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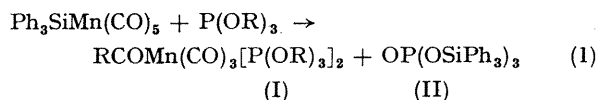
## Cleavage of Si-Mn Bonds by Phosphites

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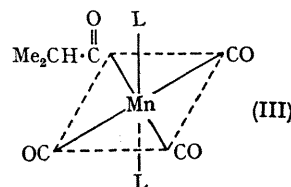
**Summary** Trialkyl and triaryl phosphites cleave the silicon-manganese bond in triphenylsilylpentacarbonylmanganese (0).

REACTIONS of  $\text{Ph}_3\text{SnMn}(\text{CO})_5^{1,2}$  and  $\text{Ph}_3\text{GeMn}(\text{CO})_5^3$  with phosphines and phosphites (phos) in the absence of solvent at elevated temperatures have been shown to give  $\text{Ph}_3\text{XMn}(\text{CO})_4(\text{phos})$  (X = Ge or Sn) products. We have found similar reactions to occur in solution. The reaction with  $\text{PPh}_3$  of  $\text{Ph}_3\text{SiMn}(\text{CO})_5^4$  in decalin at  $130^\circ$  also yields a product of this type, *trans*- $\text{Ph}_3\text{SiMn}(\text{CO})_4\text{PPh}_3$  [ $\nu(\text{CO})$  2051 (vw), 1993 (w), and 1952 (s)  $\text{cm}^{-1}$ ,  $\text{CHCl}_3$  solvent],<sup>†</sup> characterized by elemental analysis. In contrast,  $\text{Ph}_3\text{SiMn}(\text{CO})_5$  reacts with phosphites,  $\text{P}(\text{OR})_3$  (R = Ph, Me, or Pr<sup>t</sup>) according to equation (1).

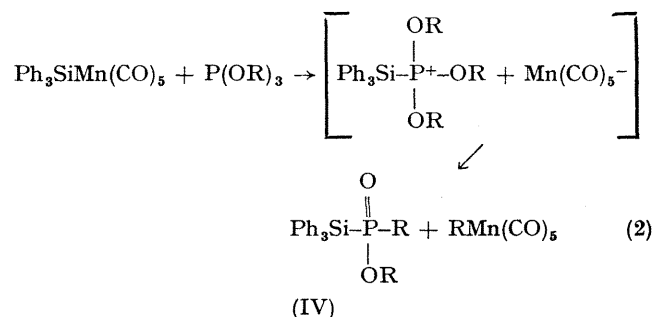


Thus, reaction of 5.44 g. of  $\text{Ph}_3\text{SiMn}(\text{CO})_5$  with 14 g. of  $\text{P}(\text{OPr}^t)_3$  (L, a ten-fold excess) in 100 ml. n-heptane at  $80^\circ$  under a CO atmosphere (to inhibit decarbonylation) gave, after 10 hr. a white precipitate of (II), which was collected by filtration, and a straw-coloured filtrate. Compound (II) was found to be identical (mixed m.p., i.r. spectrum) with an authentic sample of  $\text{OP}(\text{OSiPh}_3)_3$  prepared from  $\text{Ph}_3\text{SiOH}$  and  $\text{H}_3\text{PO}_4$  in toluene.<sup>5</sup> 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<sup>t</sup>) which slowly became yellow even under vacuum. This complex was characterized by elemental analysis, i.r. spectrum [ $\nu(\text{CO})$  2031 (w), 1948 (vs), 1906 (s)  $\text{cm}^{-1}$ ; acyl  $\nu(\text{CO})$  1600  $\text{cm}^{-1}$ , n-heptane solvent],<sup>†</sup> mass spectrum (peaks at *m/e* 598, assigned to  $[\text{Pr}^t\text{Mn}(\text{CO})_3\text{L}_2]^+$  and 583, assigned to  $[\text{COMn}(\text{CO})_3\text{L}_2]^+$ ), and <sup>1</sup>H n.m.r. spectrum. The latter (L methyl,  $\tau$  8.72, d, *J* 7 Hz.; isobutyl methyl,  $\tau$  9.18, d, *J* 7

Hz.; relative intensities 6 : 1,  $\text{CCl}_4$  solvent,  $\text{Me}_4\text{Si}$  standard) demonstrates the magnetic equivalence of the two L groups, and on the basis of the data (I) is assigned the structure (III) below.



The relatively mild conditions under which this reaction occurs (*ca.*  $80^\circ$  compared with  $>130^\circ$  for the reaction of  $\text{Ph}_3\text{SiMn}(\text{CO})_5$  with  $\text{PPh}_3$ ) suggest  $\text{RMn}(\text{CO})_5$  to be formed early in the reaction, and that this species, in turn, undergoes carbonyl insertion. Carbonyl insertion reactions of  $\text{RMn}(\text{CO})_5$  to give  $\text{RCOMn}(\text{CO})_3(\text{phos})_2$  products have been found to proceed at  $50-70^\circ$ .<sup>6</sup> Such alkylmanganese species might possibly arise through a Michaelis-Arbuzov rearrangement involving attack by the phosphite on the triphenylsilyl moiety, equation (2)



The reaction of  $\text{Et}_3\text{SiBr}$  with triethyl phosphite to give a product analogous to (IV) has been reported.<sup>7</sup> Steps which might result in the conversion of (IV) into (II) are not clear,

<sup>†</sup> 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.

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