Reactions of Dialkynyl Compounds of Group IVB Elements with Metal Carbonyls

By **S. D. Ibekwe** and **M. J. Newlands**,* † Chemistry Department, Faculty of Technology, University of Manchester

Complexes of Group IVB elements and metal carbonyls of general formulae $[R_2MFe(CO)_4]_2$, $[R_2MFe(CO)_3PPh_3]_2$, and $R_2M(C{\vdots}C{\cdot}R')_2[Co(CO)_3]_4$ (where R,R′ = alkyl or aryl; M = Si, Ge, and Sn) have been obtained from the reactions of alkynyl compounds of Group IVB elements with metal carbonyls. The preparations, properties, and reactions of these complexes are described. The structures are inferred from infrared and nuclear magnetic resonance spectra.

METAL carbonyls have long been known to react with alkynes.[1-4] Stable compounds have been isolated in which the alkyne either simply displaces carbon monoxide as ligand,[4] or combines with other alkynyl groups and sometimes with carbon monoxide also to form unsaturated cyclic hydrocarbon moieties which are bonded to the metal atom.[5]

Dimethyldivinylsilane forms complexes of the type $Me_2Si(CH{:}CH_2)_2{\cdot}M(CO)_4$ (M = W and Mo) with Group VI metal carbonyls. Co-ordination through the vinyl group is suggested.[6] However, a similar reaction between tetravinylsilane and dicobalt octacarbonyl yields the complex $CH_2{:}CHSi[Co(CO)_3]_3$, in which silicon is believed to be directly linked to three cobalt atoms by essentially σ bonds.[7]

The compounds $Me_3MN{=}C$ (M = Si, Ge, and Sn) have been reported to react with iron pentacarbonyl forming yellow crystalline complexes with the formula $(Me_3MN{\vdots}C)Fe(CO)_4$.[8]

Compounds containing a Group IVB metal with an unsaturated group and a metal carbonyl are at present restricted to the examples cited and, in particular, no example is known in which a Group IV element (other than carbon) attached to an alkynyl group was joined to a metal carbonyl. The successful preparation by Hübel and his co-workers of hydrocarbon–metal carbonyl complexes [2,5] led us to investigate the possibilities of obtaining related complexes by use of the dialkynyl derivatives of Group IVB elements. With iron and cobalt carbonyls, complexes of the types $R_2M(C{\vdots}C{\cdot}R')_2{\cdot}Fe(CO)_3$, $R_2M(C{\vdots}C{\cdot}R')_2{\cdot}Fe_2(CO)_6$, $R_2M(C{\vdots}C{\cdot}R')_2{\cdot}Fe_2(CO)_7$, and $R_2M(C{\vdots}C{\cdot}R')_2[Co(CO)_3]_4$ could be reasonably expected.

We now describe the results of these investigations briefly reported earlier.[9]

Reactions with Tri-iron Dodecacarbonyl.—Dialkyldialkynyltin compounds $R_2Sn(C{\vdots}C{\cdot}R')_2$ (I) (R = alkyl; R′ = alkyl or aryl), react with tri-iron dodecacarbonyl in anhydrous light petroleum at 110° to give yellow crystalline products of general formula $[R_2SnFe(CO)_4]_2$ (II) (R = Et, Pr^n, and Bu^n). Infrared spectroscopy and mixed melting points were used to show that these products are identical with those obtained by independent routes.[10,11]

Aryltin compounds gave only red oils from which no crystalline material could be isolated. As in the work of King and Stone,[10] it is possible that alkenyl- and alkynyl-tin compounds react with iron carbonyls to give unstable π-complexes with interaction between the unsaturated carbon centres and the iron atoms. If this were so, and there is no positive evidence to support it here or in previous work,[10] then cleavage of tin–alkynyl or –alkenyl bonds to give stable yellow products might then occur. From knowledge of the relative ease of cleavage of tin–carbon bonds,[12] it might well be expected that tin–alkenyl (alkynyl) bonds would break at a similar rate to tin–phenyl, whereas tin–alkyl bonds would be much less reactive. Thus, only the tin–alkynyl bonds of alkylalkynyltin compounds would undergo scission, whereas with arylalkynyltin compounds both types of bond might react simultaneously to give complex mixtures.

TABLE 1

Alkyltiniron carbonyl complexes

Compound	M. p.	Yield (%)	M·C–O infrared bands (ν, cm.$^{-1}$)
$[Et_2SnFe(CO)_4]_2$	138° (decomp.)	34	2058vs,* 2008vs, 2000vs, 1972s, 1942m
$[Pr^n{}_2SnFe(CO)_4]_2$	128—130	30	2058vs,* 2012vs, 2000vs, 1972sh, 1946m
$[Bu^n{}_2SnFe(CO)_4]_2$	112—113	30	2058vs,* 2000vs, 1972sh, 1946m
$[Bu^n{}_2SnFe(CO)_3PPh_3]_2$	144 (decomp.)	69	1972s,† 1942vs, 1916vs, 1876sh
$[Bu^n{}_2SnFe(CO)_4]_2$	112—113		2050vs,† 2000sh, 1950vs

* n-Hexane solution. † Nujol mull.

All the alkyltiniron tetracarbonyl compounds dissolve in organic solvents to pale yellow solutions which decompose on standing in air. The dry solids are unaffected by air during 24 hr. Hieber and Breu [11] have reported the reaction of di-n-butyltiniron tetracarbonyl dimer with triphenylphosphine in *p*-xylene at 80°. They isolated an uncharacterised reddish-brown substance which was insoluble in the usual organic solvents.

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† *Present address:* Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland, Canada.

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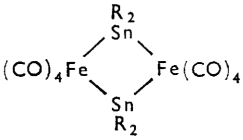


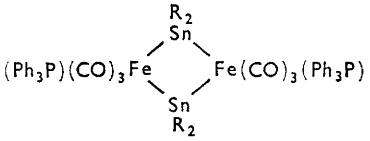
(II)

We have found that triphenylphosphine reacts with a solution of (II) ($R = Bu^n$) in light petroleum under ultraviolet irradiation to give the complex $[Bu^n{}_2SnFe(CO)_3PPh_3]_2$ (III), a yellow crystalline compound, m. p. 144° (decomp.):

$$[Bu^n{}_2SnFe(CO)_4]_2 + 2PPh_3 \longrightarrow [n\text{-}Bu_2SnFe(CO)_3PPh_3]_2 + 2CO$$

The complex (III) is not soluble in light petroleum, but is readily recrystallised from a 1 : 1 mixture of chloroform and light petroleum (b. p. 30—40°). Triphenylarsine failed to displace carbon monoxide from (II).

The shift to lower frequencies of the terminal carbonyl frequencies of $[Bu_2SnFe(CO)_3PPh_3]_2$ when compared with $[Bu_2SnFe(CO)_4]_2$ is consistent with the strongly σ-electron donating nature of triphenylphosphine.[13] Dialkynyl derivatives of silicon and germanium react with tri-iron dodecacarbonyl to give oils which could not be crystallised.



(III)

Reactions with Dicobalt Octacarbonyl.—The reactions of dicobalt octacarbonyl with $R_2M(C{\vdots}C{\cdot}R')_2$ give complexes of general formula $R_2M(C{\vdots}C{\cdot}R')_2[Co(CO)_3]_4$ (IV). These are formed by the simple displacement of the bridging carbonyl groups by alkynyl groups, in much the same way as complexes of the type $R{\cdot}C{\vdots}C{\cdot}R'[Co(CO)_3]_2$:[4]

$$R_2M(C{\vdots}C{\cdot}R')_2 + 2Co_2(CO)_8 \longrightarrow R_2M(C{\vdots}C{\cdot}R')_2[Co(CO)_3]_4 + 4CO$$

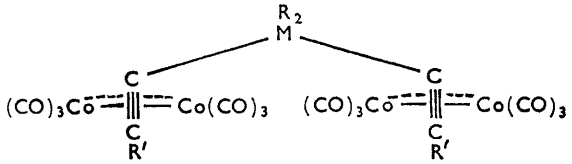
Stable crystalline complexes (generally dark brown to black) are isolated for silicon and germanium. The tin compounds are reddish-brown oils.

The infrared spectra of this series of compounds show similarities to those of the carbon analogues, $R{\cdot}C{\vdots}C{\cdot}R[Co(CO)_3]_2$ in the terminal carbonyl region.[4] The C⋮C absorptions are absent from both series of compounds suggesting that co-ordination occurs through the triple-bond system. Structure (IV) is suggested for these compounds, each cobalt atom attaining the inert-gas number of electrons. This implies a considerably modified C⋮C bond and this is believed to be shown by the medium-intensity band around 1600 cm.$^{-1}$ in the infrared spectra of all these complexes. The failure of $Me_2Si(C{\vdots}C{\cdot}Ph)_2[Co(CO)_3]_4$ to absorb hydrogen with Raney nickel as catalyst at 100°/40 atm. suggests that no discrete double bond exists in these compounds.

TABLE 2

Complexes of $R_2M(C{\vdots}C{\cdot}R')_2$ with cobalt carbonyl

Compound	M. p.	Yield (%)	M·C–O infrared bands (ν, cm.$^{-1}$; n-hexane solution)
$Et_2Ge(C{\vdots}C{\cdot}Ph)_2[Co(CO)_3]_4$	87—89°	70	2096vs, 2070vs, 2062sh, 2037vs, 2016vs, 1984w
$Ph_2Ge(C{\vdots}C{\cdot}Pr)_2[Co(CO)_3]_4$	132—134	65	2101vs, 2066vs, 2041vs, 2028vs, 2012vs, 1984w
$Ph_2Ge(C{\vdots}C{\cdot}Ph)_2[Co(CO)_3]_4$	154	66	2101vs, 2075vs, 2045vs, 2035vs, 1992w
$Me_2Si(C{\vdots}C{\cdot}Ph)_2[Co(CO)_3]_4$	144	84	2096vs, 2066vs, 2033vs, 2020sh, 1980w



(IV)

Triphenylphosphine reacts with (IV) to give $(PPh_3)_2[Co(CO)_3]_2$ and $R_2M(C{\vdots}C{\cdot}R')_2$, *e.g.*,

$$Me_2Si(C{\vdots}C{\cdot}Ph)_2[Co(CO)_3]_4 + 4PPh_3 \longrightarrow 2(PPh_3)_2[Co(CO)_3]_2 + Me_2Si(C{\vdots}C{\cdot}Ph)_2$$

That these compounds are isolated is further evidence for structure (IV). Triphenylarsine and triphenylstibine failed to react.

The nuclear magnetic resonance (n.m.r.) spectrum of (II; R = Et) shows bands at τ 8·7 and 8·2 with intensity ratios of 3 : 2 and the spectrum of (IV; M = Si, R = Me, R′ = Ph) shows bands at τ 9·1 (Me), 2·8, and 2·6 (Ph), with intensity ratios of 3 : 3 : 2.

Various other carbonyls including chromium hexacarbonyl, dimanganese decacarbonyl, and cyclopentadienyliron dicarbonyl dimer did not yield isolable complexes.

EXPERIMENTAL

All operations were carried out under nitrogen. Solvents were sodium-dried. The neutral alumina used in chromatography was obtained by shaking Spence's alumina (Type H) in ethyl acetate for at least 24 hr.

Infrared spectra were recorded on a Perkin-Elmer double-beam spectrophotometer (model 21) either in Nujol mulls or in n-hexane solution in 0·1 mm. CaF_2 cells. The nuclear magnetic resonance spectra were measured on a Perkin-Elmer (model R.10) high resolution spectrometer at 60 Mc./sec. with tetramethylsilane as internal reference.

Elemental analyses were carried out by the Microanalytical Laboratory of this Department and molecular weights were determined on a "Mechrolab" vapour-pressure osmometer.

Alkynyltin compounds were synthesised as described earlier[14] and the metal carbonyls were either prepared by established methods or from commercial sources.

Reactions of Tri-iron Dodecacarbonyl with Alkynyltin Compounds.—*With di-n-butyldihex-*1-*ynyltin.* Di-n-butyl-

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dihex-1-ynyltin (6·2 g., 16 mmoles) was added to a well-stirred suspension of tri-iron dodecacarbonyl (4·0 g., 7 mmoles) in anhydrous light petroleum (b. p. 100—120°) (100 ml.). The mixture was heated to 100°. After 3 hr. the colour of the mixture changed from dark green to dark brown. The mixture was kept at the reflux temperature for a further 8 hr., and then allowed to cool to room temperature. The solvent was removed under reduced pressure to leave an orange-brown oil.

The solution of the oil in light petroleum was chromatographed on neutral alumina and eluted with light petroleum (b. p. 60—80°). Two fractions were obtained, one pale orange and the other dark brown.

Solvent evaporation *in vacuo* from the dark brown solution gave a dark brown glue which could not be induced to crystallise. The pale orange fraction, on concentration under reduced pressure, gave yellow crystals. These were recrystallised from light petroleum (b. p. 100—120°) to give the *complex* $[Bu^n_2SnFe(CO)_4]_2$ (1·9 g., 30%), m. p. 112—113° (Found: C, 36·1; H, 5·0; ash, 57·4%; *M*, 820. $C_{12}H_{18}FeO_4Sn$ requires C, 36·0; H, 4·5; metals as oxides, 57·6%; *M*, 802).

The reactions shown in Table 3 were carried out similarly. No crystalline product was obtained from the reaction of tri-iron dodecacarbonyl with $Ph_2Sn(C{\vdots}C{\cdot}Ph)_2$, $Ph_2Sn(C{\vdots}C{\cdot}Bu)_2$, and $Bu^nSn(C{\vdots}C{\cdot}Bu)_3$.

TABLE 3

Reactions of tri-iron dodecacarbonyl with alkynyltin compounds

Reactants		Products	Yield		Analyses							
					Found (%)				Required (%)			
$Fe_3(CO)_{12}$	$R_2Sn(C{\vdots}C{\cdot}R')_2$	$[R_2SnFe(CO)_4]_2$	(%)	M. p.	C	H	Ash	*M*	C	H	Metals as oxides	*M*
4·0 g., 7 mmoles	R = Bu^n, R′ = Bu^n 6·2 g., 16 mmoles	$[Bu^n_2SnFe(CO)_4]_2$	30	112—113°	36·1	5·0	57·4	820	36·0	4·5	57·6	802
4·5 g., 9 mmoles	R = Pr^n, R′ = Bu^n 6·6 g., 18 mmoles	$[Pr^n_2SnFe(CO)_4]_2$	30	128—130	32·0	4·4	61·5	759	32·2	3·8	61·9	746
1·5 g., 3 mmoles	R = Et, R′ = Bu^n 1·9 g., 6 mmoles	$[Et_2SnFe(CO)_4]_2$	32	138 (decomp.)	27·8	2·9	66·7	695	27·8	2·9	67·0	690
2·5 g., 5 mmoles	R = Bu^n, R′ = Pr^n 3·6 g., 10 mmoles	$[Bu^n_2SnFe(CO)_4]_2$	28	112—113	36·2	4·6	56·9		36·0	4·5	57·6	
4·4 g., 9 mmoles	R = Pr^n, R′ = Pr^n 6·0 g., 18 mmoles	$[Pr^n_2SnFe(CO)_4]_2$	30	128—130	32·1	3·8	61·8		32·2	3·8	61·9	
4·4 g., 9 mmoles	R = Et, R′ = Pr^n 6·4 g., 20 mmoles	$[Et_2SnFe(CO)_4]_2$	34	138 (decomp.)	27·9	2·9	67·0		27·8	2·9	67·0	
4·4 g., 9 mmoles	R = Et, R′ = Ph 6·8 g., 18 mmoles	$[Et_2SnFe(CO)_4]_2$	12	138 (decomp.)	28·1	2·8	66·5		27·8	2·9	67·0	
1·5 g., 3 mmoles	R = Pr^n, R′ = Ph 2·6 g., 6 mmoles	$[Pr^n_2SnFe(CO)_4]_2$	10	128—130	32·3	3·7	62·0		32·2	3·8	61·9	

TABLE 4

Reactions of dicobalt octacarbonyl with alkynyl-germanes and -silanes

Reactants		Products	Yield		Analyses									
					Found (%)					Required (%)				
$Co_2(CO)_8$	$R_2M(C{\vdots}C{\cdot}R')_2$	$R_2M(C{\vdots}C{\cdot}R')_2[Co(CO)_3]_4$	(%)	M. p.	C	H	Co	Ash	*M*	C	H	Co	Metals as oxides	*M*
4·7 g., 14 mmoles	2·5 g., 7 mmoles	$Ph_2Ge(C{\vdots}C{\cdot}Pr)_2[Co(CO)_3]_4$	65	132—134°	44·3	2·7	24·5	45·3	975	43·8	2·6	24·3	45·7	933
1·6 g., 5 mmoles	1·0 g., 2 mmoles	$Ph_2Ge(C{\vdots}C{\cdot}Ph)_2[Co(CO)_3]_4$	66	154	47·8	2·2	23·3	42·3	993	48·0	2·0	23·6	42·6	1001
4·1 g., 12 mmoles	2·0 g., 6 mmoles	$Et_2Ge(C{\vdots}C{\cdot}Ph)_2[Co(CO)_3]_4$	70	87—89	42·4	2·4	25·8	46·7	906	42·4	2·3	26·1	47·1	905
5·3 g., 20 mmoles	2·0 g., 6 mmoles	$Me_2Si(C{\vdots}C{\cdot}Ph)_2[Co(CO)_3]_4$	84	144	43·1	1·7	28·3	44·9	826	43·3	1·9	28·4	45·7	832

*Reactions of Dicobalt Octacarbonyl with Alkynyl-germanes and -silanes.—With diphenyldipent-*1-*ynylgermane.* A solution of diphenyldipent-1-ynylgermane (2·5 g., 7 mmoles) in light petroleum (b. p. 30—40°) was added to a well-stirred solution of dicobalt octacarbonyl (4·7 g., 14 mmoles) in light petroleum (b. p. 30—40°) (100 ml.) at room temperature. Carbon monoxide was vigorously evolved. After being stirred for 3 hr., the mixture was concentrated under reduced pressure and chromatographed on neutral alumina. Elution with light petroleum (b. p. 30—40°) gave only one fraction. The reddish-brown solution was concentrated under reduced pressure to give dark orange crystals of the *complex* $Ph_2Ge(C{\vdots}C{\cdot}Pr)_2{\cdot}[Co(CO)_3]_4$ (4·2 g., 65%), m. p. 132—134° (Found: C, 44·3; H, 2·7; Co, 24·5; ash, 45·3%; *M*, 975. $C_{34}H_{24}Co_4GeO_{12}$ requires C, 43·8; H, 2·6; Co, 24·3; metals as oxides, 45·7%; *M*, 933).

The reactions shown in Table 4 were carried out similarly. No crystalline product could be obtained from similar reactions with $Et_2Ge(C{\vdots}C{\cdot}Bu)_2$, $Me_2Si(C{\vdots}C{\cdot}Bu)_2$, or $R_2Sn(C{\vdots}C{\cdot}R')_2$ compounds.

Reaction of Di-n-butyltiniron Tetracarbonyl Dimer with Triphenylphosphine.— Di-n-butyltiniron tetracarbonyl dimer (1·0 g., 1·2 mmoles) and triphenylphosphine (1·0 g., 3·9 mmoles) in light petroleum (b. p. 60—80°) (30 ml.) were sealed *in vacuo* in a silica tube. The mixture was irradiated with ultraviolet light with agitation for 4 days.

The tube was then opened, the solvent was removed under reduced pressure, and the residue sublimed *in vacuo*. Triphenylphosphine (0·3 g., 30% recovery), m. p. 79°, was obtained at 90—140°/0·15 mm. Chromatography of the residue on neutral alumina gave two fractions. Di-n-butyltiniron tetracarbonyl dimer ($<$0·1 g., 10% recovery) was eluted first with light petroleum, and confirmed by m. p. (112°) and infrared spectrum. Further elution with chloroform gave a yellow solution which was concentrated under reduced pressure. Light petroleum (b. p. 30—40°) was then added to make a 1 : 1 solvent mixture. The solution was warmed to boiling and allowed to cool to room temperature. Yellow crystals of the *complex* $[Bu^n_2SnFe(CO)_3PPh_3]_2$ (1·1 g., 69%, m. p. 144°, decomp.) were obtained (Found: C, 54·6; H, 5·1%; *M*, 1211. $C_{29}H_{33}FeO_3PSn$ requires C, 54·8; H, 5·2%; *M*, 1270).

Reaction of $Me_2Si(C{:}C{\cdot}Ph)_2[Co(CO)_3]_4$ *with Triphenylphosphine*.—Triphenylphosphine (5·0 g., 19 mmoles) and $Me_2Si(C{:}C{\cdot}Ph)_2[Co(CO)_3]_4$ (4·0 g., 4·8 mmoles) were dissolved in light petroleum (b. p. 30—40°) (50 ml.). The solution was cooled and the flask was evacuated and then set aside for 12 hr. Orange crystals of *bis(triphenylphospine)dicobalt hexacarbonyl* (3·0 g., 77%) were precipitated (Found: C, 62·0; H, 3·6. $C_{42}H_{30}Co_2O_6P_2$ requires C, 62·2; H, 3·7%).

The filtrate was evaporated to give a dark brown oil which was sublimed *in vacuo* at 130°/0·15 mm. to give unchanged triphenylphosphine (2·9 g., 58% recovery). The residue, dissolved in light petroleum, was then chromatographed on neutral alumina. Elution with light petroleum (b. p. 30—40°) gave an almost colourless fraction. This was concentrated under reduced pressure to give crystals of dimethyldi(phenylethynyl)silane (0·8 g., 67%, m. p. 81·5°). The infrared spectrum was identical with that of an authentic sample.

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