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MONONUCLEAR ANIONIC FORMYL COMPLEXES; SYNTHESIS AND PROPERTIES

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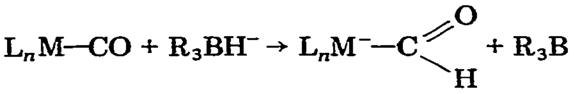
Summary

A series of kinetically unstable mononuclear anionic formyl complexes have been prepared by the action of $Li(C_2H_5)_3BH$ on neutral metal carbonyl precursors. One of these, $Li^+[(CO)_4Mn(COC_6H_5)(CHO)]^-$, is shown to decompose by a hydride transfer disproportionation mechanism involving the by-product $(C_2H_5)_3B$.

Introduction

Current interest in the synthesis and reactions of formyl-transition metal complexes derives from the postulated intermediacy of catalyst-bound formyls in certain CO reduction processes [1]. However, the two principal routes utilized to prepare acyl-transition metal complexes (alkylmetal carbonylation [2] and metal anion acylation [3]) have not proved generally applicable to the synthesis of formyl-transition metal complexes [4—6]. In 1976, the preparation of anionic formyl complexes by the attack of trialkylborohydrides or related hydride nucleophiles upon neutral metal carbonyl precursors (eq. 1) was announced by our laboratory [7] and also Casey's [5] and Winter's [8]. In this paper, we demonstrate that eq. 1 constitutes a means of considerable generality for the preparation of mononuclear anionic formyl complexes, and examine the properties of some of the complexes thus prepared. Portions of this work were the subject of a preliminary communication [9].



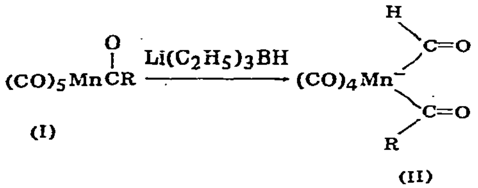
$$L_nM{-}CO + R_3BH^- \rightarrow L_nM^-{-}C\overset{\displaystyle O}{\underset{\displaystyle H}{\lessgtr}} + R_3B \qquad (1)$$

Results

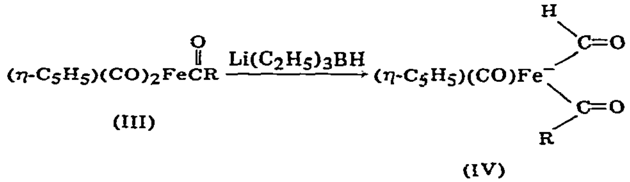
Synthesis and spectra. 0.5 *M* THF solutions of the metal carbonyl compounds depicted in Table 1 were prepared, and 1,2,4,5-tetrachlorobenzene internal

TABLE 1

DATA ON FORMYL COMPLEXES PREPARED FROM ACYL-MANGANESE AND -IRON COMPOUNDS


(I) (II)

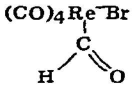
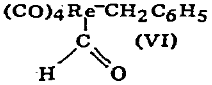
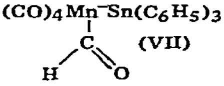
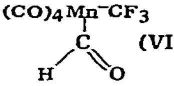
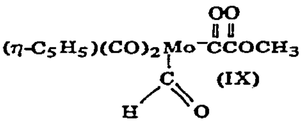
R	Yield of II (%)	^{1}H NMR (δ, —50°C)
(a) C_6H_5	98	12.80
(b) CH_2OCH_3	91	12.75
(c) $\overset{O}{\overset{\|}{C}}OCH_3$	34	12.65
(d) CF_3	26	12.43


(III) (IV)

R	Yield of IV (%)	^{1}H NMR (δ, —50°C)
(a) C_6H_5	77	12.91
(b) p-$C_6H_4OCH_3$	96	13.10
(c) CH_3	97	12.83

TABLE 2

OTHER FORMYL COMPLEXES PREPARED WITH $Li(C_2H_5)_3BH$

Starting material	Product	Product yield (%)	^{1}H NMR, δ (°C)
$(CO)_5ReBr$	 (V)	64	13.47 (—50)
$(CO)_5ReCH_2C_6H_5$	 (VI)	95	13.95 (—10)
$(CO)_5MnSn(C_6H_5)_3$	 (VII)	29	13.6 (—30)
$(CO)_5MnCF_3$	 (VIII)	54	12.40 (—59)
$(\eta\text{-}C_5H_5)(CO)_3Mo\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OCH_3$	 (IX)	17	12.90 (—50)

standard was added. These were cooled to —50°C in a ^{1}H NMR probe, and 1.2 equiv. of $Li(C_2H_5)_3BH$ was added to each. New ^{1}H NMR signals were detected in the δ 12.4—13.1 ppm range. Since ^{1}H resonances of this type had been previously established as characteristic of anionic formyl complexes [4,5,8], the tentative structural assignments depicted in Table 1 were made. Yields were calculated relative to 1,2,4,5-tetrachlorobenzene, and can be considered accurate to ±5%.

Other metal carbonyl compounds were treated with $Li(C_2H_5)_3BH$ under conditions similar to those described above. Reactions in which the formation of formyl metal products were observed are summarized in Table 2. No ^{1}H NMR evidence was obtained for the formation of formyl species from the following complexes: $(\eta\text{-}C_5H_5)(CO)_2FeSn(C_6H_5)_3$, $(\eta\text{-}C_5H_5)(CO)_3MoCH_3$, $Mn(CO)_3(PPh_3)_2Cl$, $Re(CO)_3[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Br$, and $(CO)_5CrPCl_3$.

The formyl complexes IIa—IId and IVa—IX were all unstable at room temperature, and hence could not be purified. In some cases, IR spectra supporting the indicated structural assignments could be obtained (cm^{-1}, THF): IIa, 2050w, 1949s, 1933s, 1884m, 1588w(br); IIb, 2055m, 1962s, 1929s, 1863m, 1604m; IVa, 1932s, 1555m. The absorption patterns of IIa and IIb are characteristic of *cis*-geometric isomers.

The formyl proton NMR resonances shifted non-linearly to lower field when the sample temperatures were increased (typically, 0.08—0.20 ppm/10°C increment). Satisfactory ^{13}C NMR spectra could be obtained only in the presence of $Cr(acac)_3$. Manganese formyl IIb (^{13}C NMR, —35°C, THF-d_8, ca. 0.02 *M* $Cr(acac)_3$: 302.6, 284.7 (acyl, formyl carbons) 220.1, 217.7, 215.1 (CO carbons) 92.8 (CH_2), 58.5 (CH_3) ppm) exhibited the three CO resonances expected of a *cis*-geometric isomer. In iron formyl (IVa), the formyl and acyl carbons were nearly degenerate (^{13}C NMR, —35°C, THF-d_8, ca. 0.02 *M* $Cr(acac)_3$: 295.9, 294.2 (acyl, formyl carbons), 221.8 (CO), 158.9 (*ipso*-phenyl carbon), 88.3 (C_5H_5) ppm; other phenyl carbons obscured by some remaining IIIa).

Kinetics. The rates of thermal decomposition of identically prepared solu-

TABLE 3

DECOMPOSITION RATES OF FORMYL COMPLEXES

Complex [a]	Decomposition rate, $k_{obs} \times 10^4$/sec	Temperature (°C)
IIa	15.53 ± 0.71	7
IIa	7.10 ± 0.19	—3
IIa	3.61 ± 0.23	—10
IIa	0.46 ± 0.04	—20
IIb	1.25 ± 0.17	7
IId	17.38 ± 0.64	—23
IVa	6.29 ± 0.18	7
IVb	24.87 ± 0.93	20
IVb	5.67 ± 0.15	7
IVb	0.35 ± 0.02	—18
IVc	9.94 ± 0.52	—16

[a] Li^+ salts generated using $Li(C_2H_5)_3BH$.

TABLE 4

DECOMPOSITION RATE AT —10°C OF IIa GENERATED FROM DIFFERENT TRIALKYLBOROHYDRIDES

Trialkylborohydride employed to form IIa	Decomposition rate, $k_{obs} \times 10^4$/sec
$Li(C_2H_5)_3BH$	3.72 ± 0.33
$Na(C_2H_5)_3BH$	6.93 ± 1.46
$K(C_2H_5)_3BH$	17.4 ± 6.6
$Li(s\text{-}C_4H_9)_3BH$	negligible
$Li(C_2H_5)_3BD$	1.10 ± 0.11

tions of IIa, IIb, IId, and IVa—IVc were monitored by ^1H NMR and found to be first order. The observed rate constants compiled in Table 3 (each of which was reproduced at least once) were obtained from plots with 0.981—0.996 correlation coefficients to at least 2.5 half-lives of data. The addition of 2 equiv. of $(C_2H_5)_3B$ approximately doubled the rate of disappearance of IIa, but did not alter the rate of disappearance of IVa. In these two experiments, much poorer correlation coefficients were obtained. From the rate data in Table 3, the following apparent entropies of activation ($\Delta S^{\neq}$) for the decomposition of IIa and IVb were calculated: IIa: —8.8 ± 2 eu; IVb: —16.2 ± 2 eu.

A series of experiments was conducted in which formyl IIa (or other alkali metal salts thereof) was generated from different trialkylborohydrides under comparable conditions. Utilizing $Li(C_2H_5)_3BD$, IIa-d_1 was generated. Decomposition rates were measured by ^1H or ^2H NMR and are summarized in Table 4. A marked kinetic deuterium isotope effect was observed. When Ia was treated with $Li(CH_3)_3BH$, IIa formed only in low (20—30%) yields.

Decomposition products. Metal hydride ^1H NMR resonances were not observe when formyls IIa—IId and IVa—IX were allowed to decompose. The decomposition of IIa (Li^+ salt) was IR monitored at room temperature. The primary products were observed to be $Li[Mn(CO)_5]$ and $(CO)_5Mn(COC_6H_5)$. After 2 h, $(C_6H_5)_3SnCl$ was added to the reaction mixture. Subsequently isolated were 0.42 equiv. of $(CO)_5Mn(COC_6H_5)$ and 0.55 equiv. of $(CO)_5MnSn(C_6H_5)_3$. In a separate experiment, the decomposition products were water quenched and tetradecane internal standard was added. GC analysis indicated 0.41 equiv. of benzyl alcohol to be present. When IIa was allowed to decompose for 24 h, $Li[Mn(CO)_5]$ was the only organometallic species remaining by IR, and benzyl benzoate (0.30 equiv.) was detected by GLC. Benzyl benzoate was also formed when Ia was reacted with $C_6H_5CH_2O^-Li^+$. The decomposition of IIa generated from $K(C_2H_5)_3BH$ also resulted in the formation of $K[Mn(CO)_5]$ and $(CO)_5Mn(COC_6H_5)$ by IR.

Formyl IVa, prepared from 2.005 mmol of $(\eta\text{-}C_5H_5)(CO)_2Fe(COC_6H_5)$, was allowed to decompose for 2 h at room temperature, after which $(C_6H_5)_3SnCl$ was added. Subsequently isolated were $(\eta\text{-}C_5H_5)(CO)_2Fe(COC_6H_5)$ (0.477 mmol), $(\eta\text{-}C_5H_5)(CO)_2FeSn(C_6H_5)_3$ (0.630 mmol), and $[(\eta\text{-}C_5H_5)(CO)_2Fe]_2$ (0.380 mmol). By GLC analysis, 0.392 mmol of benzyl alcohol was formed. No other organic products could be detected; specifically absent were benzaldehyde, benzoin, benzil, benzyl benzoate, and stilbene.

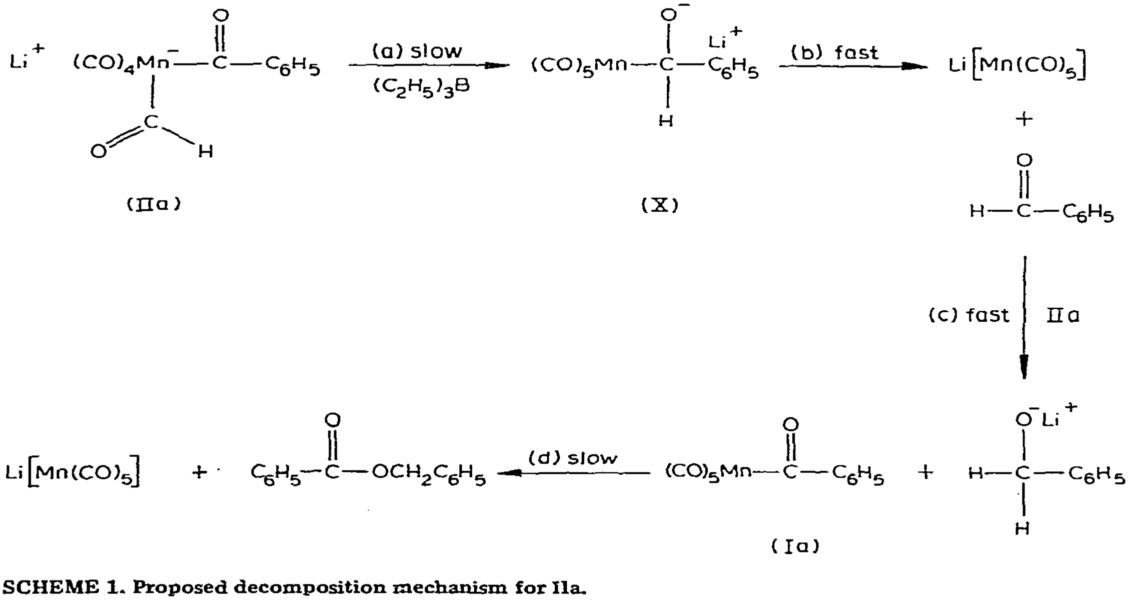
Reactions. When benzaldehyde was added to IIa at 0°C, and the reaction quenched after 5 minutes with H_2O, benzyl alcohol was obtained in 96% yield (based upon IIa) by GC. When this reaction was monitored at —70°C by ^1H NMR, IIa was completely reacted within 3 minutes.

In ^1H NMR monitored experiments, 1.1—1.4 equiv. of CF_3SO_3H completely consumed formyls IIa and IVa within 3 minutes at —20 and —40°C, respectively. In preparative scale experiments, an 83% yield of $(CO)_5Mn(COC_6H_5)$ could be isolated from the reaction of IIa with CF_3SO_3H, and a 74% yield of $(\eta\text{-}C_5H_5)(CO)_2Fe(COC_6H_5)$ could be isolated from the reaction of IVa with CF_3SO_3H. However, the observation of H_2 evolution originally reported in these reactions [9] could not be reproduced.

Discussion

Trialkylborohydride nucleophiles clearly offer access to a wide variety of mononuclear anionic formyl complexes. Additional examples have been reported by Lukehart [10], and $K(i\text{-}C_3H_7O)_3BH$ has been utilized by Casey to generate mononuclear anionic chromium, -tungsten, and -iron formyl complexes [5]. However, with the exception of the formyl $[(CO)_4Fe(CHO)]^-$ originally synthesized by Collman and Winter [4], and simple derivatives thereof [5,8], the vast majority of mononuclear anionic formyl complexes are unstable at room temperature. Hence purification cannot be readily achieved. In particular, satisfactory methods for the removal of trialkylborane by-products have not been developed. However, "formyl transfer" reactions [11] using stable, purified anionic formyls such as $[Re_2(CO)_9(CHO)]^-$ as hydride donors [12,13] offer a means of circumventing this problem.

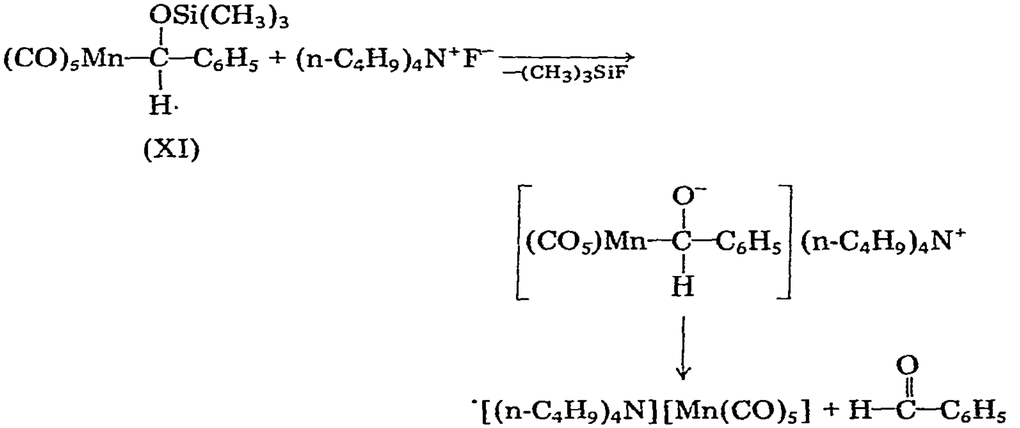
A considerable amount of direct and indirect evidence indicates that most formyl-metal complexes are thermodynamicaly unstable with respect to decar-



SCHEME 1. Proposed decomposition mechanism for IIa.

bonylation and metal hydride formation [4,5,6,8,14]. However, metal hydride products were not apparent in the ^1H NMR monitored decompositions of anionic formyl complexes reported herein. This seemingly anomalous situation merits close examination, since insight might be gained as to how catalyst-bound formyls can be diverted into more fruitful reductive reaction pathways. In a relevant preliminary study utilizing optically active trialkylborohydrides and the prochiral ketone acetophenone, we established that trialkylborane by-products can participate in hydride transfer reactions of anionic formyl complexes [15]. The possibility of trialkylborohydride involvement must therefore be kept in mind when considering decomposition mechanisms for the formyl complexes reported in this paper.

A mechanism which satisfactorily accounts for the decomposition stoichiometry and kinetics of IIa is depicted in Scheme 1. We suggest that IIa is transformed to manganese alkyl X in a rate-determining hydride transfer step. We propose that X then rapidly fragments to $Li[Mn(CO)_5]$ and benzaldehyde, as shown in step b; the former is an observed product of the decomposition. We have confirmed the viability of step b by independently generating X (R_4N^+ salt) from silyloxyalkyl XI and $(n\text{-}C_4H_9)_4N^+F^- \cdot 3\ H_2O$ (eq. 2) [16]. Under these conditions, F^- attack on silicon and alkoxide displacement are known to occur. Benzaldehyde and $[(n\text{-}C_4H_9)_4N][Mn(CO)_5]$ formed instantly [16].



$$(CO)_5Mn{-}\overset{\displaystyle OSi(CH_3)_3}{\underset{\displaystyle H}{C}}{-}C_6H_5 + (n\text{-}C_4H_9)_4N^+F^- \xrightarrow[-(CH_3)_3SiF]{}$$

(XI)

$$\left[(CO_5)Mn{-}\overset{\displaystyle O^-}{\underset{\displaystyle H}{C}}{-}C_6H_5\right](n\text{-}C_4H_9)_4N^+ \qquad (2)$$

$$\downarrow$$

$$[(n\text{-}C_4H_9)_4N][Mn(CO)_5] + H{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}C_6H_5$$

Benzaldehyde, however, is not an observed decomposition product of IIa. Hence we propose that the benzaldehyde formed in step b is immediately reduced by undecomposed IIa to alkoxide $C_6H_5CH_2O^-Li^+$ (Scheme 1). This accounts for the observed product distribution, and is compatible with the first-order decomposition kinetics. Importantly, the reaction of IIa and benzaldehyde was independently observed to be virtually instantaneous at —70°C. Finally, upon prolonged standing, $(CO)_5Mn(COC_6H_5)$ benzoylates $C_6H_5CH_2O^-Li^+$ (step d). We observed by GLC a 60% yield (theory: 0.5 equiv) of the resulting benzyl benzoate. Pearson has previously described the analogous reaction between $(CO)_5Mn(COCH_3)$ and $NaOCH_3$ [17].

Returning to the initial steps of Scheme 1, alternatives involving CO loss should be considered in light of the decomposition of $[(CO)_4Re(COCH_3)(CHO)]^-$ to $[(CO)_4Re(COCH_3)H]^-$ reported by Lukehart [10] and studies by Casey on

$[(CO)_4Mn(COC_6H_5)(COCH_3)]^-$. After a slight modification [18] of earlier work [19], the decomposition chemistry of $[(CO)_4Mn(COC_6H_5)(COCH_3)]^-$ appears well understood. Dissociation of CO has been established as the initial and rate-determining step. Subsequently, rapid (and reversible) alkyl migration occurs. Acetophenone is then produced by reductive elimination from either $[(CO)_4Mn(COC_6H_5)(CH_3)]^-$ or (preferably) $[(CO)_4Mn(C_6H_5)(COCH_3)]^-$. Hence the possibility that intermediate benzaldehyde in Scheme 1 might be formed by a similar route must be addressed.

Several lines of evidence eliminate this alternative route for benzaldehyde formation. Most importantly, the decomposition of IIa shows a reproducible kinetic deuterium isotope effect of ca. 3.3 (Table 4). This requires involvement of the formyl C—H bond prior to or during the rate determining step. Secondly, the negative $\Delta S^{\neq}$ calculated from the k_{obs} in Table 3 is inconsistent with CO dissociation as an initial, rate-determining step. Consideration might be given to CO dissociation as an initial but not rate-determining step. However, alkyl migration rapidly followed CO loss from $[(CO)_4Mn(COC_6H_5)(COCH_3)]^-$. Also metal—hydride bonds are known to be considerably more (thermodynamically) stable than metal—alkyl bonds [20], and (where comparisons are possible) [6,14a] coordinatively unsaturated metal formyls decompose to metal hydrides much more rapidly than homologous metal acyls decompose to metals alkyls. Thus it is highly improbable that hydride migration would not also be rapid if CO loss occurred from IIa. Finally, the rate of decomposition of IIa is enhanced by added $(C_2H_5)_3B$. These data strongly suggest an initial hydride transfer step, such as to form X (Scheme 1), and that this transfer is mediated by $(C_2H_5)_3B$.

A related interesting observation is that IIa generated from $Li(s\text{-}C_4H_9)_3BH$ is kinetically considerably more stable than IIa generated from $Li(C_2H_5)_3BH$ (Table 4). Since $(s\text{-}C_4H_9)_3B$ is known to be a much poorer hydride acceptor than $(C_2H_5)_3B$ [21], this provides additional support for an important trialkylborane role in the decomposition of IIa. Unfortunately, $(CH_3)_3B$ is such a good hydride acceptor that $Li(CH_3)_3BH$ is ineffective for the generation of IIa. Since $(CH_3)_3B$ is a gas, (b.p. —20°C), formyl complex purification would have been facilitated.

Several possible roles can be envisioned for the involvement of trialkylboranes in the decomposition of IIa. It may be necessary for the formation of IIa to be completely reversed prior to generation of X. Alternatively, X might form from IIa via a 4-centered transition state in which the trialkylborane is associated with the migrating hydride and/or the benzoyl oxygen. Unfortunately, these speculative possibilities are not readily distinguished by experiment.

The decomposition chemistry of the other formyl complexes was not investigated in detail. In the cases of IIc and IId, the lower yields and faster decomposition rates observed are likely due to the presence of highly electrophilic acyl groups; hence the formation of species analogous to X (Scheme 1), either upon decomposition of IIc and IId or directly from Ia and Id and $Li(C_2H_5)_3BH$, should be more favorable. Similarities in the types of decomposition products suggest that the decomposition mechanism of the iron formyl IVa shares some qualitative features with that of IIa. It is somewhat surprising that $(CO)_5ReH$ does not appear to be formed from V (Table 2). Recently, we established that the homologous anionic acyl *fac*-$Li^+[(CO)_3Re(PPh_3)(COCH_3)(Br)]^-$ can intramolecularly decompose to the alkyl *cis*-$(CO)_4Re(PPh_3)(CH_3)$ [22].

At this stage, we have no explanation for our inability to reproduce our earlier observation of H_2 formation upon protonation of IIa and IVa. Certainly the recovery of $(CO)_5Mn(COC_6H_5)$ and $(\eta\text{-}C_5H_5)(CO)_2Fe(COC_6H_5)$ from these reactions in 74—83% yields requires a reduction product. ^1H NMR monitoring indicates that the formyl is consumed virtually instantly. Our best guess is that some type of electrophile induced disproportionation, similar to that observed with the neutral formyl $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$ [23], may occur. It seems possible that hard electrophiles such as H^+ might prefer to initially attack the formyl oxygen. Oxygen protonation of homologous anionic acyl complexes has been observed [24]. Similarly, we have been unable to reproduce our reports [12] of H_2 formation upon protonation of binuclear formyl complexes [25].

In summary, it has been shown that hydride transfer properties (at least in the presence of $(C_2H_5)_3B$) of anionic formyl complexes can play an important role in their decomposition chemistry. Pathways distinctly different from homologous anionic acyl complexes are observed, adding to numerous existing contrasts between these two classes of compounds. Work with binuclear anionic formyl complexes will be presented in our subsequent full paper in this series.

Experimental

General. All reactions, filtrations, and isolations were carried out under N_2 using standard Schlenk techniques. Chromatographic separations of neutral compounds were carried out in air, limiting exposure of solutions by maintaining a nitrogen atmosphere in the collection vessel.

THF and diethyl ether were dried and deoxygenated by distillation from benzophenone ketyl immediately prior to use. Hexane was dried over $LiAlH_4$. Other solvents were commercial reagent grade and were used without further purification.

IR spectra were recorded on a Perkin—Elmer Model 521 spectrometer. Gas chromatography was carried out on a Hewlett—Packard Model 5720A instrument with a 6′ 10% DC710 (on Chromosorb W) column. NMR instrumentation employed is specified in the individual experiments.

Starting materials. $Li(C_2H_5)_3BH$, $Li(C_2H_5)_3BD$, $Li(s\text{-}C_4H_9)_3BH$, $Na(C_2H_5)_3BH$, $K(C_2H_5)_3BH$ and $(C_2H_5)_3B$ were obtained from Aldrich Chemical Company as 1.0 *M* THF solutions and used without standardization. $Li(CH_3)_3BH$ was obtained from Aldrich (custom synthesis) as a 1.0 *M* solution in 1,3-dioxolane.

The following organometallic compounds were prepared by literature methods $(CO)_5Mn(COCO_2CH_3)$ [3], $(CO)_5Mn(COCF_3)$ [26], $(CO)_5MnCF_3$ [26], $(\eta\text{-}C_5H_5)(CO)_2Fe(COC_6H_5)$ [3,27], $(\eta\text{-}C_5H_5)(CO)_2Fe(COCH_3)$ [28], $(\eta\text{-}C_5H_5)(CO)_2Fe(CO\text{-}p\text{-}C_6H_4OCH_3)$ [29], $(CO)_5ReCH_2C_6H_5$ [30], $(CO)_5MnSn(C_6H_5)_3$ [3], $(\eta\text{-}C_5H_5)(CO)_3Mo(COCO_2CH_3)$ [3], $(\eta\text{-}C_5H_5)(CO)_2FeSn(C_6H_5)_3$ [3], $(\eta\text{-}C_5H_5)(CO)_3MoCH_3$ [3].

In our hands, $(CO)_5Mn(COC_6H_5)$ (Ia) was not easily obtained pure when prepared by published methods [31]. In an IR monitored reaction sequence, we added first $Li(C_2H_5)_3BH$ and then C_6H_5COCl to $Mn_2(CO)_{10}$ according to procedures previously described [3]. Solvent removal under vacuum at room temperature, CH_2Cl_2 extraction of the residue, washing of the CH_2Cl_2 extract, concentration, and cooling to 0°C afforded crystals of Ia in 30—60% yields.

Compound Ib, $(CO)_5Mn(COCH_2OCH_3)$, was prepared in 54% yield from $Mn_2(CO)_{10}$, $Li(C_2H_5)_3BH$, and methoxyacetyl chloride by a procedure analogous to that given in ref. 3 for $(CO)_5Mn(COCOC_6H_5)$. Data: m.p. 27—30°C; IR (cm^{-1}, cyclohexane); 2116m, 2050w, 2015vs, 2002s, 1991w(sh), 1635m; ^1H NMR (δ (ppm), $CDCl_3$): 3.47 (s, 3 H), 3.67 (s, 2 H); ^{13}C NMR (ppm, $CDCl_3$): 263.1, 208.7 (broad), 89.9, 58.9; (ppm, THF-d_8, —35°C): 262.1, 210.9, 90.1, 58.7; mass spectrum (*m/e*): 223 (100%, $Mn(CO)_6^+$), 212 (41, $(CO)_3MnCOCH_2OCH_3^+$) 195, (52, $Mn(CO)_5^+$).

Preparation of formyls IIa—IId, IVa—IVc, IX. Procedure for IVa: A ^1H NMR tube was prepared by oven drying (30 min, 110°C), rinsing with $Li(C_2H_5)_3BH$ and then THF, flushing with N_2, and sealing with a septum cap. A solution of 0.070 g (0.249 mmol) of $(\eta\text{-}C_5H_5)(CO)_2Fe(COC_6H_5)$ and 0.027 g (0.127 mmol) of 1,2,4,5-tetrachlorobenzene in 0.5 ml of THF was syringed into the tube. The sample was cooled to —50°C in the variable temperature probe of a Varian A-60 spectrometer; then 0.27 ml of 1.0 *M* $Li(C_2H_5)_3BH$ in THF (0.27 mmol) was syringed directly into the sample solution in the probe via a 20 cm needle. Within 5 minutes, the formyl was present in maximum yield. A 500 Hz scan, encompassing both the formyl and the tetrachlorobenzene (δ 7.52 ppm) resonances, was recorded. Yield (77%) and chemical shift (δ 12.91 ppm) were measured relative to the tetrachlorobenzene standard.

The other formyl complexes in Table 1 and formyl IXb in Table 2 were prepared exactly as described for IVa. Each reaction was run utilizing 0.25 mmol of acyl-metal carbonyl, 0.5 ml of THF, and 0.27 ml (0.27 mmol) of $Li(C_2H_5)_3BH$. Samples for ^{13}C NMR (recorded at 50 MHz on a Bruker WP-200 Spectrometer) were prepared similarly, except that THF-d_8 which was ca. 0.02 *M* in $Cr(acac)_3$ was employed as solvent.

Preparation of formyl V. A ^1H NMR tube was prepared as described for IIa—IId above. A solution of $(CO)_5ReBr$ (0.103 g; 0.25 mmol) and *p*-di-t-butylbenzene (0.021 g; 0.11 mmol) in 0.75 ml of THF was syringed into the tube. The sample was cooled to —50°C in the variable temperature probe of a Varian A-60 spectrometer; then 0.27 ml of 1.0 *M* $Li(C_2H_5)_3BH$ in THF (0.27 mmol) was syringed directly into the sample solution in the probe via a 20 cm needle. Within 5 minutes the formyl was present in maximum yield. A 500 Hz scan, encompassing both the formyl and the *p*-di-t-butylbenzene aromatic (δ 7.27 ppm) resonances was recorded. Yield (64%) and chemical shift (δ 13.47 ppm) were measured relative to the *p*-di-t-butylbenzene standard.

Preparation of formyl VI. A ^{1}NMR tube was prepared as described for IIa—IId above. A solution of $(CO)_5ReCH_2C_6H_5$ (0.062 g; 0.148 mmol) in 0.3 ml of THF-d_8 and 0.2 ml of THF (containing $(CH_3)_4Si$) was syringed into the tube. The sample was cooled for 15 min in a dry ice/acetone bath; then 0.18 ml of 1.0 *M* $Li(C_2H_5)_3BH$ in THF (0.18 mmol) was added via syringe. The sample was quickly transferred to the probe of a Bruker WP-200 Spectrometer, which had been precooled to —40°C. The temperature was slowly raised. At —10°C, a yield of 96% was determined by integration relative to the phenyl protons in the sample. The chemical shift (δ 13.95 ppm) was measured relative to $(CH_3)_4Si$.

Preparation of formyl VII. A ^1H NMR tube was prepared as described for IIa—IId above. A solution of $(CO)_5MnSn(C_6H_5)_3$ (0.0449 g; 0.0824 mmol) and *p*-di-t-butylbenzene (0.0125 g; 0.0657 mmol) in 0.5 ml of THF was added, and the tube was cooled to −50° C in the variable temperature probe of a Varian A-60 Spectrometer. Then 0.13 ml of 1.0 *M* $Li(C_2H_5)_3BH$ in THF (0.13 mmol) was syringed directly into the sample solution while in the probe. The sample was warmed to −30° C; yield of VII (29%) was determined by integration relativ to the phenyl protons in the sample.

Preparation of formyl VIII. A ^1H NMR tube was prepared as described for IIa—IId above. A solution of $(CO)_5MnCF_3$ (0.0515 g; 0.20 mmol) and *p*-di-t-butylbenzene (0.0044 g; 0.020 mmol) in 0.3 ml THF-d_8 was syringed into the tube. The sample was cooled for 15 min in a dry ice/acetone bath; then 0.23 ml of 1.0 *M* $Li(C_2H_5)_3BH$ in THF (0.23 mmol) was syringed in. The sample was then quickly transferred to the probe of a Bruker WP-200 Spectrometer, which had been precooled to −50°C. The temperature was raised to −30°C over 10—15 minutes. Yield (54%) and chemical shift (δ 13.27 ppm) were measured relative to the *p*-di-t-butylbenzene standard (δ 7.27 ppm).

Decomposition rates of formyls IIa, IIb, IId, IVa—IVc (Table 3). Procedure for IIa: A ^1H NMR tube was charged with 0.075 g (0.25 mmol) of $(CO)_5Mn(COC_6H_5)$, 0.027 g (0.127 mmol) of 1,2,4,5-tetrachlorobenzene, and 0.5 ml of THF as described above for the preparation of formyls IIa—IId (except that argon was used instead of N_2). The probe of the A-60 spectrometer was cooled to the desired temperature, and precise temperature calibration was obtained (after equilibration) with methanol. The $(CO)_5Mn(COC_6H_5)$ sample was then placed in the probe and allowed to equilibrate. Then $Li(C_2H_5)_3BH$ (0.27 ml, 0.27 mmol) was syringed into the sample via a 20 cm needle. Integrations of both the formyl and standard resonances were recorded at intervals which allowed 20 to 40 data points to be collected over 2.5 half lives. Using the integration of the standard with each data point, formyl concentrations were calculated. The equation $\ln C_0/C = kt$ was used to calculate k_{obs}, where C_0 is the initial formyl concentration and C is the formyl concentration at time "t".

The other decomposition rates in Table 3 were determined as described for IIa, using identical molar quantities of reactants. The exact data obtained, and the equation utilized to calculate R values, have been compiled elsewhere [32].

Decomposition rates in the presence of excess $(C_2H_5)_3B$. These rates were measured as described for IIa above, except that $(CO)_5Mn(COC_6H_5)$ or $(\eta\text{-}C_5H_5)(CO)_2Fe(COC_6H_5)$ (0.25 mmol) and 1,2,4,5-tetrachlorobenzene were dissolved in 0.5 ml of 1.0 *M* $(C_2H_5)_3B$ in THF instead of pure THF. After cooling, 0.27 ml of 1.0 ml $Li(C_2H_5)_3BH$ was then added. This resulted in the generation of ca. 0.25 mmol of formyl in the presence of ca. 0.75 mmol of $(C_2H_5)_3B$.

Effect of trialkylborohydride employed to generate IIa upon its rate of decomposition (Table 4). ^1H NMR tubes were prepared by oven drying (30 min, 110°C), rinsing with $Li(C_2H_5)_3BH$ and then THF, and flushing with N_2. These were charged with between 0.030 and 0.041 g (0.10—0.14 mmol) of $(CO)_5Mn(COC_6H_5)$ and 0.010—0.019 g of 1,2,4,5-tetrachlorobenzene. The ^1H NMR tubes were transferred into a dry box, where 0.45 ml of THF and 0.05 ml of THF-d_8 (lock solvent) were added. Each tube was sealed with a septum and parafilm.

Each sample was cooled to −78°C and 1.2 equiv of $Li(C_2H_5)_3BH$, $Na(C_2H_5)_3$-

BH, $K(C_2H_5)_3BH$, or $Li(s\text{-}C_4H_9)_3BH$ added. The sample was then quickly lowered into the pre-cooled, 0°C probe of a Bruker WP-200 Spectrometer, which was then rapidly cooled to −40°C. After 5—15 minutes, the probe was warmed to −10°C where rate data were obtained. An average of 10 data points (100 scan accumulations; time of data point taken at scan #50) were recorded over a minimum of 2.0 half lives. Rate constants were obtained as described for IIa—IId above.

For the experiment employing $Li(C_2H_5)_3BD$, rate data were obtained over 2.0 half lives by ^2H NMR (30.72 MHz) on a Bruker WP-200 Spectrometer using an external frequency synthesizer. Although a larger NMR tube was required, reactant quantities (0.34 mmol $(CO)_5Mn(COC_6H_5)$, 1.6 ml THF, 0.41 ml 1.0 *M* $Li(C_2H_5)_3BD$) were adjusted so that the initial concentration of IIa-d_1 was within 8% of the corresponding experiment with $Li(C_2H_5)_3BH$.

Decomposition products of IIa. To a solution of 0.087 g (0.29 mmol) of $(CO)_5Mn(COC_6H_5)$ in 15 ml of THF under N_2 was added 0.32 ml (0.32 mmol) of 1.0 *M* $Li(C_2H_5)_3BH$ in THF. After stirring for 2 h, a solution of 0.093 g (0.24 mmol) of $(C_6H_5)_3SnCl$ in 5 ml of THF was added, and the reaction was stirred for 15 min. After solvent removal by high vacuum rotary evaporation at room temperature, the two products were isolated by column chromatography (~150 g silica gel; 5% EtOAc/hexane). $(CO)_5Mn(COC_6H_5)$ (0.036 g) and $(CO)_5MnSn(C_6H_5)_3$ (0.089 g) were identified by comparison to authentic samples.

To a solution of 0.151 g (0.50 mmol) of $(CO)_5Mn(COC_6H_5)$ in 25 ml of THF under N_2 was added 0.55 ml (0.55 mmol) of 1.0 *M* $Li(C_2H_5)_3BH$ in THF. After stirring for 2 h, the reaction mixture was added to 30 ml of diethyl ether and 20 ml of water. The organic layer was separated and dried, and the solvent was removed to give a yellow oil. Analysis of the oil (redissolved in 2 ml of diethyl ether) by GLC indicated the presence of $C_6H_5CH_2OH$; the yield (41%) was calculated against tetradecane internal standard.

To a solution of 0.151 g (0.50 mmol) of $(CO)_5Mn(COC_6H_5)$ and tetradecane (0.25 mmol) in 9.5 ml of THF under N_2 was added 0.55 ml (0.55 mmol) of 1.0 *M* $Li(C_2H_5)_3BH$ in THF. The reaction was stirred for 24 h, after which an IR assay indicated the only organometallic compound present to be $Li[Mn(CO)_5]$. GLC analysis indicated the presence of 0.15 mmol (60% based upon 0.25 mmol theoretical) of benzyl benzoate (confirmed by coinjection with an authentic sample).

In a separate experiment, $C_6H_5CH_2O^-Li^+$ was generated by the addition of 0.22 ml (0.22 mmol) of 1.0 *M* $Li(C_2H_5)_3BH$ to 0.023 g (0.22 mmol) of $C_6H_5CH_2OH$ in 2.5 ml of THF. Then 0.030 g (0.10 mmol) of $(CO)_5Mn(COC_6H_5)$ in 2.5 ml of THF was added. The formation of benzyl benzoate was noted qualitatively by GLC.

Decomposition products of IVa. In an experiment similar to those above, 0.566 g (2.01 mmol) of $(\eta\text{-}C_5H_5)(CO)_2Fe(COC_6H_5)$ was reacted with 2.1 mmol of $Li(C_2H_5)_3BH$ for 2 h, followed by addition of 0.391 g (1.01 mmol) of $(C_6H_5)_3SnCl$. Column chromatography (~150 g silica gel; 5% EtOAc/hexane) allowed isolation of the three compounds, $(\eta\text{-}C_5H_5)(CO)_2Fe(COC_6H_5)$ (0.270 g), $(\eta\text{-}C_5H_5)(CO)_2FeSn(C_6H_5)$ (0.311 g), and $[(\eta\text{-}C_5H_5)(CO)_2Fe)]_2$ (0.107 g), which were identified by comparison to authentic samples.

In an experiment to determine the yield of $C_6H_5CH_2OH$, 0.564 g (2.00 mmol) of (η-C_5H_5)(CO)$_2$Fe(COC$_6$H$_5$) was treated with 2.4 mmol of Li(C_2H_5)$_3$BH for 2 h. Aqueous work-up of the reaction mixture (described above for IIa), followed by GLC analysis (with tetradecane added as internal standard) indicated 0.392 mmol of $C_6H_5CH_2OH$ to be present.

Reaction of IIa with benzaldehyde. To 0.078 g (0.26 mmol) of (CO)$_5$Mn(COC$_6$H$_5$) in 10 ml of THF under N_2 at 0°C was added 0.26 ml (0.26 mmol) of 1.0 *M* Li(C_2H_5)$_3$BH in THF. After 2 min, 0.041 g (0.39 mmol) of C_6H_5CHO was syringed into the solution. After 5 min, the reaction mixture was quenched with diethyl ether/water. GLC analysis (with tetradecane added as internal standard) indicated 0.026 g (96% based upon IIa) of $C_6H_5CH_2OH$ to be present.

In a second, ^{1}H NMR monitored, experiment, IIa was prepared from (CO)$_5$Mn(COC$_6$H$_5$) (0.32 g, 0.105 mmol) and Li(C_2H_5)$_3$BH (0.12 ml, 0.12 mmol) in a NMR tube at —78°C as described previously. After a 200 MHz FT ^{1}H NMR spectrum, benzaldehyde (0.020 ml; 0.196 mmol) was added. A FT ^{1}H NMR spectrum recorded within the following 3 minutes indicated IIa to be completely consumed.

Reaction of IIa with CF_3SO_3H. In a ^{1}H NMR monitored experiment, IIa was prepared from (CO)$_5$Mn(COC$_6$H$_5$) (0.048 g; 0.16 mmol) and Li(C_2H_5)$_3$BH (0.19 ml; 0.19 mmol) in a NMR tube at —78°C as described previously. After a 200 MHz FT ^{1}H NMR spectrum taken at —20°C, CF_3SO_3H (0.020 ml; 0.22 mmol) was added with mixing. A FT ^{1}H NMR spectrum recorded within the following 5 minutes indicated IIa to be completely consumed.

In a second experiment, IIa was generated at —78°C by adding Li(C_2H_5)$_3$BH (0.28 ml, 0.28 mmol) to (CO)$_5$Mn(COC$_6$H$_5$) (0.070 g; 0.23 mmol) in 2 ml of THF. After 10 min, CF_3SO_3H (0.024 ml; 0.28 mmol) was added. After warming to room temperature, solvent was removed under reduced pressure and the residue column chromatographed on silica gel in CH_2Cl_2. Thus obtained was 0.058 g (83%) of (CO)$_5$Mn(COC$_6$H$_5$).

Reaction of IVa with CF_3SO_3H. In a ^{1}H NMR monitored experiment, IVa was prepared from (η-C_5H_5)(CO)$_2$Fe(COC$_6$H$_5$) (0.0755 g; 0.26 mmol) and Li(C_2H_5)$_3$BH (0.25 ml; 0.26 mmol) in a NMR tube at —42°C as described previously. After a 60 MHz ^{1}H NMR spectrum was taken at —42°C, CF_3SO_3H (0.035 ml; 0.40 mmol) was added. A ^{1}H NMR spectrum recorded within the following 3 minutes indicated IVa to be completely consumed.

In a second experiment, IVa was generated at —78°C by adding Li(C_2H_5)$_3$BH (0.50 ml; 0.50 mmol) to (η-C_5H_5)(CO)$_2$Fe(COC$_6$H$_5$) (0.140 g; 0.499 mmol) in 2 ml of THF. After 10 min, CF_3SO_3H (0.060 ml; 0.520 mmol) was added. After warming to room temperature, solvent was removed and the residue chromatographed on silica gel in CH_2Cl_2. Thus obtained was 0.103 g (74%) of (η-C_5H_5(CO)$_2$Fe(COC$_6$H$_5$).

Note added in proof

A kinetic deuterium isotope effect has also been noted in the decomposition of cluster-based anionic formyl complexes: R.C. Schoening, J.L. Vidal, and R.A. Fiato, submitted for publication.

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