

Preliminary communication.

EXCHANGE OF METAL CARBONYL MOIETIES ON GERMANES

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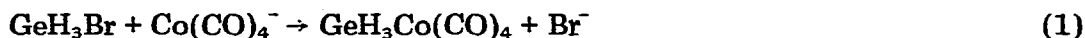
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Summary

For $R_3Ge = GeH_3, CH_3GeH_2$ or $(CH_3)_2GeH$, $R_3GeCo(CO)_4$ reacts in an ether solvent with $Mn(CO)_5^-$ to give $R_3GeMn(CO)_5$ while $Mn(CO)_5^-$ displaces $Fe(CO)_4^{2-}$ or $(GeH_3)Fe(CO)_4^-$ and $Fe(CO)_4^{2-}$ displaces $Co(CO)_4^-$.

Group IV derivatives of metal carbonyls are commonly made [1] by the halide elimination reaction, see eq. 1 for example [2]. We now report an



extension of this reaction, where one metal carbonyl anion displaces another on germanium (eq. 2). Such transition metal exchange processes are rare: one



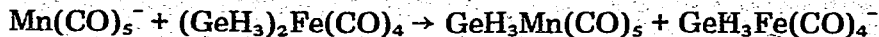
example [3] involved the displacement of $(C_5H_5)Mo(CO)_3^-$ from carbon by $(C_5H_5)Fe(CO)_2^-$.

Reactions such as 2 also occur with GeH_3 and $(CH_3)_2GeH$ derivatives. At room temperature they take 5 to 15 minutes in ether solvents on a 0.2 to 0.5 mmol scale using sodium salts of the carbonyl anion. No reaction occurs in hydrocarbons or in absence of a solvent. The products were characterised by comparison with authentic samples [4].

Using equimolar quantities, the yields of gerylmanganese compounds were about 80% after purification, suggesting (2) is near-quantitative. This was confirmed by adding HCl to the residues which yielded $HCo(CO)_4$ with only traces of $HMn(CO)_5$.

A similar reaction between $Mn(CO)_5^-$ and $(GeH_3)_2Fe(CO)_4$ in Et_2O or THF gave $GeH_3Mn(CO)_5$ corresponding to 43% of the GeH_3 groups, together with traces of $(GeH_3)HFe(CO)_4$. Addition of HCl to the residues yielded some $HMn(CO)_5$ together with $(GeH_3)HFe(CO)_4$ but little $H_2Fe(CO)_4$. The principal reaction is therefore:

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Preliminary studies indicate $\text{GeH}_3\text{Co}(\text{CO})_4$ exchanges with $\text{Fe}(\text{CO})_4^{2-}$ to yield $(\text{GeH}_3)_2\text{Fe}(\text{CO})_4$.

Taken together, these results indicate a metal carbonyl displacement series on GeH_3 and related germyls in the sense $\text{Co} \rightarrow \text{Fe} \rightarrow \text{Mn}$. If this series can be extended to other metal carbonyls and related species it will provide a useful new synthetic method. Taken in combination with reported Group IV displacements on a given transition metal such as [5] $\text{Me}_3\text{Si} \rightarrow \text{Me}_3\text{Ge} \rightarrow \text{Me}_3\text{Sn}$ in $\text{Me}_3\text{MCo}(\text{CO})_4$, a wide range of interconversions in the Group IV transition metal family is suggested. Of particular interest is the possibility of mixed ligand iron compounds $(\text{R}_3\text{M})(\text{R}'_3\text{M}')\text{Fe}(\text{CO})_4$ and as a route to new systems: for example, $\text{GeH}_3\text{Co}(\text{CO})_4$ is completely consumed when added to $\text{Cr}(\text{CO})_5^{2-}$, though $\text{Ge}-\text{Cr}$ species have not yet been isolated.

References

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