A Convenient Synthesis of Compounds containing Manganese–Zinc and Manganese–Cadmium Bonds

By N. A. D. CAREY and J. G. NOLTES

(*Institute for Organic Chemistry TNO, Croesestraat 79, Utrecht, The Netherlands*)

RECENT interest[1] in the properties of heteronuclear metal bonded compounds and the reported preparation of $[Mn(CO)]_5]_2Zn$ and $[Mn(CO)_5]_2Cd$[2] by the insertion of metal into the Mn–Mn bond of $Mn_2(CO)_{10}$ has prompted us to report the synthesis of a number of complexes of $[Mn(CO)_5]_2Zn$ and $[Mn(CO)_5]_2Cd$. These are listed in the Table.

Some complexes containing manganese–zinc and manganese–cadmium bonds

Compound	Reactants	Conditions
$[Mn(CO)_5]_2Zn$	$2\ Mn(CO)_5H + Et_2Zn$	Instantaneous reaction at temperatures > − 78°
$[Mn(CO)_5]_2Cd$	$2\ Mn(CO)_5H + Me_2Cd$	Reaction complete within 5 min. at room temperature
$[Mn(CO)_5]_2Zn$ bipy	$2\ Mn(CO)_5H + Et_2Zn$ bipy in THF	Rapid reaction at room temperature
$[Mn(CO)_5]_2Cd$ bipy	$2\ Mn(CO)_5H + Me_2Cd$ bipy in THF	Rapid reaction at room temperature
$[Ph_3PMn(CO)_4]_2Zn$ bipy ..	$2\ Ph_3PMn(CO)_4H + Et_2Zn$ bipy in THF	Reaction complete within 3 hr. at 35°
$[Ph_3PMn(CO)_4]_2Cd$ bipy ..	$2\ Ph_3PMn(CO)_4H + Me_2Cd$ bipy in THF	Reaction complete within 8 hr. at 20°
$[Ph_3SbMn(CO)_4]_2Zn$ bipy ..	$2\ Ph_3SbMn(CO)_4H + Et_2Zn$ bipy in THF	Reaction complete within 3 hr. at 35°

THF = tetrahydrofuran.

We have found that $Mn(CO)_5H$ and $Ph_3YMn(CO)_4H$ (Y = P or Sb) react quantitatively with dialkylzinc or dialkylcadmium, to give the corresponding Mn–Zn–Mn and Mn–Cd–Mn compounds, in accordance with the equation:

$$2Mn(CO)_4LH + R_2M \rightarrow [(CO)_4LMn]_2M + 2\ RH$$

$$(L = CO, Ph_3P, \text{ or } Ph_3Sb;\ M = Zn \text{ or } Cd;\ R = Me \text{ or } Et)$$

Compounds $[Mn(CO)_5]_2M$ were prepared as follows. A mixture of $Mn(CO)_5H$ (0·004 mole) and Et_2Zn (0·002 mole) was allowed to warm up from −196° *in vacuo* to room temperature, when a white solid formed on the sides of the flask. No noncondensable gas was observed and the ethane (0·004 mole) was removed by distillation and identified by i.r. spectra and molecular weight measurements. The reaction with Me_2Cd appeared to be rather slower, with the reaction starting at *ca.* 0°, while the corresponding reaction with zinc appeared to be complete at −78°.

The 2,2′-bipyridyl complexes were prepared in a similar manner by reaction of the metal hydride with the preformed complex R_2M bipy in tetrahydrofuran. No difficulty was experienced in removing the solvent on completion of the reaction.

$Ph_3PMn(CO)_4H$[3] and $Ph_3SbMn(CO)_4H$ were obtained in high yield (>90%) by the 1 : 1 reaction of Ph_3P (or Ph_3Sb) with $Mn(CO)_5H$ at room temperature and 50°,† respectively. The ν(CO) region in the infrared spectrum of $Ph_3SbMn(CO)_4H$ as a solution in cyclohexane (2067, 1990, 1975, and 1965 cm.$^{-1}$) is virtually identical with the spectrum reported for $Ph_3PMn(CO)_4H$,[3] suggesting that the structures of the two compounds are the same. The coupling constant $J_{(P\text{-}Mn\text{-}H)}$ of 34·6 Hz for $Ph_3PMn(CO)_4H$, as a solution in CS_2, is consistent in magnitude with what might be expected[3,4] for the Ph_3P being *cis* to the Mn–H bond. Owing to the relatively bulky nature of the Ph_3P and Ph_3Sb ligands, it would seem probable that in the complexes $[Ph_3YMn(CO)_4]_2M$ bipy there will be a preferred orientation of the Ph_3Y ligands with respect to one another. Unfortunately, owing to the limited solubility of these complexes in nonpolar solvents, useful structural information cannot be derived from their infrared spectra. The compounds are all air-sensitive and were handled under a dry nitrogen atmosphere. Satisfactory elemental analyses have been obtained for all these compounds.

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† At 80°, $Ph_3SbMn(CO)_4H$ dimerises with the elimination of H_2 to give $[Ph_3SbMn(CO)_4]_2$ as a dark orange solid, stable in air up to 120°, decomposing under N_2 from 150°, and entirely decomposed at 235° [*M* (C_6H_6), found: 1038; calculated: 1042]. The i.r. data [ν_{max} (CCl_4) 2062sh, 2010m, 1980s, 1953s, 1825m cm.$^{-1}$ $\nu_{(CO)}$ stretch] are in strong contrast to the spectrum of *trans*-$[Ph_3PMn(CO)_4]_2$,[5] which would suggest that the Ph_3Sb ligands are *trans* to one another and *cis* to the Mn–Mn bond.

The formation of metal–metal bonded compounds has so far been limited to the reaction of Group IVA organometallic hydrides with metal–carbon bonds. Organotin hydrides, because of their electrophilic character in the presence of appropriate substrates,[6] have been most widely used, *i.e.* Sn–Zn,[7] Sn–Cd,[7] Sn–Mg,[8] Sn–Sb,[9] and Sn–Bi.[9] Our results suggest that the reaction between acidic transition-metal hydrides and metal–carbon bonds which are susceptible to protic attack, might offer a general route to the formation of the corresponding metal–metal bonds.

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[1] G. N. Schrauzer, B. N. Bastian, and G. A. Fosselius, *J. Amer. Chem. Soc.*, 1966, **88**, 4890; D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 1968, **7**, 771 and references cited; H. C. Clark and J. H. Tsai, *Chem. Comm.*, 1965, 111.

[2] J. M. Burlitch, *Chem. Comm.*, 1968, 887.

[3] B. L. Booth and R. N. Haszeldine, *J. Chem. Soc.* (*A*), 1966, 157.

[4] A. P. Ginsberg, in "Transition Metal Chemistry", ed. R. L. Carlin, Edward Arnold, 1965, vol. I, ch. 3.

[5] A. S. Osborne and M. H. B. Stiddard, *J. Chem. Soc.*, 1964, 634.

[6] H. M. J. C. Creemers, F. Verbeek, and J. G. Noltes, *J. Organometallic Chem.*, 1967, **8**, 469.

[7] F. J. A. Des Tombe, G. J. M. van der Kerk, H. M. J. C. Creemers, and J. G. Noltes, *Chem. Comm.* 1966, 914.

[8] H. M. J. C. Creemers, J. G. Noltes, and G. J. M. van der Kerk, *J. Organometallic Chem.*, in the press.

[9] N. S. Vyazankin, G. A. Razuvaev, O. A. Kruglaia, and G. S. Semchikova, *J. Organometallic Chem.*, 1966, **6**, 473; H. M. J. C. Creemers, Ph.D. Thesis, State University of Utrecht, 1967.