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Hydride Transfer Reactions of Anionic Metal Formyl Complexes: a Mechanistic Test

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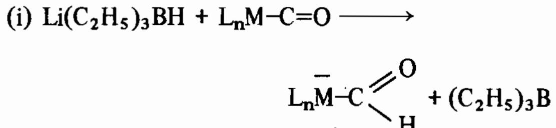
Although the initially formed intermediate in the heterogeneously catalyzed reduction of CO by H_2 is believed to be a surface-bound formyl [1], homogeneous transition metal formyl complexes have proven to be furtive entities. Their absence from the chemical literature was conspicuous until 1973, when Collman and Winter reacted $Na_2Fe(CO)_4$ with formic acetic anhydride and isolated the anionic formyl complex $[(CO)_4Fe(COH)]^-$ [2]. Subsequently, we have found that trialkylborohydrides such as $Li(C_2H_5)_3BH$ react with a variety of metal carbonyl compounds to yield anionic formyl complexes (*1*) of varying stabilities (equation i) [3–5]. Related observations have been made by Casey [6] and Winter [7]. While the binuclear rhenium formyl complex *2* has been isolated as a THF solvate [5], the vast majority of formyl complexes prepared via this route (*e.g.*, *5–7*) [3, 4] rapidly decompose at room temperature and must be characterized by low temperature spectroscopy. Hence chemical studies must be done *in situ* utilizing solutions containing the by-product triethylborane.



$$\text{(i)}\ Li(C_2H_5)_3BH + L_nM{-}C{=}O \longrightarrow L_n\bar{M}{-}C{\overset{\displaystyle O}{\underset{\displaystyle H}{\diagup\!\!\diagdown}}} + (C_2H_5)_3B$$

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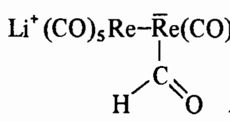
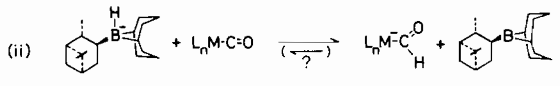


$$Li^+ (CO)_5Re{-}\bar{R}e(CO)_4{-}C(H){=}O$$

2

We have found anionic formyl complexes *1* to be potent hydride donors which reduce alkylating agents to alkanes and aldehydes and ketones to alcohols at rates much faster than their decomposition rates [3–5]. However, with unisolated complexes there exists the possibility that trialkylborane might in some way mediate the hydride transfer. Hydride donation reactions of isolable formyl complexes [2, 5, 6] also might be subject to Lewis acid catalysis. In this communication, we address ourselves to this important mechanistic question, employing a type of experiment we believe can have substantial utility for the chemical characterization of reactive organometallic species.

We have utilized the readily prepared chiral trialkylborohydride *3*, synthesized from 91% optically pure (–)-α-pinene, to generate formyl complexes as depicted in equation (ii). Brown has reported that the enantiomer of *3* reduces acetophenone to (R)-(+)-1-phenylethanol of 17% optical purity [8]. Since isolated, analytically pure formyl complexes (*e.g.*, *2*) also reduce aldehydes and ketones [5], two limiting mechanisms are possible for acetophenone reduction by these reaction mixtures if the equilibrium depicted in equation (ii) is operative.



3 1 4

The reactive formyl complexes 5–7, which have been previously prepared with $Li(C_2H_5)_3BH$, were generated using the chiral borohydride *3* (equations iii–v; IR and ^1H NMR monitored). Acetophenone was reacted with each of the reaction mixtures for 2 hr at –78 °C. After an aqueous quench, the product 1-phenylethanol was purified by column chromatography and vacuum distillation (≥80% isolated yield based upon acetophenone) and its specific rotation determined. The results, together with a control done in the absence of a metal complex, are presented in Table I.

TABLE I. Asymmetric Reduction of Acetophenone by Formyl Complex Reaction Mixtures.[a]

Metal Formyl	$[\alpha]^{25}_{D}$, 1-phenylethanol	optical purity, %
5	–5.04	11.7
6	–2.62	6.1
7	+1.33	3.1
none[b]	–6.74	15.7

[a]Typical reaction quantities: 14.65 mmol $Mn_2(CO)_{10}$, 13.38 mmol *3*, and 13.0 mmol acetophenone (equation iii). A slight excess of metal carbonyl was employed to ensure no unreacted *3* remained. [b]Reaction of *3* and acetophenone.

Formyl *5* is achiral. Yet the 1-phenylethanol produced from it has about 75% the optical purity of that produced from trialkylborohydride *3* alone (Table I). We suggest that equation (iii) is reversible and *3* performs as the kinetically active hydride donor.

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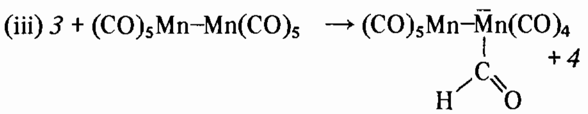
The 1-phenylethanol asymmetry induced by *6* is much less than that induced by borohydride *3*. This ***requires*** that a mechanistic pathway not involving *3* alone be operative. Since *6* is achiral, a logical mechanism is direct hydride transfer from *6* to acetophenone. The optical yield would then be rationalized by invoking direct hydride transfer *ca.* 60% of the time. Alternatively, a termolecular mechanism proceeding in lower optical yield can be invoked.



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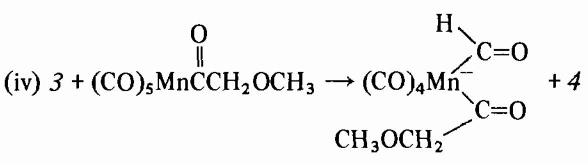

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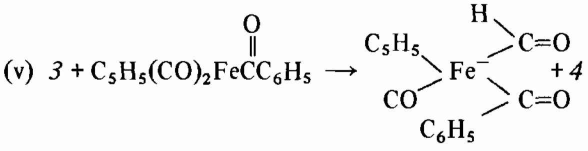

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The asymmetry induced by *7* is *opposite* in sign to that induced by *3*. This requires the intervention of a new chiral reducing system. We suggest that either significant chirality is induced into the tetrahedral formyl *7* by *3*, or a termolecular mechanism operates. Acetophenone is then reduced with predominant formation of (+)-1-phenylethanol. The possibility that *some* reduction occurs via reversal of equation (v) cannot be ruled out.

Together, the foregoing results prove that trialkylboranes can participate in hydride transfer reactions of anionic formyl complexes. On the other hand, direct hydride transfer has been unambiguously demonstrated with isolated formyl complexes [2, 5, 6]. The exact mechanisms followed should be a function both of substrate and Lewis acid: the partitioning could well be different when *5–7* are generated from $Li(C_2H_5)_3BH$.

The lability of the metal formyl hydrogen in homogeneous complexes, as evidenced by these reactions, may have analogy in surface chemistry. Interestingly, Lewis acids such as BBr_3 and $AlCl_3$ are important components of recently described homogeneous Fischer–Tropsch catalysts [9]. In addition to their previously ascribed role of coordinating CO oxygen, they might mediate hydride delivery. Finally, we note that many important mechanistic questions in organometallic chemistry and catalysis involve species of at best marginal stability. The approach taken herein for establishing the participation of trialkylboranes in hydride transfer mechanisms of reactive anionic formyls *1* is novel and potentially of broader applicability [10].

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