that this spectrum was unchanged upon addition of an equimolar quantity of water.

The data for $(C_6H_5)_3SnCo(CO)_4$ indicate that it is essentially completely dissociated in DMF. This is somewhat surprising in view of the fact that $(C_6H_5)_3SnCl$ is not appreciably ionized in this solvent.[11] A chemical reaction of $(C_6H_5)_3SnCo(CO)_4$ with the solvent or other decomposition process which might have led to the observed $Co(CO)_4^-$ was eliminated by the recovery of 94% of the pure, crystalline compound upon vacuum evaporation of the DMF and recrystallization of the cream-colored residue from hexane. Furthermore, behavior typical of a strong electrolyte was shown by a plot of $\Lambda_M$ *vs.* $\sqrt{C}$ which was linear in the region of $C = 0.04M$ to $C = 0.0002\ M$.

Systems **5**, **6**, and **7** show that pentacarbonylmanganese derivatives dissociate less readily than the corresponding tetracarbonylcobalt systems. The absorptions at 1900 and 1865 cm$^{-1}$ attributed to $Mn(CO)_5^-$ may be compared with previously reported values of 1898 and 1863 cm$^{-1}$ for this anion in tetrahydrofuran.[12] Good qualitative agreement between the intensities of these bands and the respective molar conductivities lends additional support to this assignment.

Results for systems **8**, **9**, and **10** show that the $Zn[M(CO)_3C_5H_5]_2$ compounds (M = Cr, Mo, W)[13] are largely dissociated in DMF. The observed tendency to dissociate, *viz.* Cr > Mo > W, is in qualitative agreement with the generally accepted notion that the strength of metal–metal bonds increases as one moves down a particular transition group of the periodic table. In contrast, the structurally related $Fe(CO)_2C_5H_5$ derivatives (**12** and **13**) showed little or no tendency to dissociate even under forcing conditions of excess bromide ion.[14] The previously unreported trimetallic compound $C_5H_5Fe(CO)_2ZnCo(CO)_4$ would appear to have only the $Co(CO)_4$ group ionized and would be consistent with the behavior of the symmetrical derivatives **1** and **12**. The observed ease of dissociation of the triphenyltin derivatives, *viz.* $Co(CO)_4 \gg Mn(CO)_5 \cong C_5H_5Mo(CO)_3 \gg Fe(CO)_2C_5H_5$, roughly parallels their tendency to undergo electrochemical reduction as reported by Dessy, Weissman, and Pohl.[15]

The foregoing observations, together with those from similar studies in acetonitrile,[16] suggest that the heterolytic cleavage of bonds between main group metals and certain transition metals can occur readily. Extensions to other metal and solvent systems are in progress.

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with a large solvent shift for the $E_u$ band.[10] Such behavior is entirely consistent with the known chemistry of the group IIb elements.

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## Nucleophilic Displacement of Transition Metal Carbonyl Anions from Metal–Metal Bonded Compounds

*Sir:*

During the early part of a study[1,2] of the heterolytic dissociation of bonds between main group metals and transition metals in ionizing solvents such as N,N-dimethylformamide (DMF) and acetonitrile, it was observed that the infrared spectrum in the carbonyl stretching region was highly dependent on the type of cell employed for the measurement. Thus 0.010 *M* $Hg[Co(CO)_4]_2$ in DMF showed absorptions at 2072 w, 2045 m, 1976 s, and 1891 s cm$^{-1}$ when observed in an NaCl cell whereas only two absorptions at 2065 and 1994 cm$^{-1}$ were present when Irtran-2[3] or $CaF_2$ windows were used. In view of the low conductivity of the solution before ir analysis,[1] the formation of significant amounts of $Co(CO)_4^-$, as indicated by the band at 1891 cm$^{-1}$,[4] could only be attributed to reaction of $Hg[Co(CO)_4]_2$ with the salt cell. This effect could be reproduced in a controlled manner by the addition of a soluble halide to a solution of $Hg[Co(CO)_4]_2$ in DMF and observation of the infrared spectrum in an unreactive $CaF_2$ cell. Upon addition of 5 ml of 0.01 *M* $Hg[Co(CO)_4]_2$ solution in DMF to 0.05 mmole of dry tetraethylammonium bromide in an argon atmosphere the color of the solution changed from yellow to deep orange. The appearance of a low intensity band at 1890 cm$^{-1}$ (Figure 1b) indicated that a small amount of $Co(CO)_4^-$ was present. When the above process was repeated using 0.25 mmole of $(C_2H_5)_4NBr$, a light yellow solution resulted. The infrared spectrum (Figure 1c) indicated that a large fraction of the transition metal carbonyl group was present as the anion. The spectrum of this solution was unchanged after 15 hr in the dark under argon. The limited solubility of $(C_2H_5)_4NBr$ in DMF did not permit complete conversion of the transition metal group to the ionic form although this has been accomplished in a number of other systems. For example, the addition of a fourfold molar excess of $(C_2H_5)_4NBr$ to $Zn[W(CO)_3C_5H_5]_2$ (which is partially ionized in pure DMF[1]) resulted in the complete conversion of the $W(CO)_3C_5H_5$ groups to the ionic form as indicated by the disappearance of all carbonyl bands except those at 1891 and 1774 cm$^{-1}$. These may be compared with the 1892- and 1775-cm$^{-1}$ bands observed[1] for the completely dissociated $Zn[Cr(CO)_3C_5H_5]_2$. The spectrum of the undissociated $Zn[Fe(CO)_2C_5H_5]_2$, on the other hand, was changed only slightly by the addition of excess $(C_2H_5)_4NBr$. There was no evidence for the formation of a metal carbonyl anion.

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FIG. 1

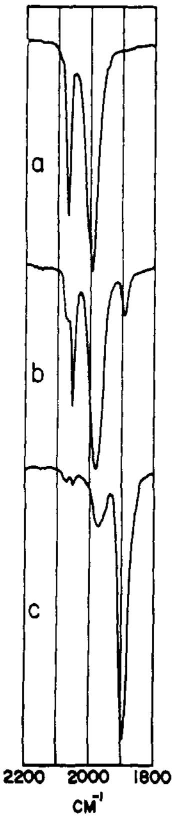

FIG. 2

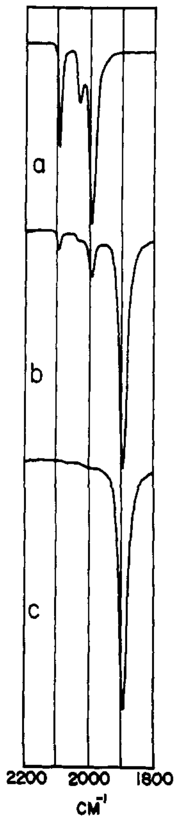

Figure 1. DMF solutions: (a) 0.01 *M* $Hg[Co(CO)_4]_2$; (b) 0.01 *M* $Hg[Co(CO)_4]_2$ + 0.01 *M* $(C_2H_5)_4NBr$; (c) 0.01 *M* $Hg[Co(CO)_4]_2$ + 0.05 *M* $(C_2H_5)_4NBr$.

Figure 2. Acetonitrile solutions: (a) 0.01 *M* $(C_6H_5)_3SnCo(CO)_4$; (b) 0.01 *M* $(C_6H_5)_3SnCo(CO)_4$ + 0.01 *M* $(C_2H_5)_4NBr$; (c) 0.01 *M* $(C_6H_5)_3SnCo(CO)_4$ + 0.05 *M* $(C_2H_5)_4NBr$.

Displacement reactions are not restricted to the group IIB metals. A particularly good example involving a group IV metal is provided by $(C_6H_5)_3SnCo(CO)_4$ in acetonitrile. Conductivity and infrared studies[2] have established that this compound was not significantly dissociated in the pure solvent at 0.01 *M*. The infrared spectrum (Figure 2a) did not differ greatly from that observed in cyclohexane.[5] Upon addition of an equimolar quantity of $(C_2H_5)_4NBr$ a strong band at 1895 $cm^{-1}$ was observed with a corresponding decrease in the intensity of the other bands (Figure 2b). A fourfold excess of bromide ion resulted in a single strong band at 1895 $cm^{-1}$ (Figure 2c) corresponding to complete conversion to $Co(CO)_4^-$. With DMF as solvent, experiments employing a fourfold excess of bromide ion resulted in partial formation of $Mn(CO)_5^-$ and $Mo(CO)_3C_5H_5^-$ with $(C_6H_5)_3SnMn(CO)_5$ and $(C_6H_5)_3SnMo(CO)_3C_5H_5$, while $(C_6H_5)_3SnFe(CO)_2C_5H_5$ was unaffected.

The foregoing observations may be interpreted as nucleophilic displacements of the transition metal carbonyl anion from the main group metal by halide ion, *e.g.*

$$(C_6H_5)_3SnCo(CO)_4 + Br^- \rightleftharpoons (C_6H_5)_3SnBr + Co(CO)_4^- \quad (1)$$

From kinetic studies with organic halides Dessy, Pohl, and King[6] established an order of nucleophilicities for the metal carbonyl anions employed in this work, *viz.* $Fe(CO)_2C_5H_5^- \gg W(CO)_3C_5H_5^- > Mo(CO)_3C_5H_5^- \cong Mn(CO)_5^- > Co(CO)_4^-$. The behavior of the compounds examined thus far is in qualitative agreement with their findings. In the triphenyltin series, with a fourfold excess of $(C_2H_5)_4NBr$ in DMF, the bromide ion was apparently not a sufficiently strong nucleophile to displace $Fe(CO)_2C_5H_5^-$. Partial displacement occurred for $Mo(CO)_3C_5H_5^-$ and $Mn(CO)_5^-$ whereas with $Co(CO)_4^-$ displacement was complete even in acetonitrile.

Although nucleophilic displacement of a transition metal group by halide ion has not been previously described as such, it seems likely that this process was responsible for the formation of $C_5H_5M(CO)_3MgBr$ (THF) (and presumably $(C_2H_5)_3GeBr$) by the action of excess $MgBr_2$ on $(C_2H_5)_3GeM(CO)_3C_5H_5$ (M = Mo, W) in THF.[7] Displacement of one transition metal carbonyl anion by another that is a stronger nucleophile has been observed in several cases. For example, electrochemically generated $Fe(CO)_2C_5H_5^-$ reacted with $(C_6H_5)_3SnMo(CO)_3C_5H_5$ to produce $(C_6H_5)_3SnFe(CO)_2C_5H_5$.[8]

From the limited number of systems examined in this work it would appear that displacement reactions of the type described are more common than previously anticipated. Some practical considerations follow from these results. First, the presence of *soluble* halides in the synthesis of metal–metal bonded compounds containing metal carbonyl groups that are weak nucleophiles may limit the conversion to the desired product by a process such as that depicted in eq 1. Secondly, the presence of a particular transition metal carbonyl group in a complex heterometallic molecule may be detectable by the characteristic infrared absorptions of the displaced anion. Finally it may be anticipated that a variety of nucleophiles will behave similarly. The scope of this type of reaction is currently under study.

**Acknowledgment**. It is a pleasure to acknowledge financial support from the National Science Foundation and the Petroleum Research Fund along with generous gifts of chemicals from Ethyl Corporation and Climax Molybdenum Company.

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## A Dihydroxo-Bridged Ferric Dimer

*Sir:*

Recent investigations have produced[1–3] a large number of dimeric complexes containing the oxo-bridged structural unit $Fe_2O^{4+}$. Here we report the isolation

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