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Preliminary Communication

# A CONVENIENT PREPARATION OF METAL CARBONYL MONOANIONS BY TRIALKYLBOROHYDRIDE CLEAVAGE OF METAL CARBONYL DIMERS; OBSERVATION AND REACTIONS OF A BIMETALLIC MANGANESE-FORMYL INTERMEDIATE

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## Summary

Commercially available $Li(C_2H_5)_3BH$ rapidly and quantitatively cleaves $[Mn(CO)_5]_2$, $[Co(CO)_4]_2$, and $[(C_5H_5)Mo(CO)_3]_2$ in THF at room temperature to the corresponding transition metal monoanions. $[(C_5H_5)Fe(CO)_2]_2$ can be cleaved in hexamethylphosphorous triamide (HMPA) or by use of $K(\underline{sec}\text{-}C_4H_9)_3BH$. The mechanism postulated for $Li[Mn(CO)_5]$ formation (Scheme I) is supported by the direct observation of a manganese-formyl intermediate (4) and rate data. 4 acts as a hydride donor toward $CH_3SO_3F$, $Fe(CO)_5$, and $HMn(CO)_5$.

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Transition metal monoanions play a pivotal role in the construction of metal-carbon bonds.[1,2] Numerous organometallic compounds have been prepared through alkylation or acylation of these highly nucleophilic[1] species. Cluster complexes and other compounds containing metal-metal bonds can be obtained by addition of an appropriate electrophile.[2]

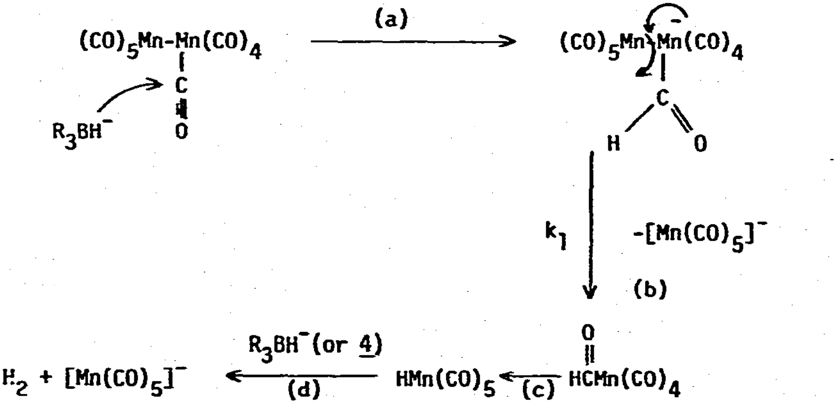
Conventionally, transition metal monoanions are prepared from the readily available corresponding metal-metal dimers. Mercury-sodium amalgam[1] or other heterogeneous metal reductant[3] is employed in a somewhat cumbersome overall procedure. Mercury-containing by-products are sometimes produced.[4] We report herein the rapid, quantitative, homogeneous, room temperature synthesis of representative monoanions $[Co(CO)_4]^-$, $[(C_5H_5)Mo(CO)_3]^-$, $[Mn(CO)_5]^-$, and $[(C_5H_5)Fe(CO)_2]^-$, utilizing inexpensive, commercially available trialkylborohydrides such as $Li(C_2H_5)_3BH$ (1). The attractiveness of this procedure is further enhanced in that only volatile by-products [$H_2$ and $(C_2H_5)_3B$ when 1 is used] are formed, enabling in theory solvent evaporation to an analytically pure product residue.

Addition of 2.5 equiv $Li(C_2H_5)_3BH$ (1)[5a] (1 M in THF) to 1.0 equiv $[Co(CO)_4]_2$, $[(C_5H_5)Mo(CO)_3]_2$, or $[Mn(CO)_5]_2$ (0.02 M in THF) afforded the corresponding lithium monoanions in quantitative yields (Initial experiments were conducted titrimetrically and ir monitored using an apparatus similar to one described by Brown.)[6] after a few minutes stirring at room temperature. During this period, 1 equiv $H_2$ evolved, as determined by manometric and mass spectral methods. Identical products were formed with Li(sec-$C_4H_9)_3BH$ (2),[5b] and potassium monoanions could be obtained from K(sec-$C_4H_9)_3BH$ (3).[5c] $Li[(C_5H_5)Fe(CO)_2]$ could not be formed using 1 or 2 unless done in ≥ 50% hexamethylphosphorous triamide (HMPA), but $K[(C_5H_5)Fe(CO)_2]$ was produced over a three hour period in THF when 3 was employed.

To the monoanions thus prepared were added THF solutions of various electrophiles. The derivatives obtained are listed in the Table and illustrate the general synthetic utility of our procedure. The yields reported are for isolated, purified products, are based upon metal, and are not optimized.

Investigation of the mechanism of $Li[Mn(CO)_5]$ formation has resulted in several remarkable observations. The following evidence supports the reaction pathway depicted in Scheme I:

SCHEME I. Proposed Mechanism of Anion Formation



4

5

Step (a) The high nucleophilicity of 1 - 3 toward organic electrophiles,[7-10] and the observance of attack on coordinated carbon monoxide by related nucleophiles,[11-13] led us to postulate the initial addition step (a). Accordingly, when $[Mn(CO)_5]_2$ was treated with one equiv 1 at -20°C in THF in a $^1H$ nmr tube, a new complex was formed in 99% yield, as indicated by the appearance of a signal at $13.66\delta$ (p-xylene reference and internal standard). This chemical shift has been established as characteristic of anionic formyl complexes,[12] and the structural assignment 4 is further supported by the observation of

Table. Monoanion Derivatives Prepared

| Hydride Reagent | Electrophile | Product | Isolated Yield (%) |
|---|---|---|---|
| 1 | $[(C_6H_5)_3P]_2N^+Cl^-$ | $[Co(CO)_4]^-[(C_6H_5)_3P]_2N^+$ | 79 |
| 1 | $(C_6H_5)_3SnCl$ | $Co(CO)_4[Sn(C_6H_5)_3]$ | 83 |
| 1 | $CH_3I$ | $(C_5H_5)Mo(CO)_3CH_3$ | $77^a$ |
| 1,2 | $CH_3O\overset{O}{C}\overset{O}{C}Cl$ | $(C_5H_5)Mo(CO)_3(\overset{O}{C}\overset{O}{C}OCH_3)$ | $77^{a,b}$ |
| 1 | $(C_6H_5)_3SnCl$ | $(C_5H_5)Mo(CO)_3[Sn(C_6H_5)_3]$ | 76 |
| 1 | $C_6H_5\overset{O}{C}\overset{O}{C}Cl$ | $Mn(CO)_5(\overset{O}{C}\overset{O}{C}C_6H_5)$ | $92^a$ |
| 1 | $(C_6H_5)_3SnCl$ | $Mn(CO)_5[Sn(C_6H_5)_3]$ | 88 |
| 1 | $CH_3O\overset{O}{C}\overset{O}{C}Cl$ | $Mn(CO)_5(\overset{O}{C}\overset{O}{C}OCH_3)$ | $81^{a,b}$ |
| 3 | $(C_6H_5)_3SnCl$ | $(C_5H_5)Fe(CO)_2[Sn(C_6H_5)_3]$ | 93 |
| 3 | $C_6H_5CH{=}CH\overset{O}{C}Cl$ | $(C_5H_5)Fe(CO)_2\overset{O}{C}CH{=}CHC_6H_5$ | $72^a$ |
| 3 | $C_6H_5\overset{O}{C}Cl$ | $(C_5H_5)Fe(CO)_2\overset{O}{C}C_6H_5$ | $67^a$ |

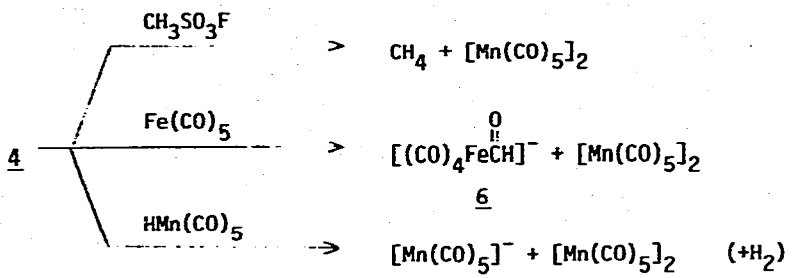
(a) electrophile added at -78° instead of room temperature

(b) new compound; satisfactory spectral and elemental analyses were obtained

the formyl $\nu_{C=O}$ in the vibrational spectrum (1540 $cm^{-1}$, THF). CO stretching frequencies at 2076 (s), 1970 (vs), 1941 (m) and 1903 (m) $cm^{-1}$ are clearly present, but 4 is unstable at room temperature and assignment of a cis or trans geometry to the disubstituted manganese cannot at this time be made with confidence.[14]

Attempted O-methylation of 4 at -20°C with $CH_3SO_3F$[15] led only to $CH_4$ (80% by manometry and mass spectroscopy) and $[Mn(CO)_5]_2$ (98%). Treatment of 4 with one equiv $Fe(CO)_5$ afforded the known iron formyl 6[12,13,16] in 76-79% yield by nmr and ir (Scheme II). The reduction of octyl iodide to octane by 6 has been previously reported.[16] These experiments suggest that anionic formyl complexes can act as hydride donors. The migration of a formyl ligand from manganese to iron in the conversion 4 → 6 is considered unlikely.

SCHEME II. Reactions of Bimetallic Manganese-Formyl 4



Steps (b)-(d) At -20°C in THF, 4 is stable for hours, but at room temperature it rapidly decomposes. One equiv $[Mn(CO)_5]^-$ and 0.5 equiv* $[Mn(CO)_5]_2$ are formed, with no detectable intermediates by $^1H$ nmr or ir. This experiment differs from preparative reactions in that no trialkylborohydride is present at this stage. At 14°C, $k_{obs}$ for the decomposition of 4 is first order ($2.03 \pm .04 \times 10^{-4}$/sec. Arrhenius $E_a = 24.8$ kcal/mol) which requires at least one intermediate between 4 and the products. We propose that the unsaturated formyl 5 is formed in the initial α-elimination step (b). The acetyl homolog of 4 has been previously generated[17,18] and fragments analogously. Rapid rearrangement of 5 to $HMn(CO)_5$ would be subsequently expected.[6] In a separate experiment, $HMn(CO)_5$ was found to react instantly with 4 at -20°C to yield one equiv each* of $[Mn(CO)_5]^-$ and $[Mn(CO)_5]_2$ (Scheme II). This accounts for the unobservability of intermediate $HMn(CO)_5$ and is consistent with the first order disappearance of 4 ($k_{obs} = 2k_1$). $HMn(CO)_5$ also reacted instantly with 1 at -20°C to form $[Mn(CO)_5]^-$; hence in the preparative reactions, this pathway may predominate. Formation of $[Mn(CO)_5]^-$ from $HMn(CO)_5$($K_a \cong 10^{-7}$)[19] may occur as an acid-base process or via hydride attack on CO. While the above body of results exclude many alternatives for steps (b)-(d), mechanistic investigations are continuing.

We postulate that the other monoanions are formed by a mechanism qualitatively similar to the one depicted for $[Mn(CO)_5]^-$. When $[(C_5H_5)Fe(CO)_2]_2$ was treated with one equiv 3 in THF at 20°C, an intermediate was formed ($\nu_{C=O}$ 1926 (s), 1745 (m), 1718 (m), 1677 (s) $cm^{-1}$) which slowly disproportionated to starting material and $K[(C_5H_5)Fe(CO)_2]$; no $^1H$ nmr resonance below δ 7.0 could be found. The less rapid formation of $[(C_5H_5)Fe(CO)_2]^-$ relative the other anions may be in part connected to the higher reduction potential of the parent dimer.[20] Anion formation from $[Co(CO)_4]_2$ and $[(C_5H_5)Mo(CO)_3]_2$ is too rapid to detect any

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*Stoichiometry was established spectroscopically and via treatment of the reaction mixture with $(C_6H_5)_3SnCl$; $Mn(CO)_5[Sn(C_6H_5)_3]$ and $[Mn(CO)_5]_2$ were subsequently isolated.

intermediates, even at -50°C by $^1H$ nmr. In terms of limitations, $[Re(CO)_5]^-$ is the only common transition metal monoanion which cannot be prepared in high yield by this methodology.

Formyl complexes such as 4 are of substantial current interest[11-13,16,21] as possible intermediates in important fuel producing catalytic processes. This investigation has established the possibility of their more widespread intermediacy in common organometallic reactions and contributed to the understanding of their fundamental chemistry. Preparative efforts are currently directed at making transition metal monoanion synthesis catalytic in trialkylborane (e.g., 3 can be generated from $(\underline{sec}\text{-}C_4H_9)_3B$ and KH)[9] and at transition metal polyanion synthesis.

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