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# THE CHEMISTRY OF METAL CARBONYL ANIONS

## III*. SODIUM—POTASSIUM ALLOY: AN EFFICIENT REAGENT FOR THE PRODUCTION OF METAL CARBONYL ANIONS

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## Summary

Reduction of several metal carbonyl dimers including $Mn_2(CO)_{10}$, $[C_5H_5Fe(CO)_2]_2$, $Co_2(CO)_8$, and $[C_5H_5M(CO)_3]_2$ (M = Cr, Mo and W) by sodium—potassium alloy (NaK) in tetrahydrofuran at room temperature provides a rapid and clean method for the production of the corresponding metal carbonyl anions in high yield. Isolation and characterization of $[n\text{-}Bu_4N][Fe(CO)_2C_5H_5]$ from the iron dimer reduction is described. Reductions of other carbonyls including $M(CO)_6$ (M = Cr, Mo and W) and $Re_2(CO)_{10}$ proceed more slowly than previously established methods and provide principally $M_2(CO)_{10}^{2-}$ and $Re(CO)_5^-$. Methods for the preparation of $Re(CO)_5^-$ are critically considered. The reaction of NaK with $[C_5H_5NiCO]_2$ is discussed in relation to previously reported results. Infrared solution spectra of a number of carbonyl anions in THF, obtained in a special infrared solution cell, are reported.

## Introduction

In the course of our work on metal carbonyl anions [1] we have developed a fast, high-yield and clean method for the generation of these species from corresponding metal carbonyls or metal carbonyl halides by reduction with sodium—potassium alloy (NaK) in ethereal solvents. This method is superior to those previously reported [2-4] for the following reasons: There is little contamination of the anions by the reducing agent (e.g., mercury compounds from sodium amalgam reduction [5], bromide ions from magnesium-1,2-dibromoethane reductions [4], or benzophenone from sodium benzophenone ketyl reductions [6]), yields are nearly quantitative, and reaction times are short at room temperature (<1½ h)

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* For Part II see ref. 22.

for $Mn_2(CO)_{10}$, $[C_5H_5Fe(CO)_2]_2$, $Co_2(CO)_8$, and $[C_5H_5M(CO)_3]_2$ (M = Cr, Mo and W). NaK reductions of other neutral carbonyls, including $M(CO)_6$ (M = Cr, Mo and W), $Re_2(CO)_{10}$ and $[C_5H_5Ni(CO)]_2$, were also investigated; however, because of relatively long reduction times, or other reasons the NaK method is not superior to other methods for these systems. Although the use of NaK as a reducing agent is well established in organic syntheses [7], there have been very few reports on the use of this reagent in organotransition metal systems [8,9].

## Experimental

### *General procedures and starting materials*

All operations were carried out under an atmosphere of purified nitrogen or argon further purified by passage through columns of activated BASF catalyst, anhydrous magnesium perchlorate and molecular sieves. Solutions were transferred by stainless steel cannulae and syringes; otherwise reactions were performed by using standard Schlenk apparatus [10]. Reagent grade tetrahydrofuran (Aldrich) was freshly distilled from the benzophenone ketyl of potassium under an argon atmosphere. All solvents and reagents except $[C_5H_5M(CO)_3]_2$ (M = Cr, Mo and W) were obtained from commercial sources. The latter substances were prepared according to published methods [11,12].

IR spectra were recorded on a Perkin—Elmer 237B Spectrometer. Solution spectra were obtained in sealed sodium chloride cells (e.g., Barnes Engineering 0.1 mm stainless steel precision pathlength sealed cell #0003-503 or 0.1 mm leakproof amalgam sealed cell #0004-664) equipped with stainless steel Luer stopcocks (e.g., Becton Dickinson #MS09, spring loaded, two-way stopcocks) to permit filling via syringe outside a glove box with essentially complete exclusion of air. Solutions of $C_5H_5Fe(CO)_2^-$ in THF could be kept for at least 0.5 h in these cells without significant oxidation (to neutral dimer) occurring. Elemental Analyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Michigan, or by Galbraith Laboratories.

### *Preparation of sodium potassium alloy ($NaK_{2.8}$)*

Potassium metal (77 g, 2.0 mol) and sodium metal (16 g, 0.7 mol) are gently heated in 100 ml of xylene which was freshly distilled from sodium. After the metals coalesce, 50 ml of dry and oxygen-free diglyme is added to help keep the alloy in one globule. Small globules of alloy may be united by adding a few drops of isopropanol to the solution. After the alloy is cooled to room temperature it may be stored indefinitely under nitrogen. Samples may be safely withdrawn from the central globule by syringe equipped with a metal stopcock. We have found NaK to be far more easy to use and dispose of than sodium amalgam; however, it must be handled carefully. For example, NaK readily ignites in moist air. A 50/50 mixture of isopropanol/petroleum ether (60-110°C) can be used to safely and quickly destroy NaK residues.

### *Reduction of metal carbonyls; chemical characterization of anions; isolation of $[(C_2H_5)_4N][C_5H_5Fe(CO)_2]$*

The procedures for all of the metal carbonyl dimers are virtually identical and will be illustrated for $[C_5H_5Fe(CO)_2]_2$. After stirring 3.5 mmol of dimer with 0.42 ml $NaK_{2.8}$ (introduced by syringe) in 75 ml of dry, oxygen-free tetrahydrofuran (THF) for 0.75 h at a moderate rate, the solution had changed from a deep brown-red to a bright red. The infrared spectrum of this exceedingly air-sensitive solution showed that the dimer was completely reduced to $C_5H_5Fe(CO)_2^-$ (Table 1). The partly solidified alloy then was cleanly filtered from the solution (medium-porosity fritted disc) to yield a clear blood-red solution. The addition of an equivalent amount of $Ph_3SnCl$ via Schlenk tube gave, after work-up and recrystallization, 3.31 g (92% yield based on dimer) of $Ph_3SnFe(CO)_2C_5H_5$. Yields of triphenyltin derivatives of other carbonyl anions are shown in Table 2. These reductions are fast and easily conducted; however, we have occasionally experienced reduced yields of anion if the stirring is continued for more than 12 h. Apparently, under these conditions, the NaK slowly destroys the carbonyl anion. No further reduced carbonyl species have been detected in solution; however, in these long-term reductions a considerable amount of metal-containing sludge forms. Also, to facilitate the filtration process, rapid stirring is to be avoided, as it breaks the alloy into very fine particles which are difficult to filter.

In similar preparations the iron anion was treated with an equivalent of tetrabutylammonium perchlorate to afford, after removal of potassium perchlorate by filtration and evaporation of the blood-red filtrate, 92-95% yields of orange-red, crystalline, analytically pure $[n\text{-}Bu_4N][Fe(CO)_2C_5H_5]$, the first reported isolation and characterization of this extremely reactive anion from reduction of the dimer. M.p. 101°C (dec.). Anal. found: C, 65.32; H, 10.01; N, 3.17. $C_{23}H_{41}FeNO_2$ calcd.: C, 65.85; H, 9.85; N, 3.34%. $\nu(CO)$: 1865s, 1788s $cm^{-1}$ (THF).

## Results and discussion

### *Reduction of $[C_5H_5Fe(CO)_2]_2$, $Co_2(CO)_8$, $Mn_2(CO)_{10}$, and $[C_5H_5M(CO)_3]_2$ ($M = Cr, Mo, W$)*

The sodium amalgam method for the reduction of metal carbonyls to anionic species has enjoyed wide popularity; however, its major drawbacks involve inconvenient handling and subsequent removal of large masses of metallic mercury and contamination of carbonyl anions by soluble mercury derivatives [5]. For these reasons, the NaK method described in this paper was deverloped. Occasionally, long reaction times have been reported for amalgam reductions [17]; however, on the basis of monitoring numerous carbonyl reductions by infrared spectroscopy, we conclude in most cases, except for $Re_2(CO)_{10}$ and $M(CO)_6$ in THF (see later) that Na/Hg and NaK reductions require similar times for completion.

The NaK method provides a rapid and clean route to $C_5H_5Fe(CO)_2^-$ and other carbonyl anions. While these may be generated and used in situ, it is possible to isolate analytically pure salts of the anions from these solutions. For example, in this paper the preparation of $Bu_4N[C_5H_5Fe(CO)_2]$ is described. This is the first reported isolation of a simple salt of $Fe(CO)_2C_5H_5^-$, although the more complex species $[C_5H_5Fe(CO)dmpe][C_5H_5Fe(CO)_2]$, prepared by the disproportionation of $[C_5H_5Fe(CO)_2]_2$ with dmpe (1,2-bis(dimethylphosphinoetane), has been known for several years [18]. The $\nu(CO)$ frequencies for the $C_5H_5Fe(CO)_2^-$ anion in the above complex agree well with ours. Similar alkylammonium salts

TABLE 1

INFRARED SOLUTION SPECTRA OF THE METAL CARBONYL ANIONS IN THE CARBONYL REGION

| Anion[a] | C—O stretching frequencies (cm$^{-1}$) |
|---|---|
| $Co(CO)_4^-$ | 1890 vs, 1857 w |
| $Mn(CO)_5^-$ | 1896 s, 1862 s, 1830 m |
| $Re(CO)_5^-$ | 1911 s, 1864 s, 1835 sh |
| $Cr(CO)_3C_5H_5^-$ | 1900 s, 1800 s, 1752 s |
| $Mo(CO)_3C_5H_5^-$ | 1898 s, 1790 s, 1750 s |
| $W(CO)_3C_5H_5^-$ | 1896 s, 1786 s, 1746 s |
| $Fe(CO)_2C_5H_5^-$[b] | 1868 s, 1792 s, 1772 s |

[a] Counterion is predominantly potassium from NaK reductions. Although these solutions have not been analyzed for sodium content, it is established that $NaK_{2.8}$ gives potassium salts [7]. For example, a preparation of $M(CO)_6^-$ (M = Nb, Ta) using NaK provides analytically pure samples of $[K(diglyme)_3][M(CO)_6]$ [8]. [b] Potassium salt consistently exhibits splitting of asymmetric CO stretch in THF. This splitting probably arises via ion pair formation, which has been reported to cause a similar splitting of $\nu(CO)$ in $Na_2Cr(CO)_5$ in THF [23]. By comparison, the sodium salt (prepared by Na(Hg) reduction of corresponding dimer) shows split bands of unequal intensity at 1882 s, 1865 m, 1810 s, 1773 m and the tetrabutylammonium salt shows bands of equal intensity at 1865 s, 1788 s in THF. These solutions were free of the corresponding neutral dimer which absorbs at 1781 cm$^{-1}$ in THF in this region.

of other carbonyl anions have been previously reported [19,20]. The synthetic utility of a readily available salt of $Fe(CO)_2C_5H_5^-$, free of THF, has yet to be established; however, there are many reports in the literature on carbonyl anion derivatives, especially of silicon, which must be prepared in the absence of ethers and other basic solvents [1].

Analogous reductions of $Co_2(CO)_8$, $Mn_2(CO)_{10}$ and $[M(CO)_3C_5H_5]_2$ (M = Cr, Mo and W) proceed smoothly and rapidly to give essentially quantitative yields of anions as shown by yields of the corresponding triphenyltin derivatives (Table 2). In most cases these are the highest reported yields for these compounds.

### *Reduction of $Re_2(CO)_{10}$*

The only binary carbonyl dimer examined that is not reduced rapidly by NaK is $Re_2(CO)_{10}$. In this case complete reduction requires 8-12 h in THF at room temperature, compared to ca. 2 h for a corresponding Na/Hg reduction. Solutions of $Re(CO)_5^-$ prepared by both methods are red-orange in color, indicating the presence of a colored impurity, possibly $Re_2(CO)_9^{2-}$ [24], and pro-

TABLE 2

YIELDS OF TRIPHENYLTIN DERIVATIVES, $Ph_3SnX$

| X | Best previously reported yield from dimer (%) | This work (%) |
|---|---|---|
| $Co(CO)_4$ | 99[a,d] [13] | 96 |
| $Mn(CO)_5$ | 81[a] [14] | 99 |
| $Cr(CO)_3C_5H_5$ | 46[b] [15] | 98 |
| $Mo(CO)_3C_5H_5$ | 65[b] [16] | 99 |
| $W(CO)_3C_5H_5$ | 57[b] [15] | 99 |
| $Fe(CO)_2C_5H_5$ | 72[c] [4] | 92 |
| $Re(CO)_5$ | 77[a] [21] | 80 |

[a] 1% Na/Hg. [b] $M(CO)_6 + NaC_5H_5$. [c] $Mg + 1,2\text{-}C_2H_4Br_2$. [d] Yield based on 0.8 mol $Ph_3SnCl$.

vide similar yields (75-80%) of $Ph_3SnRe(CO)_5$. Infrared solution spectra of $Re(CO)_5^-$ from both reduction processes show strong bands due to $Re(CO)_5^-$ (see Table 1 for that obtained by NaK method; principal $\nu$(CO) bands of $Re(CO)_5^-$ from Na/Hg are in virtually identical positions). A weak band at 1970 $cm^{-1}$ (not due to $Re_2(CO)_{10}$ or THF) also appears in the solution spectrum from the NaK reduction; a corresponding slightly more intense band at the same position, in addition to a weaker band at 2010 $cm^{-1}$ (probably due to a trace of unreacted $Re_2(CO)_{10}$, which absorbs in this region in THF at 2070m, 2010s, 1969mw) is obtained in the solution spectrum from the Na/Hg reduction.

Exposure of the above solutions to air or an equivalent of chlorotriphenylstannane causes the $\nu$(CO) bands due to $Re(CO)_5^-$ to rapidly disappear, but there is no apparent change in the red-orange color of the solution. (However, these processes were not monitored by a UV-visible spectrophotometer). Extensive air oxidation of $Re(CO)_5^-$ solutions gives bands in the infrared due to the neutral dimer as well as a broad band at ca. 1879 $cm^{-1}$ due to an uncharacterized species which may be the red-orange component.

We have been unsuccessful in attempts to obtain solutions of $Re(CO)_5^-$ which are largely free of the colored component. A reinvestigation of the reaction of $HRe(CO)_5$ with 1% sodium amalgam in THF failed to substantiate an earlier claim that $Re(CO)_5^-$ free of red-orange impurity is obtained [19]. Indeed, a careful spectral study of this reaction showed that no detectable amount of $Re(CO)_5^-$ is found after 72 h at room temperature. Addition of 1% Na/Hg to a colorless solution of $HRe(CO)_5$ in THF (the hydride prepared according to a published procedure [24]; physical and spectral properties of our sample agree well with those previously reported for $HRe(CO)_5$ [24,25]) caused the solution to slowly change to a pale yellow hue. The infrared solution spectrum in the carbonyl stretching frequency region, consisting originally of a rather broad intense band at ca. 2010 $cm^{-1}$, characteristic of $HRe(CO)_5$, changed after three hours to one that showed bands at 2011m, 1969s, 1930s, 1920(sh) and 1888m. This spectrum is very similar to that previously attributed to $NaRe(CO)_5$ in THF (see Table 1 in ref. 19). However, this attribution is incorrect as evidenced by our data (Table 1) as well as nearly identical spectra reported previously for the sodium salts of $M(CO)_5^-$ (M = Mn, Tc, Re) [25]. Continued stirring of the pale yellow solution for ca. 80 additional hours resulted in no significant change in the spectrum. The nature of the products(s) of this reaction are under investigation. Surprisingly, addition of an equivalent of butyllithium to $HRe(CO)_5$ in THF at room temperature results in a solution having a similar spectrum; however, there was no evidence for the formation of $Re(CO)_5^-$.

The p$K_a$ of $HRe(CO)_5$ is unknown [24]. Indeed, the failure of butyllithium to deprotonate it to form $Re(CO)_5^-$ suggests that the proton on $HRe(CO)_5$ may have negligible acidic character, in contrast to $HMn(CO)_5$ (p$K_a$ ~7) which is readily deprotonated under similar conditions. These observations are consistent with an earlier report that even in very basic aqueous solutions, $Re(CO)_5^-$ is completely hydrolyzed to $HRe(CO)_5$ [24].

### *Reduction of other metal carbonyls*

The NaK reductions of $M(CO)_6$ (M = Cr, Mo and W) and $[C_5H_5NiCO]_2$ in THF were also investigated under the same conditions reported for other metal carbonyls in this paper. Reduction of $M(CO)_6$ proceeded slowly; only after approximately 20 h stirring at room temperature was all $M(CO)_6$ reduced to $M_2(CO)_{10}^{2-}$. No evidence for the formation of $M(CO)_5^{2-}$ was found although it has been shown that long-term reductions of $M(CO)_6$ by sodium amalgam in THF at room temperature produce at least small quantities of these substances [22].

Reduction of $[C_5H_5NiCO]_2$ by NaK in THF provides practically quantitative yields of the green-black paramagnetic cluster $(C_5H_5Ni)_3(CO)_2$, first prepared by sodium amalgam reduction of the same dimer in methanol [26]. No spectral evidence for the production of the elusive $C_5H_5NiCO^-$ was obtained in the NaK reduction. Previously, it has been reported, without spectral confirmation, that potassium metal reacts with $[C_5H_5NiCO]_2$ in THF to yield solutions of $K[C_5H_5NiCO]$ [27]; however, our numerous attempts to obtain the spectrum of such a species with the potassium metal reduction have been uniformly unsuccessful. On this basis, we feel that the existence of $C_5H_5NiCO^-$, claimed also to have been generated electrochemically [28], is open to question.

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