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Synthesis of Metal Carbonyl Monoanions by Trialkylborohydride Cleavage of Metal Carbonyl Dimers: A Convenient One-Flask Preparation of Metal Alkyls, Metal Acyls, and Mixed-Metal Compounds

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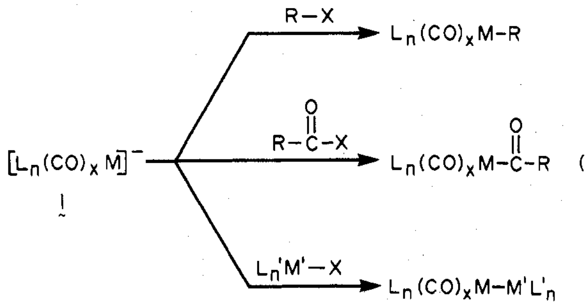
Commercially available trialkylborohydrides $Li(C_2H_5)_3BH$, $Li(sec\text{-}C_4H_9)_3BH$, and $K(sec\text{-}C_4H_9)_3BH$ effect the near-quantitative, homogeneous, room-temperature synthesis of transition-metal monoanions $[Co(CO)_4]^-$, $[(C_5H_5)Mo(CO)_3]^-$, $[Mn(CO)_5]^-$, and $[(C_5H_5)Fe(CO)_2]^-$ from the corresponding metal carbonyl dimers. Reactions are nearly instantaneous except in the case of $[(C_5H_5)Fe(CO)_2]_2$, which is reduced over a 3-h period by $K(sec\text{-}C_4H_9)_3BH$ in THF or within 2 h by $Li(C_2H_5)_3BH$ in $\geq$50% HMPA cosolvent. Metal carbonyl anions are also produced by the action of $Li(C_2H_5)_3BH$ on $[Mn(CO)_5]Br$ and $[(C_5H_5)Mo(CO)_3]Cl$. These anions are subsequently subjected in situ to a variety of alkylation, acylation, and metalation reactions. This methodology offers considerable advantage over more conventional means for the synthesis of metal carbonyl anions and their derivatives; these aspects are discussed in detail.

Introduction

Metal carbonyl monoanions (**1**) have played an important role in the development of inorganic and organometallic chemistry.[1,2] They are highly nucleophilic species[3] which may be readily alkylated, acylated, or metalated by reaction with an appropriate electrophile (eq 1).[1,2] More complex reactions, such as the formation of transition-metal cluster compounds,[1] have also been observed.



(1)

Metal carbonyl monoanions such as **1** are conventionally prepared by reduction of the corresponding metal carbonyl dimers, $L_n(CO)_xM{-}M(CO)_xL_n$. The most commonly employed reducing agent has been 1% Na/Hg amalgam,[1,2,4] although other heterogeneous reductants such as Na/K alloy[5] or Na dispersion[6] can be used as well. Several difficulties are associated with the Na/Hg amalgam procedure. These include the large amounts of mercury which must be employed, the hazards involved in Na/Hg amalgam formation (exothermicity and flammability), and the need for a special reaction apparatus.[4a] Side reactions are often encountered: when $[Mn(CO)_5]_2$ is reacted with Na/Hg, 11% $(CO)_5Mn{-}Hg{-}Mn(CO)_5$ accompanies the formation of $Na[Mn(CO)_5]$.[7] With heterogeneous metal reductants other than Na/Hg, the problems involved are mainly ones of manipulation and handling. Nonetheless, it should be noted that reducing agents of this genre have been elegantly applied by Ellis toward the synthesis of such highly reduced species as metal carbonyl dianions, trianions,[8] and even tetraanions.[9]

Simple metal carbonyl dimers and cyclopentadiene-substituted derivatives are among the least expensive organometallic starting materials at the disposal of the synthetic chemist.[10] Our contention has been that if a convenient, bench-top method employing easily handled reagents could be developed for the preparation of metal carbonyl monoanions from these starting materials, anions **1** should see increased use in the hands of organic chemists. For example, a wide variety of useful homologation and carbon–carbon bond forming reactions can be realized via the reaction of $Na_2[Fe(CO)_4]$ (Collman's reagent)[11] with organic compounds. There is ample reason to believe that these and other novel reaction types might be realized through the agency of metal carbonyl monoanions as well.[12]

We report in this paper that trialkylborohydrides $Li(C_2H_5)_3BH$, $Li(sec\text{-}C_4H_9)_3BH$, and $K(sec\text{-}C_4H_9)_3BH$, which are commercially available as THF solutions,[13] are able to effect the rapid, near-quantitative, homogeneous, room-temperature syntheses of transition-metal monoanions $[Co(CO)_4]^-$, $[(C_5H_5)Mo(CO)_3]^-$, $[Mn(CO)_5]^-$, and $[(C_5H_5)Fe(CO)_2]^-$ from the corresponding metal carbonyl dimers according to generalized eq 2.[14] We also describe the use of these anion solutions in subsequent alkylation, acylation, and metalation reactions. Mechanistic aspects of these transformations, which are known to involve intermediate metal–formyl complexes,[14-18] will be covered in a separate paper. A note describing the application of this methodology to transition-metal dianion synthesis ($K_2[Fe(CO)_4]$ from $Fe(CO)_5$) has already appeared.[19]

$$L_n(CO)_xM{-}M(CO)_xL_n + 2M'R_3BH \longrightarrow 2M'[L_n(CO)_xM] + 2R_3B + H_2 \qquad (2)$$

$$M' = Li,\ K \qquad L_n(CO)_xM = (C_5H_5)Fe(CO)_2,\ Mn(CO)_5,\ (C_5H_5)Mo(CO)_3,\ Co(CO)_4$$

Results

The metal carbonyl compounds employed in this study have, for the most part, distinct IR spectra in the CO stretching region. Therefore the simple IR reaction monitoring device depicted in Figure 1 was utilized to obtain many of the results in this section. Details of its operation are given in the Experimental Section.

The addition of 2.5 equiv of $Li(C_2H_5)_3BH$ to 1.0 equiv of $[Co(CO)_4]_2$ dissolved in THF (ca. 0.02 M) in the apparatus depicted in Figure 1 resulted in the immediate formation of $Li[Co(CO)_4]$ (IR: 1880 (vs) cm^{-1}). Under identical conditions, $Li[(C_5H_5)Mo(CO)_3]$ (IR: 1905 (s), 1807 (s), 1780 (m), 1714 (s) cm^{-1}) was formed from $[(C_5H_5)Mo(CO)_3]_2$, and $Li[Mn(CO)_5]$ (IR: 1898 (s), 1862 (s) cm^{-1}) was formed from $[Mn(CO)_5]_2$. No metal carbonyl by-products could be detected by IR.

The chemical identity of these anionic species was confirmed by derivatizing them with electrophiles in situ. Thus a variety of alkylating agents, acylating agents, and metalating agents were added to the reaction mixtures, which in some cases had

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Table I. Summary of Monoanion Derivatives Prepared

entry	starting carbonyl	hydride reagent	monoanion produced	electrophile added	product formed	isolated yield, %
1	$[Co(CO)_4]_2$	$Li(C_2H_5)_3BH$	$Li[Co(CO)_4]$	$[(C_6H_5)_3P]_2N^+Cl^-$	$[(C_6H_5)_3P]_2N^+[Co(CO)_4]^-$	79
2	$[Co(CO)_4]_2$	$Li(C_2H_5)_3BH$	$Li[Co(CO)_4]$	$(C_6H_5)_3SnCl$	$[Co(CO)_4]Sn(C_6H_5)_3$	83
3	$[(C_5H_5)Mo(CO)_3]_2$	$Li(C_2H_5)_3BH$	$Li[(C_5H_5)Mo(CO)_3]$	CH_3I	$[(C_5H_5)Mo(CO)_3]CH_3$	77
4	$[(C_5H_5)Mo(CO)_3]_2$	$Li(C_2H_5)_3BH$	$Li[(C_5H_5)Mo(CO)_3]$	$(CH_3O)COCOCl$	$[(C_5H_5)Mo(CO)_3]COCO_2CH_3$	77
5	$[(C_5H_5)Mo(CO)_3]_2$	$Li(sec\text{-}C_4H_9)_3BH$	$Li[(C_5H_5)Mo(CO)_3]$	$(CH_3O)COCOCl$	$[(C_5H_5)Mo(CO)_3]COCO_2CH_3$	77
6	$[(C_5H_5)Mo(CO)_3]_2$	$Li(C_2H_5)_3BH$	$Li[(C_5H_5)Mo(CO)_3]$	$(C_6H_5)_3SnCl$	$[(C_5H_5)Mo(CO)_3]Sn(C_6H_5)_3$	76
7	$[Mn(CO)_5]_2$	$Li(C_2H_5)_3BH$	$Li[Mn(CO)_5]$	$C_6H_5COCOCl$	$[Mn(CO)_5]COCOC_6H_5$	92
8	$[Mn(CO)_5]_2$	$Li(C_2H_5)_3BH$	$Li[Mn(CO)_5]$	$(C_6H_5)SnCl$	$[Mn(CO)_5]Sn(C_6H_5)_3$	88
9	$[Mn(CO)_5]_2$	$Li(C_2H_5)_3BH$	$Li[Mn(CO)_5]$	$(CH_3O)COCOCl$	$[Mn(CO)_5]COCO_2CH_3$	81
10	$[Mn(CO)_5]_2$	$K(sec\text{-}C_4H_9)_3BH$	$K[Mn(CO)_5]$	$[(C_6H_5)_3P]N^+Cl^-$	$[(C_6H_5)_3P]_2N^+[Mn(CO)_5]^-$	78
11	$[Mn(CO)_5]_2$	$K(sec\text{-}C_4H_9)_3BH$	$K[Mn(CO)_5]$	$(CH_3)_3SiBr$	$[Mn(CO)_5]Si(CH_3)_3$	60–80
12	$[(C_5H_5)Fe(CO)_2]_2$	$K(sec\text{-}C_4H_9)_3BH$	$K[(C_5H_5)Fe(CO)_2]$	$(C_6H_5)_3SnCl$	$[(C_5H_5)Fe(CO)_2]Sn(C_6H_5)_3$	93
13	$[(C_5H_5)Fe(CO)_2]_2$	$K(sec\text{-}C_4H_9)_3BH$	$K[(C_5H_5)Fe(CO)_2]$	$C_6H_5CH{=}CHCOCl$	$[(C_5H_5)Fe(CO)_2]COCH{=}CHC_6H_5$	72
14	$[(C_5H_5)Fe(CO)_2]_2$	$K(sec\text{-}C_4H_9)_3BH$	$K[(C_5H_5)Fe(CO)_2]$	C_6H_5COCl	$[(C_5H_5)Fe(CO)_2]COC_6H_5$	67
15	$[(C_5H_5)Fe(CO)_2]_2$	$K(C_2H_5)_3BH$	$K[(C_5H_5)Fe(CO)_2]$	CH_3I	$[(C_5H_5)Fe(CO)_2]CH_3$	56

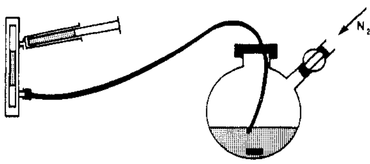

Figure 1. Apparatus for infrared monitoring of reactions.

been previously cooled. These reactions are summarized as entries 1–4 and 6–9 in Table I. The yields reported are for isolated, purified products and are in most cases unoptimized.

Reaction of $Li(sec\text{-}C_4H_9)_3BH$ (2.5 equiv) with $[Co(CO)_4]_2$, $[(C_5H_5)Mo(CO)_3]_2$, and $[Mn(CO)_5]_2$ under the same conditions similarly afforded $Li[Co(CO)_4]$, $Li[(C_5H_5)Mo(CO)_3]$, and $Li[Mn(CO)_5]$. The IR spectra of these anions matched virtually identically with those employed utilizing $Li(C_2H_5)_3BH$ (e.g., $Li[(C_5H_5)Mo(CO)_3]$: 1904 (s), 1808 (s), 1780 (m), 1713 (s) cm^{-1}). The anions $K[Co(CO)_4]$, $K[(C_5H_5)Mo(CO)_3]$, and $K[Mn(CO)_5]$ were instantly obtained when 2.5 equiv of $K(sec\text{-}C_4H_9)_3BH$ was added to the corresponding metal carbonyl dimer. The IR spectra of the potassium salts in THF agreed with those previously reported.[5]

The identity of these anions was verified by reactions with electrophiles. Thus $Li[(C_5H_5)Mo(CO)_3]$ prepared via $Li(sec\text{-}C_4H_9)_3BH$ was reacted with methyloxalyl chloride (entry 5, Table I). The new compound $[(C_5H_5)Mo(CO)_3]COCO_2CH_3$ was isolated in 77% yield. A $K[Mn(CO)_5]$ solution was reacted with $[(C_6H_5)_3P]_2N^+Cl^-$ (PPN^+Cl^-; entry 10). After KCl precipitation, $[(C_6H_5)_3P]_2N^+[Mn(CO)_5]^-$ was isolated in 78% yield.

The reaction of $[(C_5H_5)Fe(CO)_2]_2$ with $Li(C_2H_5)_3BH$ in THF did not lead to the formation of $Li[(C_5H_5)Fe(CO)_2]$.[20] $Li(sec\text{-}C_4H_9)_3BH$ reacted much more rapidly with $[(C_5H_5)Fe(CO)_2]_2$ but still did not yield $Li[(C_5H_5)Fe(CO)_2]$. However, if these reactions were run in HMPA or ≥50% HMPA in THF, $Li[(C_5H_5)Fe(CO)_2]$ formation was complete within 2 h (IR: 1862, 1788 cm^{-1}).[20] If the HMPA used was not purified, trialkylborohydride in substantial excess of the theoretical amount was required for complete conversion; however, a quantitative IR yield could always be obtained.

HMPA was not required for the preparation of $K[(C_5H_5)Fe(CO)_2]$. Addition of $K(sec\text{-}C_4H_9)_3BH$ (2.5–3.0 equiv) to $[(C_5H_5)Fe(CO)_2]_2$ resulted in the formation of the potassium anion over the course of 3 h (IR: 1868 (s), 1792–1772 (s) cm^{-1}). Transient IR absorptions at 1924 and 1675 cm^{-1} were observed and ascribed to intermediates in this reduction. A 1.0 M solution of $K(C_2H_5)_3BH$ was prepared and found to effect an identical reaction. Quicker anion formation (ca. 0.5 h) could be achieved by employing 45–65 °C reaction temperatures. The $K[(C_5H_5)Fe(CO)_2]$ system was unique in that minor amounts of by-products sporadically accompanied its formation. These did not interfere with the subsequent reactions of $K[(C_5H_5)Fe(CO)_2]$; good to high yields of various adducts could be isolated after the addition of electrophiles to these reaction mixtures (entries 12–15, Table I). For the somewhat sluggishly formed $[(C_5H_5)Fe(CO)_2]^-$ anion, yields of derivatives were generally higher if the entire reaction sequence was performed in the apparatus depicted in Figure 1.

Although there are reports of $[(C_5H_5)Ni(CO)]^-$ in the literature,[21] reaction of $[(C_5H_5)Ni(CO)]_2$ with $K(sec\text{-}C_4H_9)_3BH$ resulted in the gradual decomposition of the dimer without the appearance of any new metal carbonyl species.

In order to test for the possibility of a metal carbonyl anion–trialkylborane interaction, a THF solution of $Na[Re(CO)_5]$ was prepared using Na/Hg amalgam. $Na[Re(CO)_5]$ is known to be one of the most basic transition-metal anions[22] and one which complexes BH_3.[23] It was titrated with 1.0 M $(C_2H_5)_3B$ in THF, using the IR monitoring device in Figure 1. Except for dilution, the IR spectrum of $Na[Re(CO)_5]$ was unaffected.

Several methods were found for the removal of trialkylborane by-products from metal carbonyl anions. Triethylborane distills with THF. Thus when a triethylborohydride is employed in metal anion synthesis, subsequent evaporation of the solvent removes most of the borane. The residue is then washed with a little hydrocarbon solvent and redissolved in THF. Removal of the less volatile $(sec\text{-}C_4H_9)_3B$ at the anion stage is illustrated by the $[Mn(CO)_5]Si(CH_3)_3$ preparation (Experimental Section and entry 11, Table I). The crude $K[Mn(CO)_5]$ was precipitated from ethyl ether with pentane, under which conditions the $(sec\text{-}C_4H_9)_3B$ remained in solution.

The synthesis of $[Mn(CO)_5]^-$ could be made catalytic in trialkylborane. Thus when 1.0 mmol of $[Mn(CO)_5]_2$, 2.5 mmol of KH, and 0.25 mmol of $(C_2H_5)_3B$ were mixed in 25 mL of THF, $K[Mn(CO)_5]$ was formed in ca. 97% spectroscopic yield within 15 min.

The evolution of H_2 as a second by-product accompanying $Li[Mn(CO)_5]$ formation was confirmed by conducting the reaction between $Li(C_2H_5)_3BH$ and $[Mn(CO)_5]_2$ on a gas buret. Mass spectrometry indicated the gas formed to be H_2.

The halides $[(C_5H_5)Mo(CO)_3]Cl$ and $[Mn(CO)_5]Br$ were found to react with $Li(C_2H_5)_3BH$ (2.0 equiv) to yield $Li[(C_5H_5)Mo(CO)_3]$ and $Li[Mn(CO)_5]$, respectively. $[(C_5H_5)Fe(CO)_2]Cl$ was reacted with trialkylborohydrides under a variety of conditions, but $[(C_5H_5)Fe(CO)_2]^-$ was never formed in useful yields.

Discussion

As is evidenced by the multiple authorship of this paper, the preparative methodology detailed herein has been routinely employed in this research group over the past 18 months. Many of the entries in Table I represent compounds prepared in connection with other studies.

The advantages of our metal anion synthesis relative to other methods include the following: (a) the trialkylborohydride reducing agents are easily manipulated; (b) only a simple Schlenk flask is required; (c) reactions are rapid at room temperature; (d) only volatile by-products are produced when a triethylborohydride is employed; (e) by varying the alkali metal of the trialkylborohydride reductant, different product counterions may be obtained. Probably the major drawback to our procedure is the moderate expense of the trialkylborohydride reagents ($46/mol).

As summarized in Table I, the preparation of alkylated, acylated, or metalated derivatives of transition-metal monoanions proceeds smoothly, in high yield. Nearly all of these reactions were conducted in the same flask in which the anion was prepared.

Problems are encountered only in the synthesis of $[(C_5H_5)Fe(CO)_2]^-$ derivatives. To reduce $[(C_5H_5)Fe(CO)_2]_2$ to $Li[(C_5H_5)Fe(CO)_2]$, HMPA cosolvent must be employed, which is difficult to separate from subsequent reaction products. When $K(sec\text{-}C_4H_9)_3BH$ is used to produce $K[(C_5H_5)Fe(CO)_2]$, resulting products must be separated from $(sec\text{-}C_4H_9)_3B$, which is a high-boiling liquid (63–64 °C (3 mm)). This may be achieved by recrystallization or distillation, as indicated in the Experimental Section for entries 10–14. However, precautions must be taken (especially on large scales) because pure and/or solvent-free $(sec\text{-}C_4H_9)_3B$ is spontaneously and spectacularly flammable when exposed to air. It also tends to cochromatograph with organometallic products on silica gel columns. The use of $K(C_2H_5)_3BH$ to prepare $K[(C_5H_5)Fe(CO)_2]$ eliminates the problem of a nonvolatile borane by-product. However, $K(C_2H_5)_3BH$ is not presently commercially available.

The less rapid reduction of $[(C_5H_5)Fe(CO)_2]_2$ relative to the other metal carbonyl dimers is likely connected to its higher reduction potential.[24] We consider the $[(C_5H_5)Fe(CO)_2]^-$ anion an important system for further synthetic refinement, since many elegant and useful transformations utilizing organometallics of the $[(C_5H_5)Fe(CO)_2]R$ type have been discovered by Rosenblum.[25]

We have routinely worked up reactions involving $Li(C_2H_5)_3BH$ without special precaution and without incident. However, other researchers have recommended that care be taken to break rotary evaporatory vacuums with N_2 when it is likely that $(C_2H_5)_3B$ will be among the volatiles.[26]

Trialkylborohydrides can in most cases be prepared by reaction of an alkali metal hydride MH with a trialkylborane R_3B.[27-29] Thus anion synthesis might be realized using a catalytic amount of trialkylborane in conjunction with a stoichiometric amount of MH, since the trialkylborane would be continuously regenerated according to eq 2. We have conducted a number of exploratory reactions with KH, a metal carbonyl dimer, and $(C_2H_5)_3B$ in a molar ratio of 2.5:1:0.25. Although the formation of $K[Mn(CO)_5]$ proceeds satisfactorily, the reaction is slightly slower and requires more setup time. We have also observed KH to independently react with metal carbonyl dimers at a much slower rate.[50]

When $Li(C_2H_5)_3BH$ is reacted with organic electrophiles, it is sometimes necessary to use excess hydride to ensure a complete and rapid reduction.[30] This has been ascribed to the formation of intermediate $Li[(C_2H_5)_3B\text{–}H\text{–}B(C_2H_5)_3]$ (from $(C_2H_5)_3B + Li(C_2H_5)_3BH$), which is a much less powerful hydride donor.[30] Metal carbonyl dimers are apparently too reactive for reaction to be adversely affected by this equilibrium. Such bridging hydride species are not formed with $(sec\text{-}C_4H_9)_3B$.

The data presented in the Results fail to provide evidence for any significant metal anion–trialkylborane interaction. For instance, the IR spectrum of $Li[(C_5H_5)Mo(CO)_3]$ is invariant regardless of whether it is prepared from $Li(C_2H_5)_3BH$ or $Li(sec\text{-}C_4H_9)_3BH$. By-product $(sec\text{-}C_4H_9)_3B$ is a much more encumbered and less effective Lewis acid than $(C_2H_5)_3B$. In other studies, however, we have uncovered evidence for the participation of trialkylboranes in hydride-transfer reactions of anionic metal carbonyl formyl complexes.[31] Since trialkylboranes and their corresponding ate adducts (R_3BX^-) exhibit large ^{11}B NMR chemical shift differences, a probe exists for the degree of metal anion association.[29] At this writing, however, it is clear that the trialkylborane by-product plays no *key* role in the ensuing metal anion chemistry.

Other procedural aspects deserve mention. When $Li[Mn(CO)_5]$ is prepared by the addition of $Li(C_2H_5)_3BH$ to $[Mn(CO)_5]_2$ at room temperature, the solution produced is red. However, when $Li(C_2H_5)_3BH$ is added to a solution of $[Mn(CO)_5]_2$ which has been cooled first to 0 °C, the solution obtained after warming to room temperature is light yellow. Formation of $Li[Mn(CO)_5]$ by the inverse addition of $[Mn(CO)_5]_2$ to $Li(C_2H_5)_3BH$ also eliminates the red color. We suggest that the red color may be due to trace amounts of $Li[Mn_3(CO)_{14}]$,[32] which would have the best chance of forming under conditions where $Li[Mn(CO)_5]$ and $[Mn(CO)_5]_2$ are simultaneously present. When $Li(C_2H_5)_3BH$ is added to a solution of $[Mn(CO)_5]_2$ at or below 0 °C, a binuclear anionic formyl complex is formed rapidly in virtually quantitative yield.[14] At a much slower rate, this intermediate fragments to $Li[Mn(CO)_5]$. Thus, although the $Li[Mn(CO)_5]$ produced at room temperature appears clean by IR and is entirely satisfactory for preparative purposes, anion solutions generated at lower temperatures are undoubtedly of slightly higher purity.

Temperature can play an important role in subsequent reactions of transition-metal monoanions. We have noted in some cases that higher yields of products are obtained when electrophiles are added at −78 °C. Electron-transfer processes have been observed to compete with transition-metal monoanion alkylation.[33] The extent of these side reactions would be expected to depend upon the metal anion counterion, electrophile, solvent, and temperature. A recent study has shown that $Na[(C_5H_5)Fe(CO)_2]$ reacts much cleaner with cyclopropylcarbinyl bromide than cyclopropylcarbinyl iodide.[33]

The only common transition-metal monoanion which we are unable to prepare using trialkylborohydrides is $[Re(CO)_5]^-$. Reaction of $Li(C_2H_5)_3BH$ with $[Re(CO)_5]_2$ affords an isolable anionic binuclear formyl complex by hydride attack upon coordinated CO.[15] Further addition of trialkylborohydride reagents does not lead to rhenium–rhenium bond rupture.

We anticipate that the fact $Li(C_2H_5)_3BH$ can reduce metal carbonyl halides such as $[Mn(CO)_5]Br$ to $Li[Mn(CO)_5]$ and $[(C_5H_5)Mo(CO)_3]Cl$ to $Li[C_5H_5)Mo(CO)_3]$ will prove of occasional synthetic utility. For instance, $[Mn(CO)_5]Br$ undergoes much more rapid exchange with ^{13}CO than $[Mn(CO)_5]_2$.[34] Thus the preparation of a ^{13}CO-labeled $[Mn(CO)_5]R$ species would be most readily accomplished via initial conversion of $[Mn(CO)_5]_2$ to $[Mn(CO)_5]Br$. After ^{13}CO exchange, the desired product could be obtained in a one-flask operation from labeled $[Mn(CO)_5]Br$.

Other new methods for transition-metal monoanion synthesis have recently been reported.[50] For instance, Alper has noted that $[Co(CO)_4]_2$ can be converted to $[Co(CO)_4]^-$ by NaOH under phase-transfer catalysis conditions.[35] Mention should also be made of electroreductive techniques.[3,24,36] However, on scales where the moderate expense of trialkylborohydrides is inconsequential, we believe that the procedures detailed herein constitute the methods of choice for the preparation of monoanions $[Co(CO)_4]^-$, $[(C_5H_5)Mo(CO)_3]^-$, and $[Mn(CO)_5]^-$. We rate our procedure for $[(C_5H_5)Fe(CO)_2]^-$

as an overall toss-up with the Na/Hg amalgam technique.

In concluding, we note that trialkylborohydrides can also be used to cleave heteroatom–heteroatom bonds, enabling the synthesis of metalloid and main group element anions. For instance, nucleophilic selenium and sulfur anions can be generated by $Li(C_2H_5)_3BH$ reduction of polymeric Se_x[37] and S_8,[38] respectively. Typical reactions are eq 3 and 4.

$$S + 2Li(C_2H_5)_3BH \xrightarrow{THF} Li_2S + 2(C_2H_5)_3B + H_2 \quad (3)$$

$$2S + 2Li(C_2H_5)_3BH \xrightarrow{THF} Li_2S_2 + 2(C_2H_5)_3B + H_2 \quad (4)$$

Thus it appears that trialkylborohydrides will have at least as many uses in synthetic inorganic and organometallic chemistry as they do in synthetic organic chemistry. Our goal in this paper has been to compile a number of useful procedures in a fashion which will not only facilitate their adaptation but stimulate new ideas as well. Additional applications of trialkylborohydrides to synthetic problems on the organic–inorganic interface will be forthcoming from this laboratory and undoubtedly others as well.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of dry N_2. THF, ethyl ether, hexane, and pentane were dried and deoxygenated by distillation from sodium benzophenone ketyl. HMPA was purified by distillation from CaH_2 and again from sodium metal. IR spectra were recorded on a Perkin-Elmer Model 521 spectrometer. ^1H NMR and ^{13}C NMR spectra were obtained using Varian T-60 and CFT-20 spectrometers, respectively. Elemental analyses were conducted by Galbraith. Melting points were taken on a Büchi Schmeltzpunktbestimmungsapparat and are uncorrected.

Starting Materials. $Li(C_2H_5)_3BH$, $Li(\textit{sec}\text{-}C_4H_9)_3BH$, and $K(\textit{sec}\text{-}C_4H_9)_3BH$ were obtained from Aldrich Chemical Co. as 1.0, 1.0, and 0.5 M THF solutions, respectively, and used without further standardization. $(C_2H_5)_3B$ and $(\textit{sec}\text{-}C_4H_9)_3B$ were also purchased from Aldrich as 1.0 M THF solutions. KH was obtained from Alfa Products.

$[Co(CO)_4]_2$, $[(C_5H_5)Mo(CO)_3]_2$, $[(C_5H_5)Fe(CO)_2]_2$, and $[(C_5H_5)Ni(CO)]_2$ were purchased from Strem Chemical Co. and used without further purification. $[Mn(CO)_5]_2$ was prepared by the method of Calderazzo.[39] $[Re(CO)_5]_2$ was purchased from Pressure Chemical Co.

$[(C_6H_5)_3P]_2N^+Cl^-$ was prepared by the method of Ruff.[40] $(C_6H_5)_3SnCl$ was purchased from Alfa Products, $(CH_3)_3SiBr$ was obtained from Petrarch Systems, Inc., and methyloxalyl chloride ($CH_3OCOCOCl$) was purchased from Aldrich Chemical Co. Benzoylformyl chloride ($C_6H_5COCOCl$) was prepared from benzoylformic acid (Aldrich Chemical Co.) by the method of Ottenheijm and de Man.[41] All other electrophiles reacted with the metal anions were common commercially available materials.

IR Monitoring of Reactions. Solutions of the appropriate metal carbonyl compound were placed in a Schlenk flask fitted with a septum and a Teflon needle, as depicted in Figure 1. A standard 0.1-mm cavity IR cell was fitted to the other end of the needle utilizing a machined Teflon plug. To the other IR cell inlet was attached a syringe, preferably of the "gas-tight" variety. A slight positive pressure of nitrogen was maintained via the Schlenk flask side arm. Reagents and reactants were added as needed through the septum, and the reaction mixture could be spectroscopically sampled at any time by simply pumping on the syringe.

Preparation of $K(C_2H_5)_3BH$. An oil suspension of KH was suction filtered in a glovebox and washed with hexanes. An oven-dried, 1000-mL Schlenk flask was then charged with 20.0 g (0.5 mol) of KH and equipped with a stirring bar and a septum. A nitrogen atmosphere was maintained via the Schlenk flask side arm. Then 500 mL (0.5 mol) of a 1.0 M solution of $(C_2H_5)_3B$ in THF was slowly added with stirring over a 0.5-h period using the double-ended needle technique. Upon completion, a clear yellow solution was obtained.

Preparation of $Li[Mn(CO)_5]$. In a typical reaction, $Mn_2(CO)_{10}$ (0.195 g, 0.5 mmol) was dissolved in THF (25 mL) in the Schlenk apparatus depicted in Figure 1. A gas-tight syringe was used to slowly add 1.25 mL of 1.0 M $Li(C_2H_5)_3BH$ in THF (1.25 mmol; 2.5 equiv) to the reaction mixture. The solution was allowed to stir 15 min before reaction.

Preparation of $Li[Co(CO)_4]$. This procedure was identical with the one described for $Li[Mn(CO)_5]$ except that $[Co(CO)_4]_2$ was employed instead of $[Mn(CO)_5]_2$.

Preparation of $Li[(C_5H_5)Mo(CO)_3]$. This procedure was identical with the one described for $Li[Mn(CO)_5]$ except that $[(C_5H_5)Mo(CO)_3]_2$ was used instead of $[Mn(CO)_5]_2$.

Preparation of $K[Mn(CO)_5]$, $K[Li(CO)_4]$, and $K[(C_5H_5)Mo(CO)_3]$. The procedures employed were identical with those described for the corresponding lithium salts except that $K(\textit{sec}\text{-}C_4H_9)_3BH$ was used instead of $Li(C_2H_5)_3BH$.

Preparation of $K[Mn(CO)_5]$ from KH and $(C_2H_5)_3B$. To a stirred mixture of KH (0.1 g, 2.5 mmol) and $(C_2H_5)_3B$ (0.25 mL of a 1.0 M THF solution) in 10 mL of THF in the Schlenk apparatus depicted in Figure 1 was added $[Mn(CO)_5]_2$ (0.390 g, 1.0 mmol) dissolved in 30 mL of THF. After 15 min of reaction, the IR spectrum of the homogeneous solution indicated approximately a 97% conversion to $K[Mn(CO)_5]$.

Preparation of $Li[(C_5H_5)Fe(CO)_2]$. In a typical reaction, $[(C_5H_5)Fe(CO)_2]_2$ (0.354 g, 1.0 mmol) was dissolved in 50 mL of purified HMPA in the Schlenk apparatus depicted in Figure 1. A gas-tight syringe was used to add 2.4 mL of 1.0 M $Li(C_2H_5)_3BH$ to the reaction mixture. $Li[(C_5H_5)Fe(CO)_2]$ formation was complete after 2 h.

Preparation of $K[(C_5H_5)Fe(CO)_2]$. In a typical reaction, $[(C_5H_5)Fe(CO)_2]_2$ (0.354 g, 1.0 mmol) was dissolved in 30 mL of THF in the Schlenk apparatus depicted in Figure 1. A gas-tight syringe was used to add 5.5 mL of 0.5 M $K(\textit{sec}\text{-}C_4H_9)_3BH$ (2.75 mmol, 2.75 equiv) to the reaction mixture. $K[(C_5H_5)Fe(CO)_2]$ formed over the course of 3 h. Alternatively, $K(C_2H_5)_3BH$ (preparation above) could be employed in place of $K(\textit{sec}\text{-}C_4H_9)_3BH$.

Attempted Preparation of $K[(C_5H_5)Ni(CO)]$. $[(C_5H_5)Ni(CO)]_2$ (0.5 mmol) in 50 mL of THF was reacted with 1.25 mmol of $K(\textit{sec}\text{-}C_4H_9)_3BH$ (2.5 mL) as described for $[(C_5H_5)Fe(CO)_2]_2$. Starting material slowly disappeared without the formation of new CO-containing products.

Reaction of $Li(C_2H_5)_3BH$ with $[Mn(CO)_5]Br$ and $[(C_5H_5)Mo(CO)_3]Cl$. $[Mn(CO)_5]Br$ (0.137 g, 0.5 mmol) was dissolved in ca. 15 mL of THF in the apparatus depicted in Figure 1. One milliliter (2.0 equiv) of $Li(C_2H_5)_3BH$ was added. Formation of $Li[Mn(CO)_5]$ was immediate. The IR spectrum was identical with that obtained when $[Mn(CO)_5]_2$ was used as starting material. Similarly, $Li[(C_5H_5)Mo(CO)_3]$ was formed over the course of 5 min when $Li(C_2H_5)_3BH$ (0.6 mL, 0.6 mmol) was added to $[(C_5H_5)Mo(CO)_3]Cl$ (0.085 g, 0.3 mmol) in ca. 10 mL of THF.

$[(C_6H_5)_3P]_2N^+[Co(CO)_4]^-$. To 2.0 mmol of $Li[Co(CO)_4]$, prepared as described above, was added 2.1 mmol (1.2 g) of solid $[(C_6H_5)_3P]_2N^+Cl^-$. The reaction was stirred for 10 min and then filtered through Celite, and the solvent was removed by rotary evaporation. The resulting residue was dissolved in 15 mL of dichloromethane. Ethyl ether was added until a precipitate appeared, at which point the flask was cooled to 0 °C for 3 h. Pale lime green crystals were collected and dried under vacuum: yield 0.85 g, 79%; mp 182–186 °C dec. IR (THF): 1888 (s) cm^{-1} (lit:[40] 1890 cm^{-1}).

$[Co(CO)_4]Sn(C_6H_5)_3$. One millimole of $Li[Co(CO)_4]$ was prepared as described above and cooled to −10 °C. To this was added 0.60 g (1.55 mmol) of $(C_6H_5)_3SnCl$ in 15 mL of THF. The solution was slowly warmed to 25 °C and stirred for 2 h. The solvent was removed by rotary evaporation and the resulting residue extracted with hot, degassed hexane. Crystallization at −78 °C yielded 0.432 g (83% yield) of product, mp 119–121 °C (lit:[42] 120 °C). IR (THF): 2090 (m), 2025 (m), 1995 (s) cm^{-1}.

$[(C_5H_5)Mo(CO)_3]CH_3$. Two millimoles of $Li[(C_5H_5)Mo(CO)_3]$ was prepared as described above. The solution was cooled to −78 °C and 3.0 mmol (0.426 g) of methyl iodide was injected. After the solution was stirred for 2 h, the solvent was removed by high-vacuum rotary evaporation below room temperature. The crude product remained as a residue and was subsequently sublimed at 80 °C (0.1 torr) to give 0.434 g (77%) of yellow crystalline product, mp 124 °C dec (lit: 124 °C dec).[43]

$[(C_5H_5)Mo(CO)_3]COCOOCH_3$. Two millimoles of $Li[(C_5H_5)Mo(CO)_3]$ was prepared as described above. After the reaction was cooled to −78 °C, 3.0 mmol of methyloxalyl chloride was added. The solution was stirred for 2 h prior to solvent removal by high-vacuum rotary evaporation. The resulting yellow-brown residue was extracted with 300 mL of hot, degassed hexane. The solution was concentrated to approximately 150 mL and stored below 0 °C for 12 h. Yellow crystals of product were collected by filtration: yield 0.511 g, 77%;

mp 56–58 °C. IR (THF): 2047 (s), 1942 (s), 1727 (w), 1625 (m) cm^{-1}. ^{1}H NMR (C_6D_6): δ 3.31 (s, 3 H), 4.65 (s, 5 H). Mass spectrum: *m/e* 300 (M^+ – CO), 269 (M^+ – (CO,OCH_3)), 85 ($COCOOCH_3$). Anal. Calcd: C, 39.88; H, 2.42; Mo, 28.70. Found: C, 39.75; H, 2.50; Mo, 28.77.

$[(C_5H_5)Mo(CO)_3]Sn(C_6H_6)_3$. To 1.0 mmol of $Li[(C_5H_5)Mo(CO)_3]$, prepared as described above, was added 1.1 mmol (0.4 g) of $(C_6H_5)_3SnCl$ in 10 mL of THF. After the mixture was stirred for 30 min, the solvent was removed by rotary evaporation and the residue extracted with 25% ethyl acetate in hexane (v/v). Removal of solvent and recrystallization from hexane afforded pure product in 76% yield, mp 215–216 °C dec (lit:[44] 211–214 °C).

$[Mn(CO)_5]COCOC_6H_5$. $Li[Mn(CO)_5]$ (11.5 mmol) was prepared as described above. The solution was cooled to –78 °C and 13 mmol of benzoylformyl chloride dissolved in 10 mL of THF was added. After being stirred for 45 min, the reaction mixture was allowed to warm to room temperature after which the volume of the reaction was reduced to 10 mL by rotary evaporation. The resulting solution was chromatographed on silica gel with 1:3 (v/v) ethyl acetate–hexane. The product fraction was collected, the solvent was removed by rotary evaporation, and the resulting residue was dried under vacuum for 12 h. A 92% yield of orange-yellow product, mp 62.5–63.5 °C (lit:[45] 61.5–62.5 °C), was obtained. IR (cyclohexane): 2119 (m), 2058 (w), 2028 (vs), 2021 (s, sh), 2009 (s), 1672 (m), 1621 (m) cm^{-1}. ^{13}C NMR ($CDCl_3$): 264.0, 209–207 (broad), 191.2, 134.6, 130.5, 130.1, 129.2 ppm. Anal. Calcd: C, 47.58; H, 1.54. Found: C, 47.36; H, 1.44.

$[Mn(CO)_5]Sn(C_6H_5)_3$. One millimole of $Li[Mn(CO)_5]$ was prepared as described above. To the anion was added 0.600 g (1.55 mmol) of $(C_6H_5)_3SnCl$ in ca. 10 mL of THF. The reaction was complete by IR after 2 h at 25 °C. The solvent was removed by rotary evaporation leaving 0.650 g of the crude product. Recrystallization from degassed hexane gave 0.480 g (88%) of pure tin complex, mp 148–150 °C (lit:[46] 148–150 °C). IR (THF): 2090 (m), 1995 (vs) cm^{-1}.

$[Mn(CO)_5]COCO_2CH_3$. Two millimoles of $Li[Mn(CO)_5]$ was prepared as described above and cooled to –78 °C. Three millimoles of methyloxalyl chloride was then added dropwise. After being stirred for 1 h, the reaction mixture was warmed and the solvent removed. The resulting residue was dissolved in a minimun of hot, degassed hexane. The hexane solution was concentrated and stored at 0 °C for 48 h. Yellow crystals of the desired product were collected by filtration and vacuum dried: yield 81%; mp 48–50 °C. IR (cyclohexane): 2123 (m), 2062 (w), 2030 (s), 2013 (s), 1721 (m), 1643 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.83 (s). Anal. Calcd: C, 34.07; H, 1.07. Found: C, 33.98; H, 1.02.

$[(C_6H_5)_3P]_2N^+[Mn(CO)_5]^-$. To 0.95 g (2.5 mmol) of $[Mn(CO)_5]_2$ in THF (100 mL) at 0 °C was added 15 mL (7.5 mmol) of K(*sec*-$C_4H_9)_3BH$. The solution was stirred 3 h and allowed to warm to room temperature. Then 4.3 g (7.5 mmol) of $[(C_6H_5)_3P]_2N^+Cl^-$ was added, and the reaction was stirred until all of this material had dissolved. During this time a fine white solid formed (KCl) which was removed by filtration. Onto the THF solution was then gently layered 150 mL of petroleum ether (bp 30–60 °C). Diffusive mixing resulted in large yellow crystals of product, which were collected after 3 days: yield 2.85 g (78%). IR (THF): 1895 (m, br), 1855 (s, br) cm^{-1} (lit:[47] 1893, 1860 cm^{-1}).

$[Mn(CO)_5]Si(CH_3)_3$. A solution of $[Mn(CO)_5]_2$ (1.95 g, 5 mmol) in 50 mL of THF was cooled to 0 °C and 25 mL (12.5 mmol) of K(*sec*-$C_4H_9)_3BH$ added. The solution was stirred 2 h and allowed to warm. Solvent was then removed under vacuum at 40 °C, leaving behind a pyrophoric, (*sec*-$C_4H_9)_3B$-containing residue. In a glovebox, the residue was dissolved in 25 mL of ethyl ether and the crude $K[Mn(CO)_5]$ precipitated as a dull green solid with 100 mL of pentane. The solvents were decanted and the $K[Mn(CO)_5]$ vacuum dried, causing it to become nearly white.

To a slurry of the $K[Mn(CO)_5]$ in 25 mL of pentane (product $[Mn(CO)_5]Si(CH_3)_3$ reacts with most oxygen-containing solvents) was added 2.0 mL (2.35 g, 15 mmol) of $(CH_3)_3SiBr$ (freshly distilled from CaH_2). This mixture was stirred vigorously in a closed flask for 2 days. The reaction mixture was then filtered through 5 g of silica gel, which was flushed with an additional 50 mL of pentane. The filtered solution was concentrated to ca. 10 mL and cooled to –78 °C. After 2 h, solvent was decanted from the solid product which precipitated. The product was vacuum dried at 0 °C for 15 min and then sublimed (room temperature, 0.1 mmHg) onto a 0 °C probe. In multiple preparative runs, yields ranging from 1.60 g (60%) to 2.15 g (80%) of $[Mn(CO)_5]Si(CH_3)_3$ were obtained: mp 26.5 °C (lit:[48] 25.6–26.2 °C). IR (cyclohexane): 2098 (w), 1994 (s), 1962 (w, br) cm^{-1}. ^{1}H NMR (C_6H_6): δ 0.49 (s).

$[(C_5H_5)Fe(CO)_2]Sn(C_6H_5)_3$. $K[(C_5H_5)Fe(CO)_2]$ (2.2 mmol) was prepared as described above. One gram (2.6 mmol) of $(C_6H_5)_3SnCl$ was then added. After 0.5 h of stirring, the solvent was removed by rotary evaporation. (**Caution**: this residue contains (*sec*-$C_4H_9)_3B$.) The residue was extracted first with hexane and then with ethyl ether. The combined extracts were concentrated and cooled to 0 °C for 12 h. Crystalline product formed and was collected: yield 1.08 g, 93%; mp 139–140 °C (lit:[46] 139–141 °C). IR (THF): 1990 (s), 1940 (s) cm^{-1}.

$[(C_5H_5)Fe(CO)_2]COCH{=}CHC_6H_5$. Two millimoles of $K[(C_5H_5)Fe(CO)_2]$ was prepared as described above. After the solution was cooled to –78 °C, 2.08 mmol of cinnamoyl chloride was added. The reaction was stirred for 0.5 h and allowed to warm to room temperature. The solvent was removed by rotary evaporation and the resulting residue (**Caution**: residue contains (*sec*-$C_4H_9)_3B$) extracted with 200 mL of hexane. The solution was concentrated to half the original volume and stored for 12 h at 0 °C. The product[49] crystallized and was isolated in 72% yield. IR (THF): 2018 (s), 1958 (s), 1633 (m) cm^{-1}. ^{13}C NMR ($CDCl_3$): 250.4, 214.3, 138.7, 135.2, 129.6, 128.9, 128.3, 86.6 (C_5H_5 carbons) ppm; the substituted aryl carbon was not observed.

$[(C_5H_5)Fe(CO)_2]COC_6H_5$. Four millimoles of $K[(C_5H_5)Fe(CO)_2]$ was prepared as described above. The solution was cooled to –78 °C and benzoyl chloride (0.6 mL, 5.2 mmol) was added with a gas-tight syringe. The reaction mixture was stirred for 0.5 h and allowed to warm to room temperature. The solvent was removed by rotary evaporation leaving a red oil, which was dissolved in 25 mL of $CHCl_3$ (**Caution**: the red oil contains (*sec*-$C_4H_9)_3B$). The resulting solution was filtered through alumina. The alumina was further washed with 50 mL of $CHCl_3$. The solvent was again removed and the red oil was dissolved in a minimum of $CHCl_3$. Degassed hexane was added and the solution cooled to –78 °C. The product formed as yellow crystals (mp 63–65 °C; lit:[49] 59–62 °C), was isolated in 67% yield, and was found to be identical with an authentic sample prepared by the method of King.[49] IR (THF): 2019 (s), 1956 (s), 1613 (m) cm^{-1}. ^{13}C NMR ($CDCl_3$, ca. 0.07 M $Cr(acac)_3$): 263.5, 214.0, 150.9, 130.3, 128.1, 125.9, 86.7 (C_5H_5 carbons) ppm.

$[(C_5H_5)Fe(CO)_2]CH_3$. $[(C_5H_5)Fe(CO)_2]_2$, 1.062 g (3 mmol), was placed in a 500-mL Schlenk flask equipped with a condenser. THF, 150 mL, was then added and the solution brought to reflux. Twenty milliliters of 1 M $K(C_2H_5)_3BH$ was then added and the solution allowed to cool with stirring for 0.5 h. This was followed by the addition of 1.5 mL (20 mmol) of CH_3I. After 10 min of additional stirring, the THF was removed via water aspirator. The condenser was replaced with a cold finger which was loaded with ice. The product was sublimed at 65 °C under 0.1 mm pressure: yield 0.645 g of orange crystals (56%); mp 81–82 °C (lit:[4b] 78–82 °C). IR (THF): 2007 (s), 1944 (s) cm^{-1}. The excess $K(C_2H_5)_3BH$ employed in this specific reaction is not critical to its success.

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Registry No. $[Co(CO)_4]_2$, 10210-68-1; $[(C_5H_5)Mo(CO)_3]_2$, 12091-64-4; $[Mn(CO)_5]_2$, 10170-69-1; $[(C_5H_5)Fe(CO)_2]_2$, 12154-95-9; $[Mn(CO)_5]Br$, 14516-54-2; $[(C_5H_5)Mo(CO)_3]Cl$, 12128-23-3; $Li(C_2H_5)_3BH$, 22560-16-3; Li(*sec*-$C_4H_9)_3BH$, 38721-52-7; K(*sec*-$C_4H_9)_3BH$, 54575-49-4; $K(C_2H_5)_3BH$, 22560-21-0; $Li[Co(CO)_4]$, 15616-75-8; $Li[(C_5H_5)Mo(CO)_3]$, 68550-41-4; $Li[Mn(CO)_5]$, 15689-01-7; $K[Mn(CO)_5]$, 15693-51-3; $K[(C_5H_5)Fe(CO)_2]$, 60039-75-0; $K[Co(CO)_4]$, 14878-26-3; $K[(C_5H_5)Mo(CO)_3]$, 62866-01-7; $Li[(C_5H_5)Fe(CO)_2]$, 33361-37-4; $[(C_6H_5)_3P]_2N^+[Co(CO)_4]^-$, 53433-12-8; $[Co(CO)_4]Sn(C_6H_5)_3$, 13964-91-5; $[(C_5H_5)Mo(CO)_3]CH_3$, 12082-25-6; $[(C_5H_5)Mo(CO)_3]COCO_2CH_3$, 65106-65-2; $[(C_5H_5)Mo(CO)_3]Sn(C_6H_5)_3$, 12100-85-5; $[Mn(CO)_5]COCOC_6H_5$, 59299-81-9; $[Mn(CO)_5]Sn(C_6H_5)_3$, 14405-84-6; $[Mn(CO)_5]COCO_2CH_3$, 65106-66-3; $[(C_6H_5)_3P]_2N^+[Mn(CO)_5]^-$, 52542-59-3; [$Mn(CO)_5$]$Si(CH_3)_3$, 26500-16-3; [$(C_5H_5)Fe(CO)_2$]$Sn(C_6H_5)_3$, 12132-09-1; [$(C_5H_5)Fe(CO)_2$]$COCHCHC_6H_5$, 12216-33-0; [$(C_5H_5)Fe(CO)_2$]$COC_6H_5$, 12154-94-8; [$(C_5H_5)Fe(CO)_2$]$CH_3$, 12080-06-7.

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Adduct Formation and Further Reactivity of Iron Carbonyl Complexes Introduced into a Zeolite Matrix

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$Fe(CO)_5$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ have been introduced into a dehydrated HY type zeolite. The iron content in the samples ranged from 1 to 4 wt %. During adsorption the iron complexes retain a molecular structure as shown by IR spectroscopy. For $Fe(CO)_5$ and $Fe_2(CO)_9$, a vacuum treatment leads to the evolution of CO and the formation of $Fe(CO)_4$ bonded to the zeolite while in the case of $Fe_3(CO)_{12}$ no CO is evolved. Treating $Fe_3(CO)_{12}$/zeolite under CO atmosphere restores the IR spectra of the $Fe(CO)_5$ or $Fe_2(CO)_9$/zeolite system. Thereafter the zeolite acts both as an oxygen-containing ligand leading to L–$Fe(CO)_4$ species and as a Lewis acid able to form adducts with $Fe_3(CO)_{12}$ units via the oxygens of the bridging carbonyls. Heating the loaded zeolite (100–200 °C) produces a dehydroxylation of the support which is promoted by the iron carbonyls. The subsequent formation of CO_2 and hydrogen is explained by the water–gas shift reaction. Some CO_2 remains chemisorbed on the surface as evidenced by the presence of carbonate species. These species can be desorbed by hydrogen treatments with concomitant formation of CH_4. Heating up to 250 °C leads to total decarbonylation of the iron carbonyl/HY systems and subsequent oxidation of Fe(0) to Fe(II) as evidenced by complexes formed with NO and CO. The oxidation process involves the protons of the zeolite. The Fe^{2+} ions are mainly located in the supercage in contrast to a conventional Fe^{2+}/Y sample.

Introduction

Coordination compounds supported on both organic and inorganic materials are attracting attention for the two main purposes of (i) anchoring coordination compounds in attempts to combine the advantages of homogeneous and heterogeneous catalysis[1,2] and (ii) utilizing coordination complexes as precursors for the preparation of dispersed metallic catalysts.[3,6]

The interaction between the support and the complex and the redox behavior of these partners are important factors which will influence the type of catalyst formed. With an inorganic matrix, ions or metallic particles are obtained. Several types of inorganic matrices can be used, and among them the zeolites exhibit interesting properties associated with their unique structural features. The cavities, the inner electrostatic fields, and acidic and redox properties of the zeolites allow the introduction of transition-metal centers in sites of varying accessibilities.

Earlier work from this laboratory[7] has shown that the adsorption of certain transition-metal carbonyls into an HY zeolite framework and subsequent thermal desorption leads

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