forcing a preference for some configurations of the chain. Perfluoroalkyl peroxides and disulfides are well known, in general being more stable than the corresponding hydrocarbon-based compounds. The fluorinated thioperoxides reported here are among the first of this class of compound to be reported.

The gentle reaction of CF_3OF with elemental sulfur is very interesting in that several compounds related to the recently characterized S_2F_2 isomers apparently were formed.

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The Preparation of Sodium Cobalt Tetracarbonyl[1]

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In the course of spectroscopic studies, numerous preparations of $NaCo(CO)_4$ were made in this laboratory. Many of these were carried out by the reaction of Na amalgam and $Co_2(CO)_8$ in THF.[2] This is a standard preparation of a salt widely used in synthetic work.[3] At first, the reaction proceeded smoothly and in reasonable time, as indicated in the literature. In time, however, we were unable to make the reaction proceed. The difficulties are indicated here, some of their implications are discussed, and a better method of preparation is given.

Results

At the beginning of the work, a portion of a sample of solid Na amalgam, prepared several years earlier in the usual manner,[4] was added to $Co_2(CO)_8$ dissolved in THF which had been dried over CaH_2–$LiAlH_4$ and the mixture was shaken. The reaction proceeded smoothly from the original very dark brown solution of $Co_2(CO)_8$ to the light yellow solution of $NaCo(CO)_4$ in THF in about 1 hr. In an "improvement" of our technique, we prepared the amalgam *in situ*, added a more concentrated THF solution of $Co_2(CO)_8$ to it, and then shook the mixture. When the solution did not turn yellow after shaking for about 2 hr, it was transferred to another tube with its freshly prepared amalgam and subjected to another period of shaking. The desired yellow color was usually obtained after one to three transfers.

In time, the development of the spectroscopic work led to a need to ensure the absence of traces of H_2O (and O_2) in the $NaCo(CO)_4$ solutions. Consequently, the THF was dried and deoxygenated in a rigorous manner (see Experimental Section) and the method of preparing the amalgam and handling the materials were improved. As a result of these precautions, there was no visual evidence for a reaction even after long standing. However, after several weeks of stirring a mixture of amalgam and $Co_2(CO)_8$ solution prepared under these conditions, an infrared spectrum of the still dark brown solution showed that the $Co_2(CO)_8$ had been consumed and that $Co(CO)_4^-$ ion had been formed. The same reaction was found to take place in a THF solution of $Co_2(CO)_8$ to which *no* sodium amalgam had been added.

As these difficulties were becoming serious, we began to investigate other methods of preparing $NaCo(CO)_4$ which would be suitable for the present purposes. The use of Na in place of Na amalgam seems to lead to the same reaction difficulties. It was found, however, that powdered NaOH reacts with $Co_2(CO)_8$ in THF to yield the desired yellow solution of $NaCo(CO)_4$ in 1–2 hr. The reaction gives a clean solution of the salt. In particular, no NaOH is present in solution in significant amount although there are some traces of water. A white, solid salt may be isolated by vacuum removal of the solvent. A dry solution of $NaCo(CO)_4$ in THF may be prepared by dissolving the solid salt, prepared as above, in dry THF.

Discussion

The reaction between Na amalgam and $Co_2(CO)_8$ in THF is viewed as taking place by eq 1.[2] The results

$$2Na + Co_2(CO)_8 \longrightarrow 2Na^+ + 2Co(CO)_4^- \qquad (1)$$

cited here show that the reaction is more complicated than indicated by this equation. The reaction to form $NaCo(CO)_4$ is slow or does not proceed when the THF is effectively dried and the Na amalgam is formed under conditions which discourage the formation of NaOH. In fact, it is difficult to escape the conclusion that our success with the amalgam reaction in the early phases of our work was due to the presence of NaOH either brought in with the amalgam and/or formed from water in the solvent.

THF is a Lewis base and hence it is capable of undergoing the reaction with $Co_2(CO)_8$ reported for a number of such bases[5–7] and shown in eq 2. Our results, obtained by stirring a THF solution of $Co_2(CO)_8$ for several days, show that this reaction takes place slowly at room temperature. This reaction forms an explanation for the slow consumption of the $Co_2(CO)_8$ with the formation of $Co(CO)_4^-$ under the more stringent conditions of preparing and stirring a mixture of Na amalgam and $Co_2(CO)_8$ in THF.

$$3Co_2(CO)_8 + 12THF \longrightarrow 2Co(THF)_6[Co(CO)_4]_2 + 8CO \qquad (2)$$

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(1) Based in part upon the Ph.D. thesis of John Lyford, IV, Purdue University, Aug 1969.

(2) W. Heiber, O. Vohler, and G. Braun, *Z. Naturforsch. B*, **13**, 192 (1958).

(3) For a recent review of the chemistry of this salt, see R. B. King, *Advan. Organometal. Chem.*, **2**, 157 (1965).

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(5) I. Wender, H. W. Sternberg, and M. Orchin, *J. Amer. Chem. Soc.*, **74**, 1216 (1952).

(6) W. Hieber and J. Sedlmeier, *Chem. Ber.*, **87**, 25 (1954).

(7) W. Hieber, W. Abeck, and J. Sedlmeier, *Angew. Chem.*, **64**, 480 (1952).

The preparation of $NaCo(CO)_4$ by the reaction of powdered NaOH with $Co_2(CO)_8$ in dry THF has a number of desirable features. It is rapid and yields a clean product. The solid salt is readily obtained and its dissolution in dry solvents yields dry solutions. It avoids the preparation and handling of quantities of Na amalgam while eliminating the formation of $Hg[Co(CO)_4]_2$, an impurity often found in the preparations with amalgam.[8,9]

Hieber and coworkers[10] have studied the reaction of $Co_2(CO)_8$ with alcoholic and aqueous hydroxide. The reaction outlined here for the preparation of $NaCo(CO)_4$ probably proceeds in a similar manner. The objections which have been raised to the use of alcoholic or aqueous hydroxide for the preparation of the salt when employed in the synthesis of other materials relate to the fact that a hydrolytic solvent is used and that the solubility of the hydroxide results in the presence of excess hydroxide in the final solution. Neither of these objections applies to the preparation outlined here. Note that the only reaction product soluble in dry THF is $NaCo(CO)_4$.

The basic method of preparation outlined here can be expected to be general for the alkali metal salts of metal carbonylate anions. We have used it to date to prepare THF solutions of $LiCo(CO)_4$ and $KCo(CO)_4$ as well as those of $NaCo(CO)_4$.

Experimental Section

Preparation of $NaCo(CO)_4$ with NaOH.—For these experiments, the THF was dried and deoxygenated by a sequential procedure involving storage over Na ribbon, distillation in a stream of dry N_2, deaeration on a vacuum line, and distillation *in vacuo* onto Linde 4A Molecular Sieves. Prior to use, the sieves were activated by heating to at least 300° and pumping on the vacuum line. Excess NaOH (Mallinckrodt analytical reagent) was quickly powdered and put in a 100-ml round-bottom flask which was placed at once on a vacuum line and pumped. After thorough evacuation, the flask was opened in an N_2-filled polyethylene bag and charged with 1.66 g of $Co_2(CO)_8$. *Caution! Then, 40 ml of THF was added slowly.* Care must be exercised in the addition of THF since considerable ebullition can take place at this point. The flask was attached to a vacuum line by means of a fitting which allowed the transfer from the N_2-filled bag to the vacuum line without admission of air to the sample. After evacuation, the line was filled with N_2, the flask was opened to the line, and stirring was begun by means of a Teflon-coated magnetic stirring bar, while a gentle stream of N_2 was maintained. After the solution had stirred for 1–2 hr, a pinkish purple precipitate had formed. The light yellow solution which remained was separated from the precipitate by centrifuging, and the precipitate was washed with THF. This wash was combined with the solution.

In typical preparations, the solution was returned to the vacuum line and the solvent removed by pumping. The white salt which resulted was stored in the absence of air and light until use.

Analysis.—Aliquots of the $NaCo(CO)_4$ solutions were allowed to decompose in the air and were then treated with sufficient 3% H_2O_2 to ensure complete decomposition of the metal carbonyl. After the residue had been dissolved in concentrated HNO_3, the resulting solutions were diluted with a small amount of H_2O and heated until evolution of brown fumes ceased. Analysis of a typical $NaCo(CO)_4$ solution prepared as above gave 7.19×10^{-2} and 7.25×10^{-2} mol/l. for Co and Na, respectively. This result corresponded to a 75% conversion of $Co_2(CO)_8$ to $Co(CO)_4^-$ and showed the presence of no detectable amount of NaOH in the THF solution of the salt.

Unsuccessful Preparation Using Sodium Amalgam.—A 1% amalgam was prepared in a 500-ml, three-necked, round-bottom flask which was provided with a dropping funnel in one inlet, a connection suitable for attachment to a vacuum line without exposure to the air in a second inlet, and a glass stopper in the third inlet. The flask was placed on a vacuum line and thoroughly flamed. After cooling, it was placed in an N_2-filled polyethylene bag where 10 ml of Hg was added to the dropping funnel. After the oxide and hydroxide coating had been removed from a piece of Na (1.73 g) in the N_2-filled bag, it was placed in the flask. The flask was then replaced on the vacuum line, the line was filled with dry N_2, and a few milliliters of Hg was run into the flask. The sodium was then heated until amalgamation began. Then, the remainder of the Hg was added at such a rate that amalgamation proceeded smoothly. The resulting amalgam was a liquid.

After the flask had cooled, it was once again placed in an N_2-filled polyethylene bag and the dropping funnel was replaced by a straight-bore stopcock through which samples could be removed. Twenty milliliters of THF, treated as indicated above, was added and then 6.35 g of $Co_2(CO)_8$ was added followed by a wash of an additional 10 ml of THF. The flask was placed on an N_2-filled vacuum line and stirring by means of a Teflon-coated magnetic stirring bar was begun. After several weeks of stirring, the solution still retained its original brown color. The infrared spectrum of the solution, however, showed only those bands associated with the $Co(CO)_4^-$ ion in the 5-μ region.

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Spectroscopic Characterization of Pentaammineruthenium Complexes of Acrylonitrile

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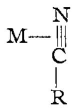
A recent contribution[2] from these laboratories described the syntheses and properties of substituted benzonitrile and acetonitrile complexes of ruthenium(II) and ruthenium(III) ammines. In that article, it was concluded that the "abnormal" decrease in the C≡N stretching frequency, ν(CN), observed for the pentaammineruthenium(II)-coordinated nitriles was the result of ruthenium-to-nitrile π back-bonding in a linear metal–nitrogen–carbon array (A) rather than the result of a perpendicular π-bond configuration (B). We

$$M-N\equiv C-R$$

A



$M-(N\equiv C)-R$

B

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[1] Author to whom inquiries should be addressed.

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