Chemical
Communications

NUMBER 21/1969 5 NOVEMBER

Cleavage of Si–Mn Bonds by Phosphites

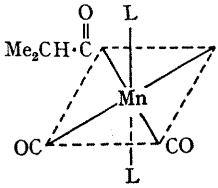
By Earl P. Ross and Gerard R. Dobson*
(*Department of Chemistry, University of South Dakota, Vermillion, South Dakota* 57069)

Summary Trialkyl and triaryl phosphites cleave the silicon–manganese bond in triphenylsilylpentacarbonylmanganese (0).

Reactions of $Ph_3SnMn(CO)_5$[1,2] and $Ph_3GeMn(CO)_5$[3] with phosphines and phosphites (phos) in the absence of solvent at elevated temperatures have been shown to give $Ph_3XMn(CO)_4$(phos) (X = Ge or Sn) products. We have found similar reactions to occur in solution. The reaction with PPh_3 of $Ph_3SiMn(CO)_5$[4] in decalin at 130° also yields a product of this type, *trans*-$Ph_3SiMn(CO)_4PPh_3$ [ν(CO) 2051 (vw), 1993 (w), and 1952 (s) cm.$^{-1}$, $CHCl_3$ solvent],† characterized by elemental analysis. In contrast, $Ph_3SiMn(CO)_5$ reacts with phosphites, $P(OR)_3$ (R = Ph, Me, or Pr^i) according to equation (1).

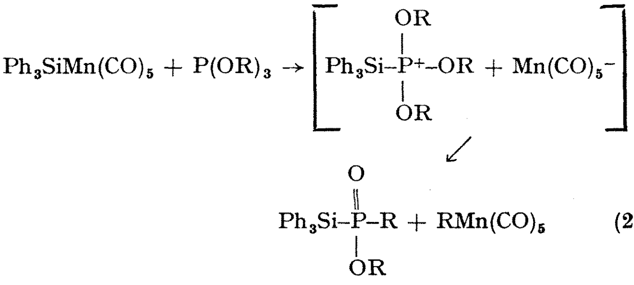
$$Ph_3SiMn(CO)_5 + P(OR)_3 \rightarrow \underset{(I)}{RCOMn(CO)_3[P(OR)_3]_2} + \underset{(II)}{OP(OSiPh_3)_3} \qquad (1)$$

Thus, reaction of 5·44 g. of $Ph_3SiMn(CO)_5$ with 14 g. of $P(OPr^i)_3$ (L, a ten-fold excess)in 100 ml. n-heptane at 80° under a CO atmosphere (to inhibit decarbonylation) gave, after 10 hr. a white precipitate of (II), which was collected by filtration, and a straw-coloured filtrate. Compound (II) was found to be identical (mixed m.p., i.r. spectrum) with an authentic sample of $OP(OSiPh_3)_3$ prepared from Ph_3SiOH and H_3PO_4 in toluene.[5] The filtrate was chromatographed under CO on silica (n-heptane–diethyl ether eluant), and after evaporation of the solvent the residue was recrystallized from n-heptane to give colourless crystals of (I; R = Pr^i) which slowly became yellow even under vacuum. This complex was characterized by elemental analysis, i.r. spectrum [ν(CO) 2031 (w), 1948 (vs), 1906 (s) cm.$^{-1}$; acyl ν(CO) 1600 cm.$^{-1}$, n-heptane solvent],† mass spectrum (peaks at *m/e* 598, assigned to $[Pr^iMn(CO)_3L_2]^+$ and 583, assigned to $[COMn(CO)_3L_2]^+$), and ^1H n.m.r. spectrum. The latter (L methyl, τ 8·72, d, J 7 Hz.; isobutyl methyl, τ 9·18, d, J 7 Hz.; relative intensities 6 : 1, CCl_4 solvent, Me_4Si standard) demonstrates the magnetic equivalence of the two L groups, and on the basis of the data (I) is assigned the structure (III) below.



(III)

The relatively mild conditions under which this reaction occurs (*ca.* 80° compared with >130° for the reaction of $Ph_3SiMn(CO)_5$ with PPh_3) suggest $RMn(CO)_5$ to be formed early in the reaction, and that this species, in turn, undergoes carbonyl insertion. Carbonyl insertion reactions of $RMn(CO)_5$ to give $RCOMn(CO)_3(phos)_2$ products have been found to proceed at 50—70°.[6] Such alkylmanganese species might possibly arise through a Michaelis–Arbuzov rearrangement involving attack by the phosphite on the triphenylsilicon moiety, equation (2)



$$Ph_3SiMn(CO)_5 + P(OR)_3 \rightarrow \left[Ph_3Si\text{–}P^{+}(OR)_3 + Mn(CO)_5^{-} \right] \rightarrow Ph_3Si\text{–}P(=O)(OR)\text{–}R + RMn(CO)_5 \qquad (2)$$

(IV)

The reaction of Et_3SiBr with triethyl phosphite to give a product analogous to (IV) has been reported.[7] Steps which might result in the conversion of (IV) into (II) are not clear,

---

† Relative band intensities: s = strong; m = medium; w = weak; v = very.

but the observed ligand dependency of the reaction rate and the formation of a phosphate, and not a phosphite product are consistent with an Arbuzov mechanism.

We thank the Petroleum Research Fund, administered by The American Chemical Society, for financial support, the University of South Dakota for a research assistantship (to E. P. R.) and Professor John G. Verkade, Iowa State University of Science and Technology, for the mass spectrum.

(*Received, August 7th*, 1969; *Com.* 1217.)

[1] R. D. Gorsich, *J. Amer. Chem. Soc.*, 1962, **84**, 2468.
[2] L. M. Bower and M. H. B. Stiddard, *J. Chem. Soc.* (*A*), 1968, 760.
[3] A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and A. B. Antonova, *Izvest. Akad. Nauk S.S.S.R., Ser. Khim.*, 1966, 139.
[4] W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, 1966, **5**, 2217.
[5] N. F. Orlov and M. G. Voronkov, *Zhur. obshch. Khim.*, 1960, **30**, 2223.
[6] P. K. Maples and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1968, **90**, 6645, and references cited therein.
[7] A. B. Arbuzov and A. N. Pudovik, *Doklady. Akad. Nauk S.S.S.R.*, 1948, **59**, 1433.