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The Ionic Dissociation of Some Compounds Containing Covalent Metal-Metal Bonds

Sir:

The covalent nature of bonds between transition metals and many main group metals has been firmly established by numerous structural, spectroscopic, and chemical studies. Recent X-ray crystallographic studies have confirmed the presence of covalent metal-to-metal bonds in $\text{Hg}[\text{Co}(\text{CO})_4]_2$,¹ $\text{Zn}[\text{Co}(\text{CO})_4]_2$,² $(\text{C}_6\text{H}_5)_3$ -

$\text{cm}^2 \text{mole}^{-1}$ indicated that essentially complete dissociation had occurred. The air-sensitive solution exhibited a single, strong infrared absorption in the carbonyl stretching region at $1920 \pm 2 \text{ cm}^{-1}$. In a recent study, Edgell, Yang, and Koizumi⁷ showed that in aqueous solutions of $\text{NaCo}(\text{CO})_4$ the tetracarbonylcobaltate(−I) anion was characterized by a single infrared carbonyl stretching absorption at 1919 cm^{-1} in agreement with that predicted for a regular tetrahedral structure.

The foregoing observations suggested that the heterolytic cleavage of metal-metal bonds might be more common than previously anticipated. Because of the limited water solubility of many compounds of interest, especially those containing organic substituents, a study was undertaken using carefully purified N,N-dimethylformamide (DMF) as the ionizing solvent. Infrared and conductance data for some representative compounds are shown in Table I. It is obvious that

Table I. Conductivity and Infrared Data in DMF

No.	Compound	Λ_M^a	Infrared absorptions, cm^{-1} b,c
1	$\text{Zn}[\text{Co}(\text{CO})_4]_2$	111	1892 vs
2	$\text{Cd}[\text{Co}(\text{CO})_4]_2$	99	2051 vw, 1961 m, 1891 vs
3	$\text{Hg}[\text{Co}(\text{CO})_4]_2$	0.17	2065 m, 1994 s
4	$(\text{C}_6\text{H}_5)_3\text{SnCo}(\text{CO})_4$	56	1893 vs
5	$\text{Zn}[\text{Mn}(\text{CO})_5]_2$	103	2015 w, 1950 vw (sh), 1900 vs, 1865 vs
6	$\text{Cd}[\text{Mn}(\text{CO})_5]_2$	2.0	2075 w, 2052 m, 1960 vs, 1940 s (sh), 1900 w (sh), 1865 w
7	$(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_5$	0.63	2102 m, 2040 w (sh), 1997 s, 1900 vw, 1867 vw
8	$\text{Zn}[\text{Cr}(\text{CO})_3\text{C}_5\text{H}_5]_2^d$	91	1892 s, 1775 s
9	$\text{Zn}[\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5]_2^d$	78	1957 vw, 1897 s, 1871 vw (sh), 1840 vw, 1779 vs
10	$\text{Zn}[\text{W}(\text{CO})_3\text{C}_5\text{H}_5]_2^d$	64	1957 m, 1892 s, 1866 m, 1828 m, 1774 vs
11	$(\text{C}_6\text{H}_5)_3\text{SnMo}(\text{CO})_3\text{C}_5\text{H}_5$	0.27	1998 s, 1925 m, 1899 s
12	$\text{Zn}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2^d$	0.14	2016 vw, 1937 s, 1926 s, 1869 s
13	$(\text{C}_6\text{H}_5)_3\text{SnFe}(\text{CO})_2\text{C}_5\text{H}_5$	0.015	1990 m, 1939 m
14	$\text{C}_5\text{H}_5(\text{CO})_2\text{FeZnCo}(\text{CO})_4^d$	55	1948 m, 1892 vs

^a Molar conductivity values are $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$. All measurements were made at 1000 cps on 0.010 M solutions under an argon atmosphere. ^b Infrared spectra of the solutions used for the conductance measurements were observed under argon in a 0.1-mm sealed cell employing CaF_2 windows; the estimated accuracy is $\pm 1 \text{ cm}^{-1}$. ^c Absorptions assigned to ionic species are italicized. ^d This compound was prepared by a metal exchange reaction starting with the analogous mercury compound.¹³

$\text{SnMn}(\text{CO})_5$,³ and $(\text{C}_6\text{H}_5)_3\text{SnMo}(\text{CO})_3\text{C}_5\text{H}_5$ ⁴ to mention only a few. In addition to obvious structural relationships, the chemical properties of compounds containing metal-to-metal bonds have been shown to be similar in many ways to those containing well-established metal-to-carbon covalent bonds.⁵

This communication describes the preliminary results of a study of the heterolytic cleavage of transition metal-to-main group metal covalent bonds. Contrary to a previous report concerning $\text{Zn}[\text{Co}(\text{CO})_4]_2$ which stated "Von Wasser wird die Substanz nicht benetzt,"⁶ we have observed that yellow, crystalline $\text{Zn}[\text{Co}(\text{CO})_4]_2$ dissolved readily in deaerated water, without gas evolution, to give a colorless solution. At a concentration of 0.010 M the observed molar conductivity of 132 ohm^{-1}

a wide spectrum of behavior is observed. The tetracarbonylcobalt derivatives (1 through 4) were particularly useful in this study because the single well-characterized absorption of $\text{Co}(\text{CO})_4^-$ at 1892 cm^{-1} in DMF⁷ was shifted from absorptions due to undissociated species. In DMF as in water $\text{Zn}[\text{Co}(\text{CO})_4]_2$ dissolved to give a stable (though somewhat air-sensitive) colorless solution. The infrared and conductance data showed that dissociation was essentially complete. As expected the Hg and Cd analogs showed less tendency to ionize. The infrared spectrum of $\text{Hg}[\text{Co}(\text{CO})_4]_2$ in DMF was very similar to that obtained in heptane⁸ and, in agreement with the low conductivity, no absorption due to $\text{Co}(\text{CO})_4^-$ was observed. With $\text{Cd}[\text{Co}(\text{CO})_4]_2$, on the other hand, in addition to the strong anion absorption at 1891 cm^{-1} , bands were observed at 2051 and 1961 cm^{-1} which we attribute to nondissociated or partly dissociated species shifted by strong interaction with the solvent.⁹ It may be noted

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(9) Our experience has shown that $\text{Cd}[\text{Co}(\text{CO})_4]_2$ and $\text{Zn}[\text{Co}(\text{CO})_4]_2$ (but not $\text{Hg}[\text{Co}(\text{CO})_4]_2$) form complexes with a number of polar solvents such as tetrahydrofuran and acetonitrile. This is always associated

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 Λ_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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gifts of chemicals from Ethyl Corporation and Climax Molybdenum Company.

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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-2³ 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 DMF¹) 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 observed¹ 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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