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Preliminary communication

EXCHANGE OF METAL CARBONYL MOIETIES ON GERMANES

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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

$$GeH_3Br + Co(CO)_4^- \rightarrow GeH_3Co(CO)_4 + Br^- \quad (1)$$

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

$$CH_3GeH_2Co(CO)_4 + Mn(CO)_5^- \rightarrow CH_3GeH_2Mn(CO)_5 + Co(CO)_4^- \quad (2)$$

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 germylmanganese 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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$Mn(CO)_5^- + (GeH_3)_2Fe(CO)_4 \rightarrow GeH_3Mn(CO)_5 + GeH_3Fe(CO)_4^-$

Preliminary studies indicate $GeH_3Co(CO)_4$ exchanges with $Fe(CO)_4^{2-}$ to yield $(GeH_3)_2Fe(CO)_4$.

Taken together, these results indicate a metal carbonyl displacement series on GeH_3 and related germyls in the sense Co → Fe → 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] $Me_3Si \rightarrow Me_3Ge \rightarrow Me_3Sn$ in $Me_3MCo(CO)_4$, 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 $(R_3M)(R'_3M')Fe(CO)_4$ and as a route to new systems: for example, $GeH_3Co(CO)_4$ is completely consumed when added to $Cr(CO)_5^{2-}$, though Ge—Cr species have not yet been isolated.

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