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Preliminary communication

The nature of metal carbonyl – Group III halide interactions. $Co_2(CO)_8 \cdot AlBr_3$ and related compounds

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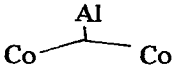
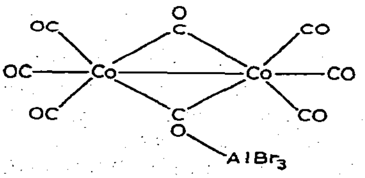
In 1958 Chini and Ercoli isolated an adduct of dicobaltoctacarbonyl $Co_2(CO)_8 \cdot AlBr_3$, for which an unusual 3-center 2-electron  donor–acceptor bond was proposed[1]. A similar bonding scheme was invoked for boron halide adducts of some iron carbonyl compounds, $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ and $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ [2] To date all these adducts have evaded detailed examination. Two reports have appeared containing some infrared data for $Co_2(CO)_8 \cdot AlBr_3$ [3,4], however the observations were incidental to other work. In both studies the structure and position of bands around 2050 and 1860 cm^{-1} were reported to be similar to those of $Co_2(CO)_8$. In the work of Whyman[4] an additional band was observed at 1600 cm^{-1} and the similarity was noted between this band and the low frequency CO stretch of C- and O-bonded bridging carbonyls[5].

Composition of the air sensitive $Co_2(CO)_8 \cdot AlBr_3$ adduct, prepared by the method of Chini and Ercoli[1], was verified by a tensimetric back titration with dimethyl ether $Co_2(CO)_8/AlBr_3 = 1/1.05$. Infrared spectra for Nujol mulls of $Co_2(CO)_8 \cdot AlBr_3$ display bands at 2025 ms, 2040 ms, 2062 s, 2070 s, 2082 sh, 2095 ms, 2105 ms, and 2138 ms cm^{-1} for terminal ν(CO) and 1867 s cm^{-1} for the bridging ν(CO) (Fig. 1). These represent a change in the number of bands as well as an increase of ca. 30 cm^{-1} for terminal ν(CO) and ca. 10 cm^{-1} for bridging ν(CO). An additional strong carbonyl stretch is noted at 1600 cm^{-1}. This pattern is exactly that expected for the interaction of a Lewis acid with one of the two bridging carbonyl oxygens (I)[5,6]. Thus the stretching



(I)

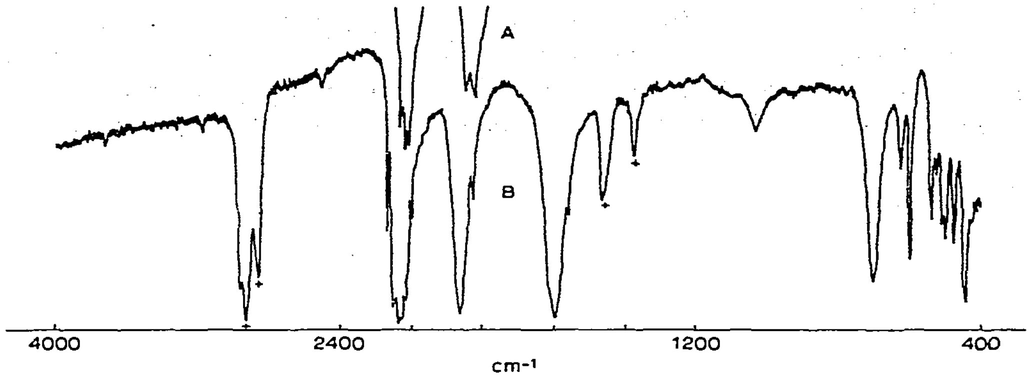
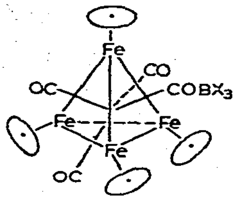


Fig. 1. Nujol mull infrared spectra of (A) $Co_2(CO)_8$, and (B) $Co_2(CO)_8 \cdot AlBr_3$. Nujol peaks are indicated by +. The ca. 1000 cm^{-1} band is not seen in all spectra and therefore may be spurious.

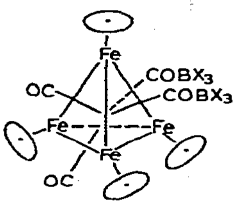
frequencies for carbonyls which are not bonded to the acid undergo a small frequency increase, while the C- and O-coordinated carbonyl stretch occurs at greatly reduced frequency. By contrast, 3-center metal base—$AlBr_3$ interaction should lead to an increase for all of the CO stretching frequencies[2]. In the far infrared three prominent new bands are observed at 448, 325 and 280 cm^{-1}. The latter feature is similar in position to a band found in organic carbonyl—aluminum halide adducts[7]. Judging from the assignments for $AlBr_3N(CH_3)_3$ [8], the 448 and 280 cm^{-1} bands are associated with asymmetric and symmetric $AlBr_3$ stretch. Thus the far infrared data agree with the O-bonded structure.

Pressure volume temperature measurements of initial and unconsumed boron trifluoride demonstrate 1/1.07 complex formation between $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ and BF_3. This stoichiometry also is demonstrated by elemental analysis for BBr_3 adduct. Found: C, 26.31; H, 2.09; B, 1.78; Fe, 18.80. $C_{14}H_{10}Fe_2O_4 \cdot BBr_3$ calcd.: C, 27.80; H, 1.66; B, 1.79; Fe, 18.47%. The BF_3 adduct displays a significant vapor pressure above -62° and the BCl_3 compound is susceptible to irreversible cleavage reactions, which render characterization difficult. Infrared spectra for mulls of the BBr_3 complex exhibit the same general pattern of CO stretching frequencies which has been found for $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 \cdot AlR_3$ systems[6]: terminal ν(CO) around 2020 cm^{-1} and one bridging ν(CO) at increased frequency (1849 cm^{-1}) and a new low frequency ν(CO) (1437 cm^{-1}).

As judged by pressure volume temperature measurements and elemental analyses, both 1/1 and 1/2 adducts may be formed between $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ and BF_3, BCl_3, or BBr_3 (1/2.01, 1/1.91, and 1/2.02 respectively for the 1/2 adducts). Infrared spectra for mulls reveal one new strong band in the 1300–1400 cm^{-1} region for the 1/1 adducts and two new bands for the 1/2 compound in this same region. These observations agree with the presence of one and two C- and O-bonded carbonyl groups respectively. Spectra in the 1650–1750 cm^{-1} region for CH_2Cl_2 solutions of these adducts show two bands for both the 1/1 and 1/2 complexes. Data in both regions agree with selection rules for C-and O-bonded adducts of C_{3v} idealized symmetry for the 1/1 complex (II) and C_{2v} idealized symmetry for the 1/2 complex (III). Furthermore the results are inconsistent with the 3-center metal-bonded structures having C_{2v} symmetry for 1/1 complex formation and D_{2d} symmetry for 1/2. While 3-center 2-electron interactions involving the proton with metal–metal bonds are known, the present work demonstrates that this type of interaction has yet to be realized with other acids. Previously only aluminum alkyls[5,6] and rare earth shift reagents[9] were known to form complexes with bridging carbonyls. The list is now extended to include boron halides and aluminum bromide.



(II)



(III)

ACKNOWLEDGEMENTS

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