

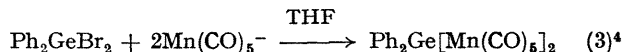
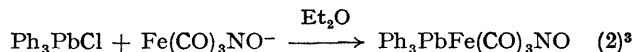
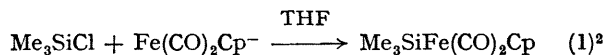
Germanium-Transition-metal Bonds: the Importance of the Leaving Group in the Preparation of Metal-Metal Bonded Compounds by Nucleophilic Displacement Reactions

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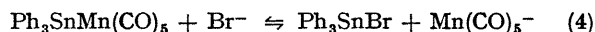
Summary Preparation of the complexes Ph_2GeQ_2 from Ph_2GeX_2 (Q = transition-metal carbonyl group, X = Cl or Br) is found to be dependent upon X.

THE preparation of complexes containing metal-metal bonds has attracted much recent interest.¹ One of the simplest methods of synthesising such compounds involves the nucleophilic displacement of a halide ion from a main group metal by a transition-metal carbonyl anion. Such reactions [*e.g.* reactions (1) (Cp = cyclopentadienyl), (2), and (3)] normally proceed readily at room temperature with formation of the desired products.



We attempted to repeat reaction (3) using Ph_2GeCl_2 in place of Ph_2GeBr_2 , but only $\text{Ph}_2\text{ClGeMn}(\text{CO})_5$ was formed, together with a small amount of $\text{Mn}_2(\text{CO})_{10}$. No $\text{Ph}_2\text{Ge}[\text{Mn}(\text{CO})_5]_2$ was observed even when an excess of $\text{Mn}(\text{CO})_5^-$ was used and the mixture allowed to react for 16 h. One possible explanation for this could be the known nucleophilic displacement of transition-metal carbonyl anions from main-group metals by soluble halides in ionizing solvents⁵

such as dimethylformamide [*e.g.* reaction (4)]. A similar



reaction between Cl^- and $\text{Ph}_2\text{Ge}[\text{Mn}(\text{CO})_5]_2$ might explain the failure to obtain the latter compound. Reaction (3) was therefore repeated using Ph_2GeCl_2 and the less polar solvent diethyl ether but despite the immediate precipitation of NaCl, the only reaction product was $\text{Ph}_2\text{ClGeMn}(\text{CO})_5$. On using Ph_2GeBr_2 in Et_2O or tetrahydrofuran, however, the bis-complex was obtained as originally reported.⁴ A reaction similar to (4) is therefore not responsible for the absence of $\text{Ph}_2\text{Ge}[\text{Mn}(\text{CO})_5]_2$. Rather the choice of the leaving group on germanium is more important.

We studied the reactions of Ph_2GeX_2 (X = Cl or Br) with the anions $\text{Fe}(\text{CO})_2\text{Cp}^-$, $\text{Fe}(\text{CO})_3\text{NO}^-$, $\text{Co}(\text{CO})_4^-$, and $\text{Co}(\text{CO})_3\text{PBU}_3^-$; for X = Cl, only $\text{Fe}(\text{CO})_2\text{Cp}^-$ yielded a bis-derivative, whereas for X = Br, the desired product was obtained in all cases,[†] although $\text{Co}(\text{CO})_4^-$ gave only a small amount of $\text{Ph}_2\text{Ge}[\text{Co}(\text{CO})_4]_2$ even with a fourfold excess of anion and a reaction time of two days.

These results, together with those for $\text{Mn}(\text{CO})_5^-$, are consistent with the order of nucleophilicities for metal carbonyl anions established from kinetic studies with alkyl halides, *viz.* $\text{Fe}(\text{CO})_2\text{Cp}^- \gg \text{Mn}(\text{CO})_5^- > \text{Co}(\text{CO})_4^-$.⁶ They also confirm the recent observation⁷ that the nucleophilicity of $\text{Co}(\text{CO})_4^-$ may be increased by the replacement of CO with tervalent phosphorus ligands which are stronger electron donors. More important, however, they illustrate the need

[†] Satisfactory elemental analyses have been obtained for all new compounds.

to choose suitable leaving groups in the synthesis of metal-metal bonded compounds by nucleophilic displacement reactions. Although this has not been previously emphasised, the leaving group was probably responsible for the formation of only $\text{Ph}_2\text{ClGeCo}(\text{CO})_4$ from Ph_2GeCl_2 .⁸

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