Chemical
Communications

NUMBER 23/1965 8 DECEMBER

Novel Insertion Reactions of Indium(I) Bromide

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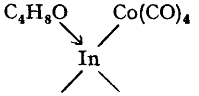
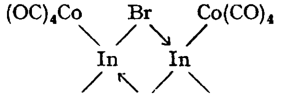
RECENTLY the "insertion" of tin(II) chloride and of germanium(II) iodide into the iron–iron bond of dicarbonyl-π-cyclopentadienyliron dimer has been reported.[1] We have observed that these halides take part in similar reactions with other metal–metal bonds,[2] and as an extension of our studies in this field, we now report that indium(I) bromide undergoes what appears to be an insertion reaction with dicobalt octacarbonyl.

When InBr and $Co_2(CO)_8$ react at room temperature in tetrahydrofuran, the bromide quickly dissolves forming an orange solution. Removal of solvent followed by pentane extraction and recrystallization affords yellow needles, reasonably stable in air, m.p. 50—55° (with decomposition). Analytical and molecular weight results agree closely with the formula $[(OC)_4Co]_2InBr,C_4H_8O$, the insertion compound in the form of its tetrahydrofuran adduct (I).



(I)



(II)

The infrared spectrum of (I) in cyclohexane shows carbonyl stretching bands at 2091 (m), 2073 (s), 2056 (w), 2035 (w), 2026 (m), 2018 (m), 2004 (s), and 1999 (s) cm.$^{-1}$ These resemble in their positions and relative intensities the bands observed for structurally related compounds of the $XYSn[CO(CO)_4]_2$ type.[2]

In high vacuum, the adduct $[(OC)_4Co]_2InBr,C_4H_8O$ slowly loses tetrahydrofuran affording a material which upon recrystallization from benzene forms orange crystals, m.p. 140° (with decomposition). The results of total elemental analysis agree with those expected for the simple insertion product $[(OC)_4Co]_2InBr$, to which the dimeric structure (II) is tentatively assigned. The infrared spectrum of (II) (cyclohexane, slight solubility) shows carbonyl stretching bands at 2093 (m), 2080 (s), 2075 (w.sh.), 2069 (w.sh.), 2039 (w), 2026 (w), 2006 (s), and 1995 (vw.sh.) cm.$^{-1}$, which resemble in pattern those found for the structurally related $X_2Sn[Co(CO)_4]_2$ series of compounds.[2]

Reaction of InBr with $Co_2(CO)_8$ in benzene proceeds much more slowly than in tetrahydrofuran, affording a product of empirical formula $[(OC)_4Co]_4In_3Br_3$ on the basis of complete elemental analysis. The infrared spectrum shows carbonyl stretching bands at 2097 (w.sh.), 2088 (s), 2081 (vw.sh.), 2054 (s), 2033 (s), 2022 (s), and 2008 (s) cm.$^{-1}$, differing markedly from those of (I) and (II). Present evidence does not permit a structure to be assigned.

(*Received October 26th*, 1965; *Com.* 678.)

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[1] F. Bonati and G. Wilkinson, *J. Chem. Soc.*, **1964**, 179; F. G. A. Stone, *Pure Appl. Chem.*, 1965, **10**, 37.
[2] D. J. Patmore and W. A. G. Graham, submitted for publication.