prolonged heating and suggests that (**1**) is the only organomolybdenum species present in solution. This suggests that the equilibrium in equation (1) must lie far to the left, the reason reaction is observed with $[Mo\{(CH_2)_3Br\}(CO)_3(\eta\text{-}C_5H_5)]$ being that subsequent rearrangements of the small instantaneous concentrations of its associated acyl are sufficiently rapid and irreversible to allow the overall reaction to proceed to completion.

$$[MoR(CO)_3(\eta\text{-}C_5H_5)] + I^- \rightleftharpoons [MoI(COR)(CO)_2(\eta\text{-}C_5H_5)]^- \quad (1)$$

Reactions of (**1**) *with Hydride Sources.*—In most reactions of hydride sources with organotransition-metal complexes the source of hydride is critical, this is the case for (**1**). The hydride reagents $LiAlH_4$, LiH, $NaBHPr^i_3$, $KBHPr^i_3$, $NaBH_4$, $NaBH_3(CN)$, and $NaBH(OMe)_3$ all react with (**1**) in thf by the elimination of $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ (indicated by comparison of i.r. spectra with authentic samples). This is accompanied by the formation of methane and confirmed by g.c.–mass spectrometry.

The hydride source $LiBHEt_3$ behaves very differently. Reaction of $LiBHEt_3$ with (**1**) at ambient temperature proceeds smoothly in thf to give a solution containing predominantly the anion (**2**) which is a complex of acetaldehyde. Justification for the structure (**2**) is given later. This reaction has been monitored by low-temperature i.r. and n.m.r. spectroscopy.

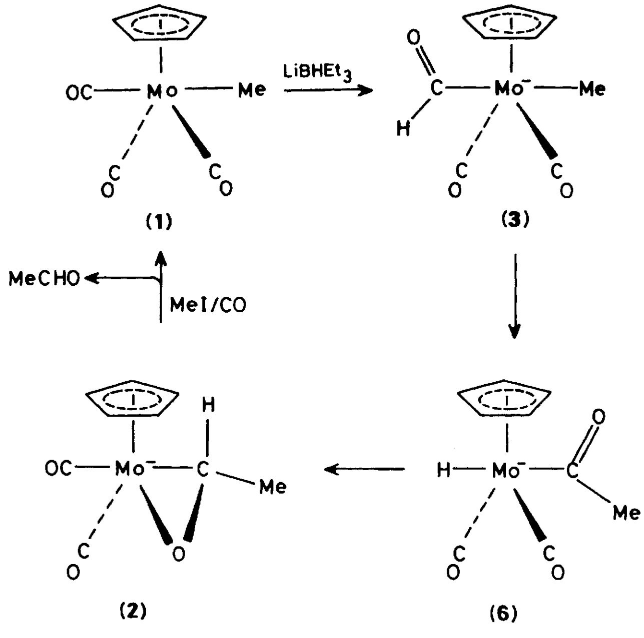
Addition of a slight excess of a solution of $LiBHEt_3$ in thf to a solution of (**1**) in thf at −78 °C followed by warming to −66 °C results in rapid formation of the anionic formyl $[MoMe(CHO)(CO)_2(\eta\text{-}C_5H_5)]^-$ (**3**) (Scheme 1), with no change in colour from the pale yellow of the initial solution. Formyl (**3**) is not isolable as a solid, owing to rapid rearrangement upon warming a solution above −40 °C, but has been characterised by i.r., ^1H n.m.r., and ^{13}C n.m.r. spectroscopy on *in situ* generated samples at low temperatures (Table).

The i.r. spectrum of the reaction mixture at −50 °C shows, after computer subtraction of signals assignable to solvent and any remaining (**1**) (Figure), only two bands. These are clearly indicative of a *trans* dicarbonyl[8] for a molybdenum complex of the type depicted by (**3**). At similar temperatures a high-frequency signal (δ 14.3) in the ^1H n.m.r. spectrum is in a position characteristic of a formyl proton. We are only aware of two examples of related molybdenum formyls, the unstable

Table. Spectroscopic data for the new complexes recorded in thf solution *

Complex	$\nu(CO)_{max.}/cm^{-1}$	^1H N.m.r. (δ/p.p.m.)	^{13}C N.m.r. (δ/p.p.m.)	Complex	^2H N.m.: (δ/p.p.m.)
(3)	^{a} 1 922m, 1 833s	^{b} 14.3 (br s, 1 H, CHO), 5.00 (s, 5 H, C_5H_5)	^{c} 287.7 (br, CHO), 229.8 (2 CO), 94.4 (C_5H_5), −19.6 (Me)	**(3-D)** **(6-D)**	^{h} 13.2 (s, CDO) ^{h} −4.9 (s, Mo–D)
(6)	^{d} 1 906m, 1 816s	^{e} 4.90 (s, 5 H, C_5H_5), 2.25 (s, 3 H, Me), −5.15 (s, 1 H, Mo–H)	^{a} 306.9 (*C*OMe), 237.9 (2 CO), 92.1 (C_5H_5), 51.8 (Me)	**(2-D)** **(3-D$_3$)** **(6-D$_3$)**	^{i} 3.5 (s, MeCDO) ^{i} −0.3 (s, CD_3) ^{i} 2.3 (s, CD_3)
(2)	^{f} 1 870s, 1 766s	^{g} 5.06 (s, 5 H, C_5H_5)	^{a} 255.5 (CO), 254.4 (CO), 92.5 (C_5H_5), 56.2 [Me*C*HO, ^1J(CH) 156 Hz]	**(2-D$_3$)**	^{i} 1.6 (s, CD_3)

* Nominal temperatures: measured at ^{a} −50, ^{b} −60, ^{c} −90, ^{d} −20, ^{e} −25, ^{f} −10, ^{g} ambient, ^{h} −40 °C, and ^{i} −30 °C.



Scheme 1.

$[Mo(CHO)(COCO_2Me)(CO)_2(\eta\text{-}C_5H_5)]^-$ (4), for which the corresponding signal is at δ 12.9[9] and the neutral $[Mo(CHO)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ (5) characterised by a resonance at δ 14.7.[10] Assignment of a formyl structure for (3) is also supported by the ^{13}C n.m.r. spectrum which contains a very high frequency signal (δ 287.7) while a single carbonyl resonance (δ 229.8) is as expected for the *trans* geometry depicted.

The reaction leading to (3) is clean, any side products must be present to an extent of less than approximately 2%. There is no indication of the corresponding *cis* isomer of (3), neither is there any evidence for any attack at the cyclopentadienyl ring.

At temperatures higher than −40 °C (3) rearranges to the hydrido-acyl (6). This is indicated by changes in both i.r. and n.m.r. spectra. In the i.r. spectrum computer subtraction of bands assignable to solvent, unreacted (1), unreacted (3), and the ultimate product (2) (below) leaves just two signals (Figure) assigned to the hydrido-acyl *trans*-(6). Evidence for the presence of a hydride ligand comes from a low-frequency signal (δ −5.15) characteristic of a metal hydride.[11] The ^{13}C n.m.r. spectrum is diagnostically useful. In addition to signals readily assignable to (1), (3), and the final product (2), (see below) it contains a high-frequency signal (δ 306.9) assigned to the acyl carbon[12] and a single carbonyl resonance which supports the *trans* geometry indicated by the intensities of the two carbonyl stretching bands.[8]

It is not possible to obtain solutions of (6) free from other organomolybdenum compounds since it undergoes rearrangement before it itself is completely formed through isomerisation of (3). Instantaneous concentrations of around 60% (measured by comparison of integrated cyclopentadienyl signals in the ^1H n.m.r. spectrum) have been observed.

At this stage very small quantities of $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ (approximately 2%) are evident and identified by comparison with the ^1H n.m.r. spectrum of an authentic sample generated by cleavage of $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ with LiBHEt$_3$ in thf.[13] Under our i.r.-monitoring conditions the 2% quantity formed is too small for detection.

Further warming of the reaction mixture to ambient temperature gives the major ultimate product (2) together with small quantities (approximately 3%) of $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ as the only observed organomolybdenum species. We have yet to succeed in isolating (2) as a salt precipitated out by large cations, consequently all spectroscopic data for (2) and its derivatives mentioned below are from *in situ* generated material. The i.r. spectrum (Figure) after removal of signals assigned to solvent contains two carbonyl bands whose relative intensities suggest a *cis*-dicarbonyl.[8] The n.m.r. spectra were only assignable with the aid of isotopic labelling experiments.

The nature of this experiment requires n.m.r. monitoring in perhydro thf since LiBHEt$_3$ is supplied as a solution in thf. Identification of product resonances which occur in the region of thf or boron ethyl signals would be tentative owing to the multiplicity and strength of such signals. However analogous experiments employing appropriately deuteriated or ^{13}C-enriched samples with monitoring by ^2H n.m.r. (61.42 MHz) and ^{13}C n.m.r. (25.15 MHz) spectroscopy circumvents the problem.

Addition of LiBDEt$_3$ to a solution of (1) at −78 °C gives a solution containing $[MoMe(CDO)(CO)_2(\eta\text{-}C_5H_5)]^-$ **(3-D)** (^2H n.m.r., δ 13.2) which upon warming converts successively to $[MoD(COMe)(CO)_2(\eta\text{-}C_5H_5)]^-$ **(6-D)** (^2H n.m.r., δ −4.9) and $[Mo(\eta^2\text{-}MeCDO)(CO)_2(\eta\text{-}C_5H_5)]^-$ **(2-D)** (^2H n.m.r., δ 3.5). The latter signal explains why no signal is observed for (2) since that for (2) would be virtually coincident with the higher-frequency thf resonance.

In a similar fashion addition of LiBHEt$_3$ to a solution of $[Mo(CD_3)(CO)_3(\eta\text{-}C_5H_5)]$ **(1-D$_3$)** at −78 °C, with monitoring by ^2H n.m.r. spectroscopy upon slow warming, results in the successive observation of $[Mo(CD_3)(CHO)(CO)_2(\eta\text{-}C_5H_5)]^-$ **(3-D$_3$)** (^2H n.m.r., δ −0.3), $[MoH(COCD_3)(CO)_2(\eta\text{-}C_5H_5)]^-$ **(6-D$_3$)** (^2H n.m.r., δ 2.3), and $[Mo(\eta^2\text{-}CD_3CHO)(CO)_2(\eta\text{-}C_5H_5)]^-$ **(2-D$_3$)** (^2H n.m.r., δ 1.6). Therefore the corresponding methyl signal for (2) is expected to be coincident with the low-frequency thf signal accounting for the failure to assign such a signal in the ^1H n.m.r. monitoring experiments.

Useful results are also obtained by monitoring the reaction of (1) enriched in ^{13}C, denoted (1*), at the carbonyl positions. Use of (1*) with each position enriched in ^{13}C to 10% (compared to a natural abundance of 1.1%) apart from giving significantly shorter data acquisition times allows the unambiguous identi-

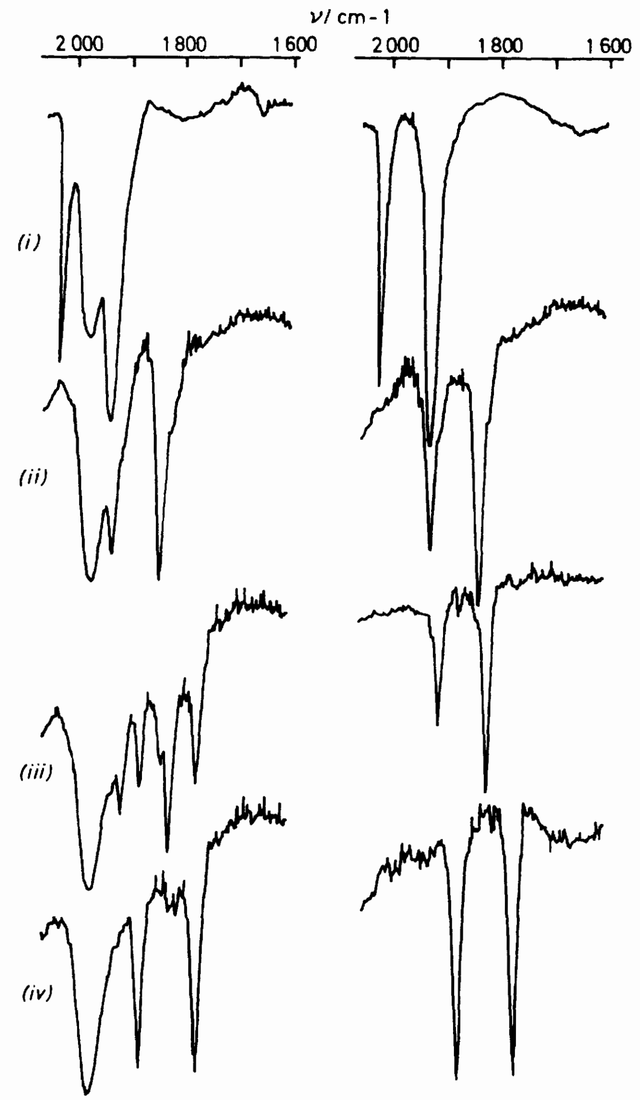
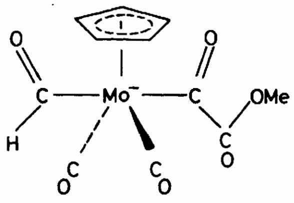


Figure. Infrared spectra during the reaction of [$MoMe(CO)_3(\eta-C_5H_5)$] (**1**) with $LiBHEt_3$ in thf. Those on the left are untreated data, those on the right after subtraction of signals assigned as solvent and organomolybdenum complexes. The spectra remaining represent: (*i*) alkyl (**1**) (at −50 °C), (*ii*) formyl (**3**) at −50 °C, (*iii*) hydrido-acyl (**6**) at −20 °C, and (*iv*) η^2-acetaldehyde anion (**2**) at −10 °C (all temperatures nominal)



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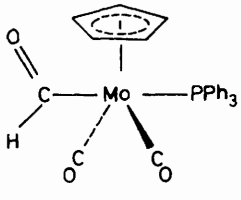
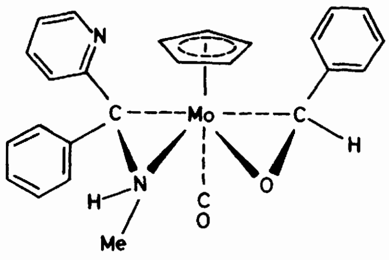


(5)

fication of product carbon-atom signals that originate from a carbonyl. Thus reaction of (**1***) with $LiBHEt_3$ results in a solution containing (**2***) and whose ^{13}C n.m.r. spectrum contains a strong doublet [^{13}C n.m.r., δ 56.2, $^1J(CH)$ 165 Hz] which is assigned to the co-ordinated carbon of the η^2-MeCHO ligand. Since we have not carried out experiments using (**1**) enriched in ^{13}C at the methyl position we have not assigned a signal in



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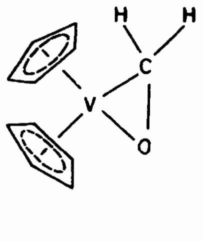

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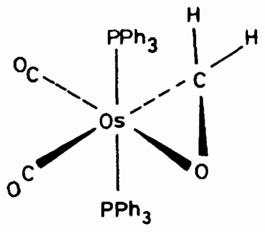

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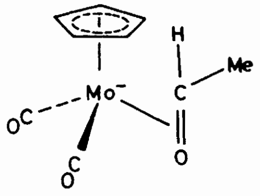

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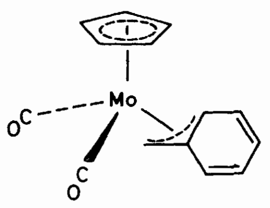

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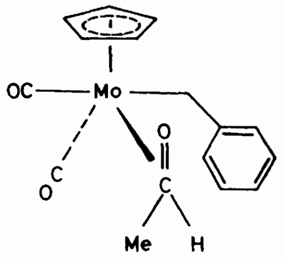

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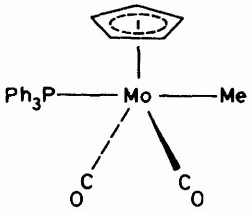
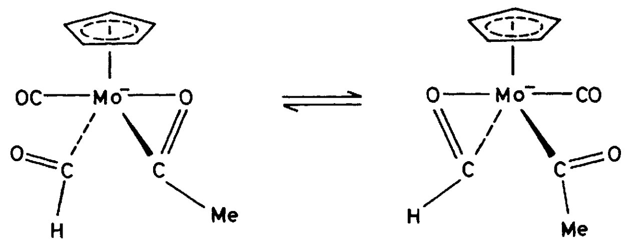


(13)

the ^{13}C n.m.r. spectrum of (**2**) to that group. It is probably coincident with the various boron ethyl resonances.

There are relatively few η^2-aldehyde complexes with which one can compare spectroscopic properties. The most clearly related example is the neutral molybdenum benzaldehyde complex (**7**) which has been crystallographically characterised.[14] For (**7**) the aldehyde proton is identified by a signal at δ 5.26 in the ^1H n.m.r. spectrum and δ 81.3 in the ^{13}C n.m.r. spectrum, both somewhat to higher frequency than those for (**2**).[15] There are also few crystallographically characterised aldehyde complexes, the structures of species such as (**8**)[16] and (**9**)[17] as well as (**7**) are represented as metallaoxiranes; for this reason we do the same although the alternative representation given for (**10**) is also reasonable.

Before considering the reaction sequence above in more detail it is necessary to discuss a few aspects of the chemistry of (**2**), one of which is its nucleophilic behaviour towards $PhCH_2Br$. Addition of a slight excess of $PhCH_2Br$ to a solution of (**2**) at ambient temperature causes a rapid reaction and the formation of a reasonable yield (63%) of the known η^3-benzyl (**11**)[18,19] in



Scheme 2.

addition to very minor quantities of $[Mo(\sigma\text{-}CH_2Ph)(CO)_3(\eta\text{-}C_5H_5)]$[18] and the dimolybdenum species $[Mo_2(CO)_4(\mu\text{-}\eta^2\text{-}MeCHO)(\eta\text{-}C_5H_5)_2]$ discussed elsewhere.[20]

It is reasonable to postulate that nucleophilic attack of (**2**) at $PhCH_2Br$ would produce the neutral σ-benzyl (**12**). Lack of back-bonding as a consequence of loss of the negative charge in the neutral (**12**) renders the aldehyde ligand labile and therefore liable to replacement by another ligand. In this case the aromatic ring provides such a ligand and displacement of acetaldehyde leads to (**11**). Although we have not detected the intermediate (**12**), acetaldehyde is evolved and quantified by g.l.c. and g.c.–mass spectrometry against appropriate standards to give a yield of 52%. We assume $[Mo(\sigma\text{-}CH_2Ph)(CO)_3(\eta\text{-}C_5H_5)]$ is produced through the reaction of the small quantities of $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ present in solution with $PhCH_2Br$.

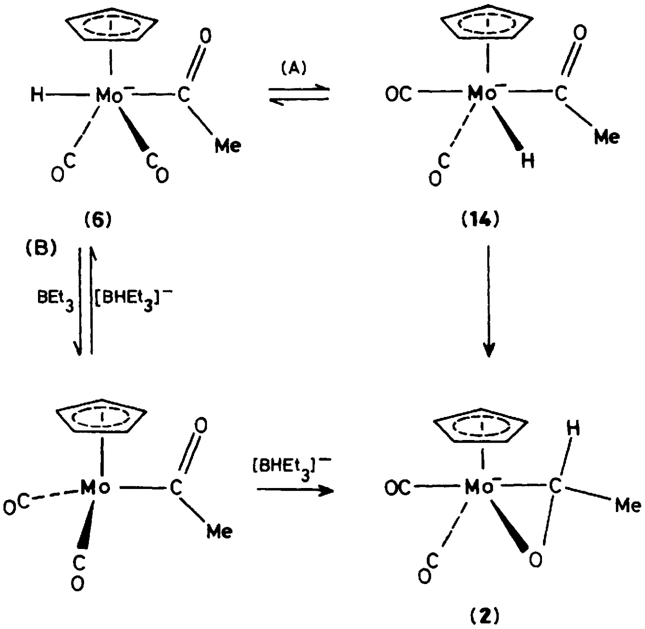
Reactions of the deuteriated analogues of (**2**) with $PhCH_2Br$ also result in the evolution of acetaldehydes. Thus treatment of a solution containing (**2-D**) with $PhCH_2Br$ leads to the evolution of MeCDO while the corresponding reaction with (**2-D$_3$**) leads to the evolution of CD_3CHO, in both cases the identities were confirmed by g.c.–mass spectrometry.

In a related reaction addition of MeI and PPh_3 simultaneously to a solution of (**2**) rapidly gives the phosphine complex (**13**)[21] together with small amounts of (**1**) as the only organomolybdenum complexes detected. It is presumed that $[MoMe(CO)_2(MeCHO)(\eta\text{-}C_5H_5)]$ is an undetected intermediate from which acetaldehyde is displaced by PPh_3, again this is detectable by g.l.c. and g.c.–mass spectrometry. The initial reaction is definitely with MeI since in separate experiments (**2**) does not react with PPh_3.

The reaction of (**2**) with MeI under a CO atmosphere is particularly significant. The only organomolybdenum product detected is (**1**) isolated in good yield while acetaldehyde is again evolved. Again the complex $[MoMe(CO)_2(MeCHO)(\eta\text{-}C_5H_5)]$ is presumed to be an intermediate. The significance of this reaction is that a stoicheiometric cycle (Scheme 1) is completed for the synthesis of acetaldehyde. It can in principle be extended to the synthesis of other aldehydes. The difficulty of producing a useful catalytic process here is the incompatibility of $LiBHEt_3$ with alkyl halides.

There are several points which require comment concerning the synthesis of (**2**). There is ample literature precedent for the formation of metal formyls by attack of hydride at a metal carbonyl,[1] although there are few molybdenum examples (see above). One report does mention the reaction of (**1**) with $LiBHEt_3$;[9b] the comment is made that no formyl is detectable after mixing the reagents at low temperature, our results suggest this to be a consequence of the further reaction of formyl (**3**) before spectrum accumulation.

The formyl (**3**) is capable of functioning as a hydride donor in its own right. This phenomenon has been noted in connection with other formyl systems. Addition of $LiBHEt_3$ to a solution of excess (**1**) at −70 °C gives a solution containing the formyl (**3**) together with excess (**1**). Addition of $[MoEt(CO)_3(\eta\text{-}C_5H_5)]$ to such a solution at −70 °C followed by warming to ambient temperature results in a reaction mixture with i.r. bands assignable to a tricarbonyl of the type $[MoR(CO)_3(\eta\text{-}C_5H_5)]$ (R = alkyl), presumed to be a mixture of (**1**) and $[MoEt(CO)_3(\eta\text{-}C_5H_5)]$, together with low-frequency signals similar to those of (**2**). In fact these two signals correspond to a mixture of (**2**) and $[Mo(\eta^2\text{-}EtCHO)(CO)_2(\eta\text{-}C_5H_5)]^-$ since addition of $PhCH_2Br$ to the solution results in the evolution of both MeCHO and EtCHO in roughly equal proportions. Since there was excess (**1**) under conditions where the formyl (**3**) is formed, and therefore no $LiBHEt_3$ present, we suggest that $[MoEt(CHO)(CO)_2(\eta\text{-}C_5H_5)]^-$, which is the precursor of $[Mo(\eta^2\text{-}EtCHO)(CO)_2(\eta\text{-}C_5H_5)]^-$, must be formed by hydride transfer from (**2**). It is not unreasonable that such a transfer would proceed through donation to BEt_3 forming $[BHEt_3]^-$ which therefore acts as a vehicle for hydride transfer. We feel that hydride transfer from the hydrido-acyl (**6**) is rather less likely (see below) but were it to happen this would nullify this argument.



Scheme 3.

The conversion of (**3**) to (**6**) is unusual, we are not aware of other examples of formyl alkyl complexes isomerising to hydrido-acyl species. However it is not unusual for a formyl complex to convert into a hydride carbonyl.[22] In this way the 18-electron rule is observed through the loss of a carbonyl ligand. In the present case the 18-electron rule is preserved through migration of methyl to carbonyl, a vacant co-ordination site is generated as a result, to which the hydrogen atom may migrate. The migratory insertion step proceeds at a temperature (approximately −40 °C) well below that of the related migratory insertion[23] of methyl to carbonyl in (**1**) induced by PPh_3, and producing $[Mo(COMe)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ which requires elevated temperatures around 70 °C. Conceivably the formyl affects the insertion step in the (**3**) $\longrightarrow$ (**6**) reaction. Bearing in mind suggestions that η^2-acyl interactions could stabilise an intermediate during migratory insertion reactions and that examples of such interactions are well characterised[24] it is tentatively suggested that an equilibrium between η^2-acyl and η^2-formyl (Scheme 2) is involved in this interconversion. In order to account for the reaction being driven in the direction of (**6**) one could invoke the presumably stronger metal–hydride interaction when compared to the metal–methyl bond as well as the fact that (6) is removed by its further reaction around these temperatures to (2).

Inter- and intra-molecular processes are conceivable for the (6) ⟶ (2) step. An intramolecular process (A) (Scheme 3) requires a hydride migration from the metal to the carbenoid acyl atom as oxygen enters into the molybdenum co-ordination sphere. This would have to take place from (14), the *cis* isomer of (6). Although we have not detected (14) even small concentrations in an equilibrium between (6) and (14) would suffice for the reaction to proceed towards (2). The suggestion of an equilibrium between (6) and (14) has precedent since several molybdenum systems of the type $[Mo(R)(CO)_2L(\eta\text{-}C_5H_5)]$ do exist as *cis*- and *trans*-equilibrium mixtures.[25]

An intermolecular process, (B), is also feasible although perhaps less likely and relies upon the presence of BEt_3 in solution. Hydride abstraction from (6) by BEt_3 would generate $[BHEt_3]^-$ which could then donate hydride to the resulting $[Mo(COMe)(CO)_2(\eta\text{-}C_5H_5)]$ or possibly $[Mo(COMe)(CO)_2(thf)(\eta\text{-}C_5H_5)]$ at the acyl carbon as oxygen binds to molybdenum. Addition of NEt_3 to the reaction mixture after the formation of (3) in order to complex out BEt_3, followed by warming still results in the formation of (6); this tends to rule out the possibility of such an intermolecular process but it is not completely conclusive.

Experimental

Infrared spectra were recorded using either a Perkin-Elmer 257 spectrometer calibrated using the 1 601.4 cm^{-1} absorption of polystyrene film or on a Perkin-Elmer 684 instrument linked to a Perkin-Elmer 3600 Data Station. Variable-temperature spectra were recorded using the 684 instrument with a Specac cell whose temperature was controlled by a Specac 20.100 temperature controller.

Proton n.m.r. spectra were recorded using JEOL PFT-100 (100.00 MHz), Bruker WP-80SY (80.13 MHz), Bruker WH-400 (400.13 MHz), and Perkin-Elmer R34 (220 MHz) instruments. Carbon-13 n.m.r. spectra were recorded using a JEOL PFT-100 (25.15 MHz) instrument while ^2H n.m.r. spectra were recorded on the WH-400 instrument at 61.42 MHz.

Mass spectra and g.c.–mass spectra were obtained using a Kratos MS 25 instrument. All g.c. work was performed on columns packed with Porapak Q under isothermal conditions at 150 °C.

All reactions were performed under a nitrogen atmosphere generally using glassware that had been flame dried under vacuum. Solvents were used as supplied except thf, which was distilled from sodium–benzophenone immediately prior to use, and light petroleum (b.p. 40–60 °C throughout), which was distilled from $LiAlH_4$. Alumina was Brockmann activity I deactivated with water (5%, w/w) to activity II. The reagents $LiBHEt_3$ and $LiBDEt_3$ (Aldrich 'Super Hydride' and 'Super Deuteride') were used as supplied. The compounds $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$,[26] $[MoR(CO)_3(\eta\text{-}C_5H_5)]$ (R = Me, CD_3, or Et),[27] $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$,[27] and $Li[Mo(CO)_3(\eta\text{-}C_5H_5)]$[13] were synthesised according to literature procedures. Complexes enriched with ^{13}C were prepared from $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ ^{13}C-enriched to approximately 10% at each of the carbonyl positions.[28]

Preparation of $[Mo(\eta^2\text{-}MeCHO)(CO)_2(\eta\text{-}C_5H_5)]^-$ (2).—$LiBHEt_3$ (2.5 cm^3, 1.0 mol dm^{-3} solution in thf, 2.5 mmol) was added to a stirred pale yellow solution of $[MoMe(CO)_3(\eta\text{-}C_5H_5)]$ (1) (0.5 g, 1.9 mmol) in thf (100 cm^3) at ambient temperature. Stirring (5 min) resulted in an orange-brown solution containing predominantly $[Mo(\eta^2\text{-}MeCHO)(CO)_2(\eta\text{-}C_5H_5)]^-$ (2) [ν(CO) 1 876s and 1 774s cm^{-1}] together with very small quantities of $Li[Mo(CO)_3(\eta\text{-}C_5H_5)]$ [ν(CO) 1 901s, 1 894(sh), 1 808s, 1 783m, and 1 717s cm^{-1}].[13]

Infrared Monitoring Experiments.—Reaction mixtures were prepared cold in a standard Schlenk tube and samples drawn into the precooled cell through poly(tetrafluoroethylene) capillary tubing. This method considerably reduced problems associated with bubble formation when performing the reaction in the i.r. cell itself.

N.M.R. Monitoring Experiments.—In a typical experiment $[MoMe(CO)_3(\eta\text{-}C_5H_5)]$ (1) (0.12 g, 0.48 mmol) was dissolved in thf and filtered into the n.m.r. tube. The volume of the solution was reduced under a stream of nitrogen to approximately 0.2 cm^3. After cooling, a solution of $LiBHEt_3$ (0.5 cm^3, 0.5 mmol) was added slowly down the side of the tube through a syringe. Proton spectra were run in the continuous-wave mode unlocked at 220 MHz. A sealed capillary tube containing $[^2H_2]$dichloromethane or $[^2H_6]$acetone inserted into the sample through a vortex plug provided the deuterium necessary to achieve a lock signal for ^{13}C and some ^1H n.m.r. experiments. For the ^{13}C n.m.r. work the solution was generally recooled after raising to a particular temperature in order to prevent further reaction at that temperature prior to data acquisition and also to benefit from the resulting improvement in signal-to-noise ratio.

Reaction of $[Mo(\eta^2\text{-}MeCHO)(CO)_2(\eta\text{-}C_5H_5)]^-$ (2) *with* $PhCH_2Br$.—Addition of $PhCH_2Br$ (0.4 cm^3, 0.57 g, 3.33 mmol) to a solution of (2) prepared as above from $[MoMe(CO)_3(\eta\text{-}C_5H_5)]$ (1) (0.5 g, 1.9 mmol), at ambient temperature resulted in a dark brown solution after stirring for 4 h. Analysis of a portion of the reaction mixture by g.l.c. and g.c.–mass spectrometry indicated the presence of acetaldehyde (52%) (identified by comparison with a library spectrum and retention times of appropriate standards, quantified by comparison of integrals of g.l.c. signals against standards). Removal of solvent followed by chromatography on alumina (30 × 3 cm) provided yellow $[Mo(\sigma\text{-}CH_2Ph)(CO)_3(\eta\text{-}C_5H_5)]$ (15 mg, 2%) followed by orange $[Mo(CO)_2(\eta^3\text{-}CH_2Ph)(\eta\text{-}C_5H_5)]$ (11) (0.39 g, 63%) upon elution with light petroleum–dichloromethane (7:1). Continued elution with light petroleum–dichloromethane (4:1) gave a green solution containing $[Mo_2(CO)_4(\mu\text{-}\eta^2\text{-}MeCHO)(\eta\text{-}C_5H_5)_2]$[20] which was crystallised from light petroleum (20 mg, 3%).

Reaction of $[Mo(\eta^2\text{-}MeCHO)(CO)_2(\eta\text{-}C_5H_5)]^-$ (2) *with* MeI *and* PPh_3.—Addition of PPh_3 (0.52 g, 2.0 mmol) and MeI (0.25 cm^3, 0.57 g, 4.0 mmol) to a solution of (2), prepared as above from $[MoMe(CO)_3(\eta\text{-}C_5H_5)]$ (1) (0.5 g, 1.9 mmol), at ambient temperature resulted in a brown solution after stirring (4 h). Analysis of a portion of the reaction mixture by g.c.–mass spectrometry indicated the presence of acetaldehyde. Removal of solvent followed by chromatography on alumina (20 × 3 cm) provided traces of (1) (20 mg, 4%) upon elution with light petroleum. Continued elution with dichloromethane–light petroleum (1:1) provided yellow $[MoMe(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ (13) (0.49 g, 52%).

Reaction of $[Mo(\eta^2\text{-}MeCHO)(CO)_2(\eta\text{-}C_5H_5)]^-$ (2) *with* MeI *and* CO.—Addition of MeI (0.25 cm^3, 0.57 g, 4.0 mmol) to a solution of (2), prepared as above from $[MoMe(CO)_3(\eta\text{-}C_5H_5)]$ (1) (0.5, 1.9 mmol), maintained under a CO atmosphere gave a brown solution after stirring (4 h). Analysis of a portion of the reaction mixture by g.c.–mass spectrometry revealed the presence of acetaldehyde. Removal of solvent and sublimation (40 °C, 0.05 Torr) gave yellow crystalline $[MoMe(CO)_3(\eta\text{-}C_5H_5)]$ (1) (0.425 g, 85%).

Reaction of $[\mathrm{MoMe(CHO)(CO)_2(\eta\text{-}C_5H_5)}]^-$ **(3)** *with* $[\mathrm{MoEt(CO)_3(\eta\text{-}C_5H_5)}]$.—A solution of **(3)** was prepared by the addition of $\mathrm{LiBHEt_3}$ (0.8 cm^3, 0.8 mmol) to a solution of $[\mathrm{MoMe(CO)_3(\eta\text{-}C_5H_5)}]$ **(1)** (0.26 g, 1.00 mmol) in thf at −70 °C. Addition of $[\mathrm{MoEt(CO)_3(\eta\text{-}C_5H_5)}]$ (0.2 g, 0.73 mmol) followed by warming to ambient temperature resulted in a brown solution. Addition of $\mathrm{PhCH_2Br}$ (0.5 cm^3, 0.75 g, 4.42 mmol) and brief stirring gave a red solution for which analysis by g.l.c. and g.c.–mass spectrometry indicated the presence of both MeCHO and EtCHO.

Acknowledgements

We are most grateful to the S.E.R.C. for substantial support and one of us (J. T. G.) is grateful to the S.E.R.C. for a research studentship.

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Received 26*th November* 1984; *Paper* 4/2013