Reactions of Dialkynyl Derivatives of Elements of Group IVB with Metal Carbonyls

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DIALKYLDIALKYNYLTINS (I; M = Sn) react with tri-iron dodecacarbonyl in petroleum at about 110° to give the known compounds (II)[1] (33%) by loss of the alkynyl groups. The products react

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[1] R. B. King and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 3833.

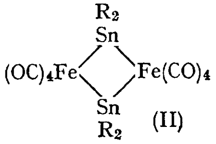
with triphenylphosphine in good yield (69%) under ultraviolet irradiation to give (III). Triphenylarsine gave no reaction.

The dialkynyl compounds of group IVB elements react with dicobalt octacarbonyl in petroleum at room temperature without loss of alkynyl groups in yields of up to 70% to give compounds which, from elemental analysis, infrared and n.m.r. spectroscopy, molecular weight determination, and reaction with triphenylphosphine, appear to have the structure (IV). For example, bis-(hexacarbonyldicobalt)dimethyldi(phenylethynyl)silane (IV; M = Si, R = Me, R′ = Ph), m.p. 87—89°, has ν_{CO} 2096, 2066, 2033, 2020, and 1980 cm^{-1} (hexane), *M*, 826 ($C_{30}H_{16}O_{12}Co_4Si$ requires 832), and reacts with triphenylphosphine to give bis(hexacarbonyldicobalt) bistriphenylphosphine[2] (77%) and dimethyldi(phenylethynyl)silane (67%). The n.m.r. spectrum of (IV; M = Si, R = Me, R′ = Ph) showed bands at τ 9·1 (Si–Me), 2·8 and 2·6 (Ph) with intensity ratios of 3 : 3 : 2. Similar compounds of germanium were prepared (R = Et, R′ = Ph; R = Ph, R′ = Pr^n; R = R′ = Ph), but the corresponding tin compounds could not be crystallised.

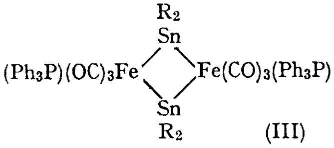
Tetravinylsilane is known to react with dicobalt octacarbonyl to give nonacarbonyl(vinylsilicon)-tricobalt.[3] n-Butyltrialkynyltins only gave intractable gums, but n-butyltin trichloride gave nonacarbonyl-(n-butyltin)tricobalt (V) (47%) m.p. 62—64°, ν_{CO} 2105, 2088, 2024, 2012, and 1965 cm.$^{-1}$; $\lambda_{max.}$ 207 mμ (ϵ 41800), and 363·5 mμ (ϵ 7100). The n.m.r. spectrum is complex because of Sn–H coupling.

$R_2Sn(C{:}CR')_2$

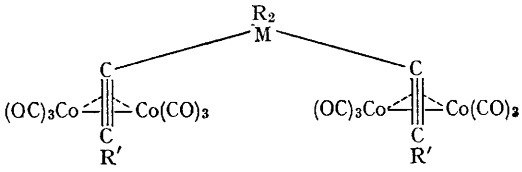
(I)



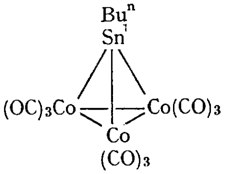
(II)



(III)



(IV)



(V)

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[2] O. Vohler, *Chem. Ber.*, 1958, **91**, 1235; W. Hieber and W. Freyer, *Chem. Ber.*, 1958, **91**, 1230.

[3] S. F. A. Kettle and J. A. Khan, *Proc. Chem. Soc.*, 1962, 82.

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