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Preliminary communication

The reaction of $CpWMe(CO)_3$ with $LiEt_3BH$. Formation of the formyl complex *trans*-$[CpWMe(CHO)(CO)_2]^-$ and the (hydrido)(acyl) complex *trans*-$[CpWH(COMe)(CO)_2]^-$

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Abstract

Addition of $LiEt_3BH$ to $CpWMe(CO)_3$ results in consecutive formation of *trans*-$[CpWMe(CHO)(CO)_2]^-$ (some of which exists in solution as two rotamers of a BEt_3 adduct) and *trans*-$[CpWH(COMe)(CO)_2]^-$. Reaction of the latter with CHI_3 and subsequent treatment of the product with either (i) Me_3SiCl, followed by filtration through SiO_2 or (ii) Me_3OBF_4 gives hydroxy- or methoxy-carbenes $CpWI[{=}C(OR)Me](CO)_2$ (R = H or Me), respectively.

The reactions of formylmetal species [1] are of considerable current interest. We are interested in the interactions of formyl ligands, once formed, with other functions within the molecule, such as methyl [2]. We report here that $CpWMe(CO)_3$ (**1**) reacts with $LiEt_3BH$ [3] to form the synthetically useful anionic hydridoacyl complex *trans*-$[CpWH(COMe)(CO)_2]^-$ (**2**) in a reaction proceeding via the formyl complex *trans*-$[CpWMe(CHO)(CO)_2]^-$ (3).

Addition of $LiEt_3BH$ to a tetrahydrofuran (THF) solution of **1** at −70 °C results in a solution containing the spectroscopically identified formyl **3** *. The carbonyl bands in the IR spectrum indicate the presence of a single *trans* [4] dicarbonyl species. However, the ^1H NMR spectrum in THF shows three formyl signals (Fig. 1. Warming of the reaction mixture to −30 °C results in a collapse of the formyl resonances, and this is reversible on recooling. Spin saturation transfer experiments at −50 °C show that all three formyls undergo chemical exchange. Addition of BEt_3 to the reaction mixture at −60 °C causes the central resonance to disappear, while the relative intensities of the outer two signals remain approximately constant.

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* $[CpWMe(CHO)(CO)_2]^-$ (**3**): IR: ν(CO) (THF, −70 °C) 1917m and 1826s cm^{-1}; ^1H NMR: formyl signals displayed in Fig. 1, other signals, δ (THF, −50 °C) 5.05 ppm (s, 5H, Cp), methyl signal obscured by BEt_3 resonances; ^{13}C NMR: δ (THF-d_8, −50 °C) 276.9 (formyl), 268.5 (formyl), 227.3 (CO), 225.1 (CO), 221.4 (CO), 95.0 (Cp), 93.2 (Cp), 92.8 (Cp), −29.8 (Me), −30.0 (shoulder, Me), and −31.4 (Me) ppm.

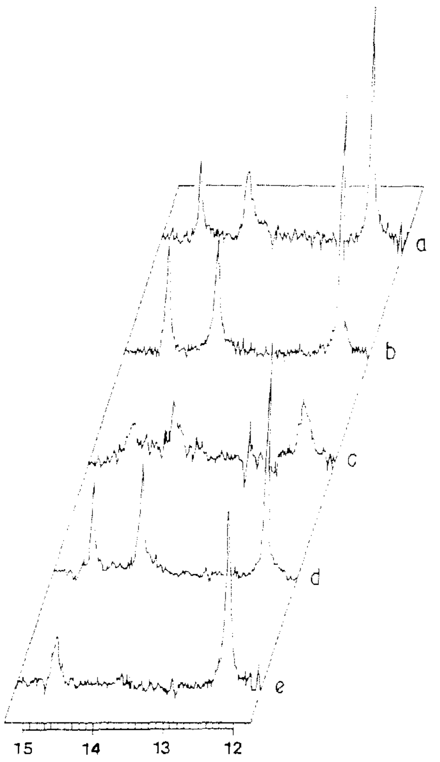
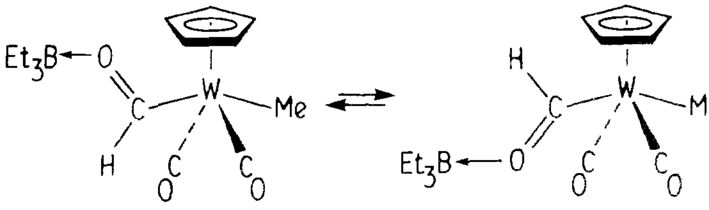


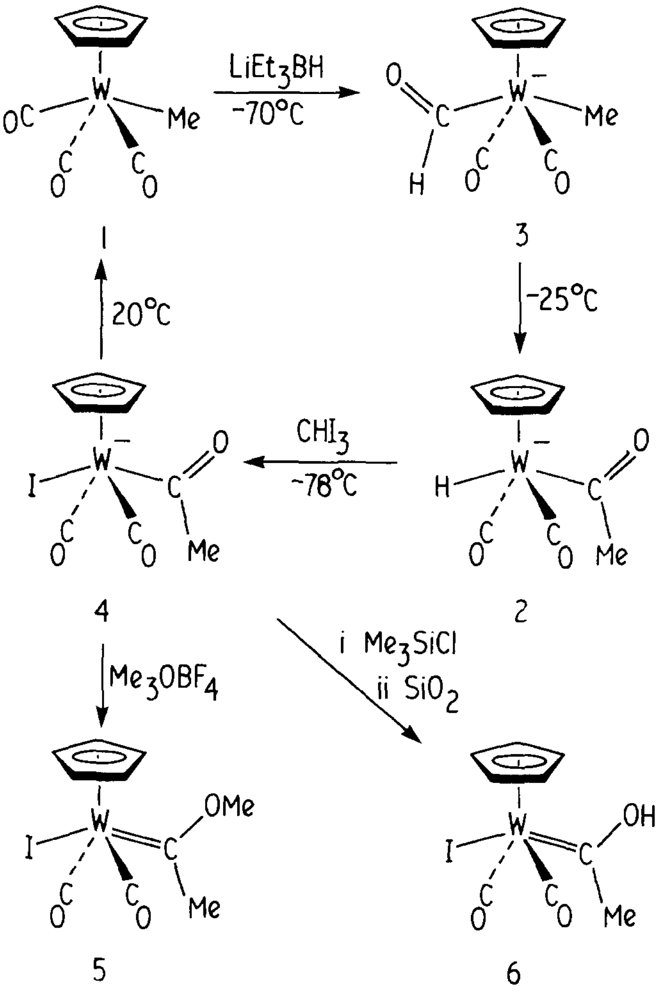
Fig. 1. ^{1}H NMR spectra in the formyl region of the reaction between **1** and $LiEt_3BH$. (a) immediately after mixing at −70 °C, (b) warming to −50 °C, (c) warming to −30 °C, (d) recooling to −50 °C, and (e) after addition of BEt_3 at −60 °C, spectrum recorded at −60 °C.

These results are consistent with some of the formyl species **3** being present as a complex with BEt_3, probably coordinated through the formyl oxygen.

Since there is no sign [4] of a *cis*-dicarbonyl in the IR or ^{13}C NMR spectra of the reaction mixture at −70 °C, the two formyl signals remaining after addition of BEt_3 are accounted for by the presence of two rotamers of the **3**-BEt_3 complex that are (Scheme 1 undergoing slow interconversion. It is possible that the uncomplexed formyl species **3** also exists as a pair of rotamers, which, however, undergo more rapid interconvertion, resulting in just a single formyl resonance (the central one) in the ^{1}H NMR spectrum. These conclusions are reinforced by ^{13}C NMR spectra,



Scheme 1.



Scheme 2.

which show three signals for each of the carbonyl, cyclopentadienyl, and methyl groups at $-50\,^\circ$C in similar proportions to the three proton formyl resonances in Fig. 1. There are only two formyl signals, probably due to an overlap of two of the expected three signals. Direct observation of formyl-boron adducts in this way is surprisingly rare, but there is a report which mentions BH_3 adducts of two rotamers of the formyl $Fe(CHO)(CO)(PMe_3)(\eta\text{-}C_5Me_5)$ [5].

Warming the reaction solution containing **3** to $-25\,^\circ$C results in rearrangement to the hydridoacyl *trans*-**2**, can be isolated as a stable boron-free 12-crown-4 adduct $[Li(12\text{-crown-}4)_2]$-(**2**) *, which, rather unusually, contains two complexed crown

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* $[Li(12\text{-crown-}4)_2][CpWH(COMe)(CO)_2]$, $[Li(12\text{-crown-}4)_2]$ (**2**): IR ν(CO) (CH_2Cl_2) 1902m and 1803s cm^{-1}; ^{1}H NMR: δ (CD_2Cl_2) 5.10 (s, 5 H, Cp), 3.75 (s, 32 H, crown OCH_2), 2.31 (s, 3 H, Me), and -6.22 ppm (s, 1H, ^1J(WH) 46 Hz); ^{13}C NMR: δ (CD_3OD, $-50\,^\circ$C) 295.2 (*C*OMe), 230.0 (CO), 90.9 (Cp), 70.2 (12-crown-4), and 54.6 ppm (Me).

ethers for the one lithium cation [6*]. The negative ion FAB mass spectrum of this material shows a good tungsten ion pattern centered at *m/e* 349 associated with $[CpWH(COMe)(CO)_2]^-$. The isomerisation of **3** to **2** is probably driven by the strength of the W–H bond in **3** relative to that of the W–Me bond in **2** [7]. A similar isomerization is observed in the analogous molybdenum reaction, although in that case $[CpMoH(COMe)(CO)_2]^-$ is a transient intermediate on the way to $[CpMo(CO)_2(MeCHO)]^-$ and is never seen pure [2]. Complex **2** shows no sign of rearranging to an analogous $[CpW(CO)_2(MeCHO)]^-$ anion.

The hydridoacyl **2** is extremely moisture sensitive. Traces of water cause formation of $Li[CpW(CO)_3]$ (confirmed by IR, ^1H NMR, and ^{13}C NMR spectroscopic comparisons with an authentic sample synthesised as described in reference 3a), and (presumably) methane.

Complex **2** is a useful synthetic precursor for carbene complexes, and allows synthesis of useful carbenes not directly available by more conventional methods. Treatment of $[Li(12\text{-crown-}4)_2]$ (**2**) with CHI_3 at −78°C gives solutions of an unisolated, thermally unstable species whose IR and NMR spectra suggest the structure *trans*-$[CpWI(COMe)(CO)_2]^-$ (**4**). Many hydrides are known to exchange with CCl_4, CBr_4, or CHI_3 [8]. The assignment of structure **4** is further based on the elimination of halide on warming, so regenerating **1**, and the addition of Me_3OBF_4 to a THF solution of **4** which gives a moderate (22%) yield of the new spectroscopically characterised iodocarbene **5**. This carbene cannot be synthesized more directly via treatment of $CpWI(CO)_3$ with MeLi followed by Me_3OBF_4, since the first step gives **1** rather than **4**.

Addition of Me_3SiCl to **4** followed by low temperature filtration through silica gives the spectroscopically characterised hydroxycarbene **6**, apparently by desilylation during filtration. This is a much better approach to **6** than direct protonation of **4** with HBF_4, which gives a number of other unidentified products and only low yields of **6**.

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