Relative Reactivities of Manganese–Silicon, –Germanium, –Tin and –Lead Bonds with Iodine: a 'Pseudo Aromatic' Substitution

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Summary The rates of reaction of [$Me_3MMn(CO)_5$] (M = Si, Ge, Sn, or Pb), studied under identical conditions show that, as in aromatic substitution, the relative reactivities depend principally on the electron-releasing power of the Me_3M group.

In 1960 Eaborn and Pande[1] showed that the relative rate coefficients, $k_{rel}^{protodemetallation}$, of the acid-catalysed hydrolysis [equation (1)] of $(alkyl)_3M(aryl)$ compounds (M = Si, Ge, Sn, or Pb) were Si : Ge : Sn : Pb = 1 : 36 : 3.5 × 10^5 : 2 × 10^8. They now interpret this order of protodemetallation in terms of the electron-releasing abilities of

$$(alkyl)_3M(aryl) \xrightarrow{H_2O,\ EtOH,\ HClO_4} (alkyl)_3M(OEt) + (aryl)H \qquad (1)$$

MMe_3 groups,[2] and stabilisation of the intermediate such as (I) by structure (II) involving σ–π conjugation (vertical hyperconjugation).[3,4] Because of the very large changes in rate when M was changed Eaborn and Pande could not study the reactions of four compounds where the only difference was in the M atom, and the relative rates were obtained by comparing the rate data of 13 different compounds in various media.

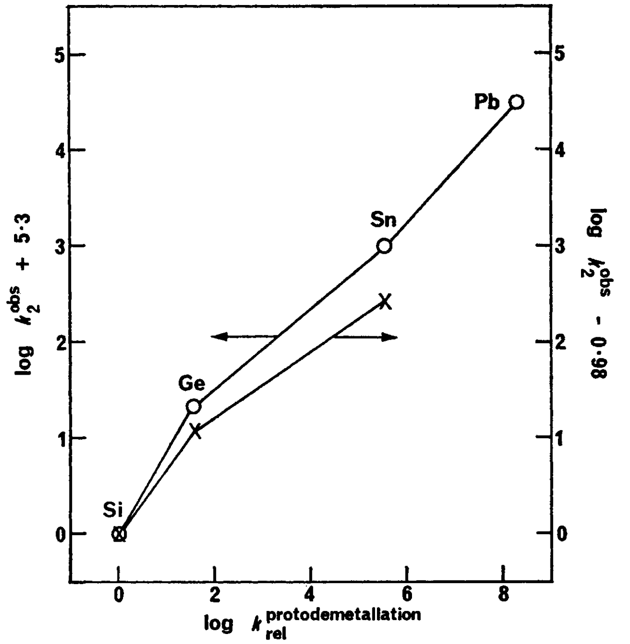


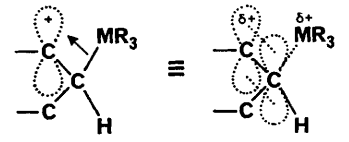
Figure. Plots of log k_2^{obs} for iodination of [$Me_3MMn(CO)_5$] (○) and $Me_3MFe(CO)_2(\eta\text{-}C_5H_5)$ (×) against log $k_{rel}^{protodemetallation}$.

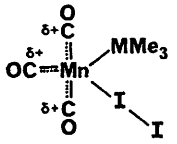
We now report a rate study of an electrophilic reaction [equation (2)] (M = Si, Ge, Sn, or Pb) where the reaction rates of four analogous compounds were measured under identical conditions. For this reaction we find the relative

$$[Me_3MMn(CO)_5] + I_2 \xrightarrow[CCl_4,\ 30\ °C]{k_2^{obs}} Me_3MI + [IMn(CO)_5] \qquad (2)$$

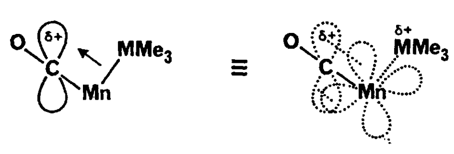
rates are Si : Ge : Sn : Pb = 1 : 21 : 10^3 : 3 × 10^4 (k_2^{obs} for Si = 5·0 × 10^{-6} l mol^{-1} s^{-1}). A plot of log k_2^{obs} against log $k_{rel}^{protodemetallation}$ is almost linear (Figure) although the two studies use solvents of differing polarity (CCl_4 and aq. EtOH), different electrophiles (I_2 and H^+), and substantially different compounds.


(I)


(II)


(III)

(For clarity the CO groups above and below the plane of the paper have been omitted.)


(IV)

This correlation suggests that a similar mechanism is operating in these two reactions. For our reaction we have postulated an intermediate where the iodine has carried out an electrophilic attack on the t_{2g} orbitals of the manganese.[5,6] The positive charge generated on the manganese is delocalised onto the co-ordinated CO ligands as shown in (III). This intermediate may be stabilised by σ–π conjugation of the Mn–M σ-bond with the π-orbitals of the carbonyl groups (IV) in an analogous manner to that postulated for the protodemetallation of the aromatic compounds, the manganese here utilising the *d*-orbital compared with the *p*-orbital of the aromatic ring. Relative rates are determined by the electron-releasing power of the Me_3M group and the contribution of structure (IV) becomes increasingly important from silicon to lead as the stability of Me_3M^+ increases. Solvent effects and the nature of the reactants play only a secondary role in determining the rate order.

The slight deviation from a linear plot of the point for germanium (Figure) confirms the empirical observations that aryl germanes are similar to their silane analogues whereas compounds containing transition metals bonded to germanium or tin are similar and much easier to work with than their silicon analogues.

We have observed the same features for reaction (3) (relative rates Si:Ge:Sn = 1:12:290, k_2^{obs} for Si = 9·6 l mol^{-1} s^{-1}).

$$[Me_3MFe(CO)_2(\eta\text{-}C_5H_5)] + I_2 \xrightarrow[CCl_4,\ 30\ ^\circ C]{k_2^{obs}} Me_3MI + [IFe(CO)_2(\eta\text{-}C_5H_5)] \quad (3)$$

Reactions of this type are remarkably similar to electrophilic aromatic substitutions, *i.e.* reactions of electrophiles at transition metals can be compared with reactions at carbon in an aromatic ring. For this reason we call these reactions 'pseudo-aromatic' substitutions.

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[6] J. R. Chipperfield, A. C. Hayter, and D. E. Webster, *J.C.S. Dalton*, in the press.