Metal Insertion into the Mn–Mn Bond of $Mn_2(CO)_{10}$

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Prior to the present work the manganese-to-manganese bond in dimanganese decacarbonyl has proved to be rather resistant toward insertion reactions of metal or metalloid species. Stannous chloride, a reagent found to undergo ready insertion into the metal–metal bonds of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$,[1] $Co_2(CO)_8$,[2] and $[\pi\text{-}C_5H_5Ni(CO)]_2$,[2] did not insert into $Mn_2(CO)_{10}$ under similar conditions.[1] Recently Hoyano, Patmore, and Graham[3] reported that $SnCl_2$ and InBr react with $Mn_2(CO)_{10}$ under forcing conditions (180—190°, sealed tube) to afford the expected insertion products.

Systematic studies in this laboratory on a variety of systems have led to the conclusion that in certain cases the "insertion" of a main-group metal into the bond between two transition metals can occur under moderate conditions.

We describe the convenient synthesis of the new compounds, $Zn[Mn(CO)_5]_2$ and $Cd[Mn(CO)_5]_2$ *via* the reaction of a main-group metal with $Mn_2(CO)_{10}$. These results are presented at this time in view of the current interest in the catalytic properties of similar zinc derivatives of transition-metal carbonyls.[4] The only other reported insertion reactions of zinc and cadmium occurred in the preparation of $Zn[Co(CO)_4]_2$ and $Cd[Co(CO)_4]_2$ from $Co_2(CO)_8$ and the metals at high CO pressure and high temperature.[5]

Upon stirring a mixture of 0·010 mole of $Mn_2(CO)_{10}$ and 0·10 g.-atom of powdered zinc metal in 60 ml. of diglyme, under argon, at 120°† for 10 hr. the colour of the solution gradually changed from light yellow to a very light pink. The cooled mixture was filtered through a "fine" fritted tube under argon and the solvent was removed by vacuum evaporation at ambient temperature. The resulting light salmon-coloured residue was sublimed twice at 120°/0·001 mm. and afforded an 84% yield of white $Zn[Mn(CO)_5]_2$, m.p. 208—209·5° (sealed, argon-filled tube). In dry air the solid product was stable for short periods but solutions in polar solvents decomposed rapidly.

Under the same conditions a similar reaction was observed between powdered cadmium metal and $Mn_2(CO)_{10}$ whereby white $Cd[Mn(CO)_5]_2$, m.p. 249—251° (partial decomp. in sealed, argon-filled tube) was obtained in 90% yield after a single sublimation at 130°/0·001 mm. The cadmium compound was considerably more air-stable than its zinc analogue. Satisfactory elemental analyses have been obtained for both derivatives and their exact composition was readily obtained from their mass spectra.‡ Both compounds exhibited moderately strong parent ions with the expected isotopic distributions and showed very similar fragmentation patterns corresponding to the successive loss of the ten CO groups. The most abundant

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† The temperature of the present process is not the only important factor in the formation of $Zn[Mn(CO)_5]_2$ because when toluene was used as the solvent, negligible conversion of $Mn_2(CO)_{10}$ to the desired product was observed after three days at the reflux temperature.

‡ The mass spectra were obtained on an Associated Electrical Industries MS 902 mass spectrometer by direct insertion of the solid sample into the ion source at 160° and 70 ev.

TABLE

Compound	I.r. absorptions (cm.$^{-1}$)[a]
$Zn[Mn(CO)_5]_2$	2065m, 1985ms (sh), 1945vs, 645m
$Cd[Mn(CO)_5]_2$	2060s, 1978s (sh), 1930vs, 648m
$Hg[Mn(CO)_5]_2$[b]	2065s, 1995s (sh), 1955vs, 645m

[a] Spectra observed in KBr pellets; estimated accuracy is ±3 cm.$^{-1}$. Limited solubility in nonpolar solvents precluded determination of solution spectra.

[b] Ref. 6 gives 2067s, 2008s (sh) and 1975vs.

fragments containing three metal atoms were $M^{II}Mn_2(CO)_5^+$ and $M^{II}Mn_2^+$ in addition to the molecular ion. Under high resolution, accurate mass measurement on the parent ion corresponding to the most abundant isotope of Zn or Cd gave the following results: calc. *m/e* for $^{64}Zn^{55}Mn_2{}^{12}C_{10}{}^{16}O_{10}$, 453·7544; found *m/e*, 453·7543; and calc. *m/e* for $^{114}Cd^{55}Mn_2{}^{12}C_{10}{}^{16}O_{10}$, 503·7286; found *m/e*, 503·7291.

Hieber and Schropp[6] have reported the i.r. spectrum of $Hg[Mn(CO)_5]_2$ and concluded that the three observed bands in the carbonyl stretching region were consistent with D_{4h} or D_{4d} molecular symmetry. The i.r. spectra of the zinc and cadmium analogues closely resemble that of $Hg[Mn(CO)_5]_2$, as shown in the Table. These observations suggest that all three molecules have the same symmetry.

Recent *X*-ray structural studies have established the linearity of the cobalt–M^{II}–cobalt covalent bonds in $Zn[Co(CO)_4]_2$[7] and in $Hg[Co(CO)_4]_2$.[8] It seems likely, therefore, that the structures of the new compounds contain linear, Mn–metal–Mn covalent bonds with pseudo-octahedral co-ordination about each manganese atom. The properties of the new compounds and the scope of the metal insertion reaction are presently under investigation.

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