Organotin Reagents for the Synthesis of π-Allyl, π-Cyclopentadienyl, π-Indenyl, and Other Related π-Enyl Carbonyl Derivatives of the Transition Metals

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Organotin compounds such as allyltrimethyltin, cyclopentadienyl trimethyltin, indenyltrimethyltin *etc.*, react with a wide variety of metal carbonyl halides and other metal carbonyl compounds to afford the corresponding π-enyl metal carbonyl derivatives. In many cases conditions are very mild and yields are high, thus commending the reactions for extensive synthetic applications. The possible mechanisms of these reactions are discussed.

DURING the past decade much work has been done on the synthesis of π-allyl carbonyl derivatives of the transition metals,[1-12] and a number of synthetic routes have been used. Most of the methods for the metal carbonyl derivatives involve a decarbonylation[1-6] of the previously prepared σ-bonded allyl derivative as exemplified below,[1,5]

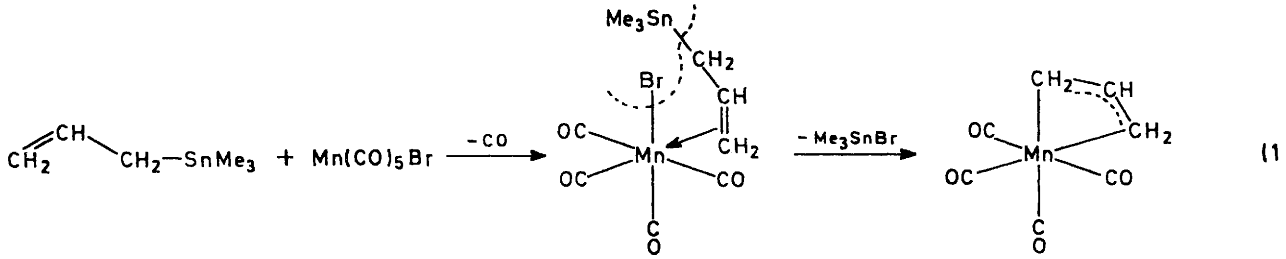
$$CH_2{=}CH{-}CH_2Cl + NaMn(CO)_5 \longrightarrow \sigma\text{-}CH_2{=}CH{-}CH_2{-}Mn(CO)_5$$
$$\Big\downarrow h\nu$$
$$(\pi\text{-}CH_2{\cdots}CH{\cdots}CH_2)Mn(CO)_4$$

$$CH_2{=}CH{-}CH{=}CH_2 + (\pi\text{-}C_5H_5)Fe(CO)_2H \longrightarrow \sigma\text{-}CH_3CH{=}CH{-}CH_2Fe(CO)_2(\pi\text{-}C_5H_5)$$
$$\Big\downarrow h\nu$$
$$(\pi\text{-}CH_3{\cdot}CH{\cdots}CH{\cdots}CH_2)Fe(CO)(\pi\text{-}C_5H_5)$$

However, it is not always possible to bring about the decarbonylation of the σ-allyl metal carbonyl. Thus, for example, σ-allylpentacarbonylrhenium is reported not to undergo conversion into π-allyltetracarbonylrhenium, either by heat or irradiation.[6]

Herein we report the use of allyltrimethyltin and other related organotins as valuable intermediates for the synthesis of a very wide range of π-enyl metal carbonyl complexes. We have previously published[13] a short communication on the method, and we note also the usage of tetra-allyltin as a source of π-allyl groups for palladium[14] and for iron nitrosyl compounds.[15] The convenience of the method lies in the fact that the syntheses involve reaction of two reagents with excellent shelf life, to form the product directly.

Allyltrimethyltin and bromopentacarbonylmanganese undergo complete reaction under reflux in tetrahydrofuran (*ca.* 70 °C) in 4 h to produce π-allyltetracarbonylmanganese in 82% yield. The same reaction takes place at 20 °C in about 10 days. As σ-allylpentacarbonylmanganese is only decarbonylated[1] at 80 °C in vacuum over 12 h, we believe it unlikely that σ-allylpentacarbonylmanganese is present as an intermediate in this reaction. Further, at no stage in a continuously monitored reaction was it possible to detect any trace of σ-allylpentacarbonylmanganese by i.r. spectroscopy. From these arguments we rule out the likelihood that the initial step involves elimination of organotin halide to produce σ-allylpentacarbonylmanganese, followed by a decarbonylation. More in accordance with our observations is a mechanism involving initial olefin co-ordination of the double bond of allyltrimethyltin along with carbonyl displacement, followed by elimination of bromotrimethyltin.



(1)

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[1] H. D. Kaesz, R. B. King, and F. G. A. Stone, *Z. Naturforsch.*, 1960, **15b**, 682.

[2] W. R. McClellan, H. N. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *J. Amer. Chem. Soc.*, 1961, **83**, 1601.

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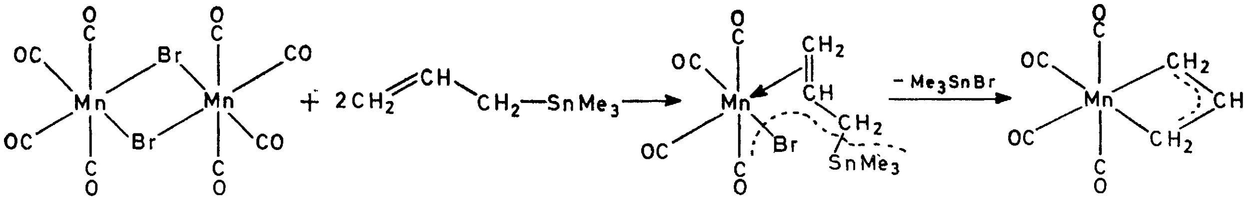
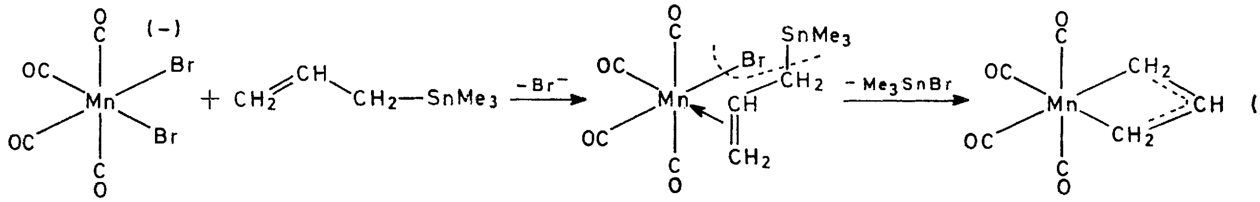
In this way π-allyltetracarbonylmanganese is made without the necessity of proceeding *via* σ-allylpentacarbonylmanganese. Thus, although σ-allylpentacarbonylrhenium will not undergo decarbonylation π-allyltetracarbonylrhenium is easily made in 80% yield *via* the organotin method.

When allyltrimethyltin undergoes reaction with dimeric dibromo-octacarbonyldimanganese no carbon monoxide is evolved, and π-$C_3H_5Mn(CO)_4$ is formed in 70% yield. Here the first step in the reaction appears to be fission of the halogen bridges, followed by intramolecular elimination of bromotrimethyltin.

In a similar manner, the dibromotetracarbonylmanganese anion gives a 66% yield of π-$C_3H_5Mn(CO)_4$.

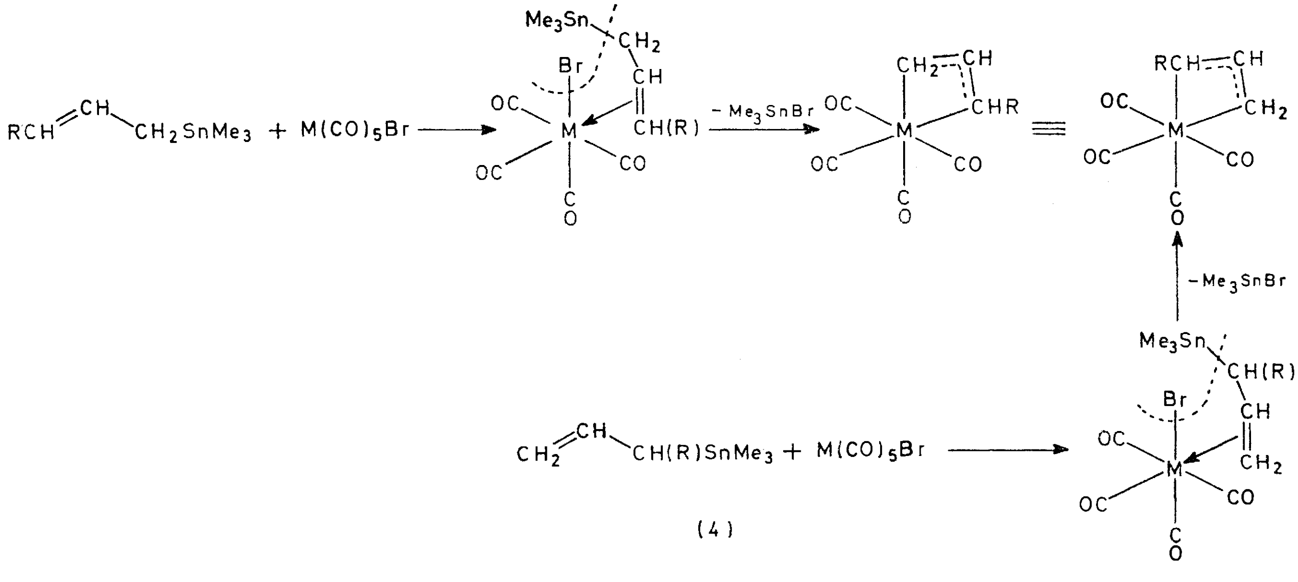

(2)


(3)

In the case of $Mn(CO)_4Br_2^-$ olefins are known[16] to displace bromide anion in preference to carbon monoxide, which accords with our proposed scheme of reaction in equation (3).

The interaction of bromopentacarbonylmanganese with a good range of allyltriorganotins, CH_2=CH–CH_2-SnR_3 (R = Me, Et, Pr^n, Bu^n, and Ph) and with $(CH_2{=}CH{-}CH_2)_2SnMe_2$ produced π-$C_3H_5Mn(CO)_4$, with only small variations in the yield of product (Table 2).

The use of alkyl and aryl substituted allyltrimethyltins produced very good yields of the corresponding substituted π-allyltetracarbonyls of manganese and rhenium. In the case of 2-substituted allyltrimethyltins it was possible to obtain the pure starting material, as the fluxional nature of the substituted allyl Grignard used to prepare the organotin did not affect the nature of the product. In the case of 1 and 3 substituted allyl groups, however, the fluxional nature of the Grignard reagent meant that a mixture of 1 and 3 substituted alkyl- or aryl-allyltrimethyltins was produced. The presence of a mixture of isomers in these reagents could be seen from their n.m.r. spectra. No attempt was made to separate the isomers, however, and the mixture was used as the reagent. Equation (4) illustrates how the two


(4)

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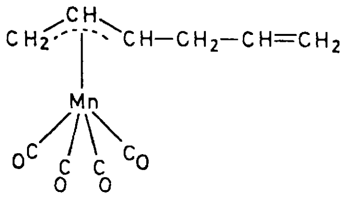
[16] F. E. Smith and I. S. Butler, *Canad. J. Chem.*, 1969, **47**, 1311.

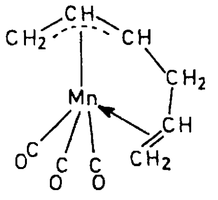
different isomeric substituted allyltrimethyltins produce the identical substituted π-allyltetracarbonylmetal.

Both products, however, consisted of the expected[2] mixture of *syn*- and *anti*-isomers.

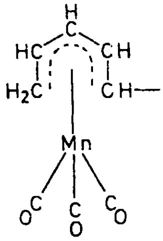
A similar problem with mixtures arose in the utilization of a diene system. Thus from the Grignard reagent of 3-bromohexa-1,5-diene and chlorotrimethyltin we obtained a mixture of 3-trimethylstannyl-hexa-1,5-diene and 1-trimethylstannylhexa-2,5-diene. This mixture was treated with bromopentacarbonylmanganese and as explained above, the π-allyl products obtained from the isomeric precursors were identical (I). In addition to this π-allyl product, π-$C_6H_9Mn(CO)_4$, a decarbonylated product π-$C_6H_9Mn(CO)_3$ was also isolated. Further, it was found that the π-allyl-tetracarbonyl species was decarbonylated to the tricarbonyl. This decarbonylation may be rationalized by the unco-ordinated olefin group in (I) displacing carbon monoxide, to form a complex (II), such decarbonylations being not uncommon. However, whilst the reaction may proceed *via* (II), we believe this undergoes immediate rearrangement by a 1—3 proton shift to form the methyl-pentadienyl ligand system. The i.r. and n.m.r. spectra of the hydrocarbon part of this complex are both complex, but are much more in accord with structure (III) rather than structure (II), especially the evidence for the presence of a methyl group.



(I)



(II)



(III)

In addition to their utility for the formation of π-allyl metal carbonyls, organotin compounds have been found to be very useful precursors for other π-enyl metal carbonyl complexes. Although a mechanism similar to that proposed for the π-allyl systems above may be applicable, the low stability of σ-bonded cyclopentadienyls, indenyls, and fluorenyls make it more difficult to rule out the alternative of an initial fission reaction followed by carbonyl displacement. Table 2 indicates the range of π-cyclopentadienyl, π-indenyl-, and π-fluorenyl-metal carbonyl complexes that have been synthesised by this method. In the main, the method provided a high yield synthesis of the desired product, though in some cases side reactions produced an interesting range of by-products.

Notable is the extraordinary reactivity of $[Rh(CO)_2Cl]_2$ which undergoes reaction with allyltrimethyltin and cyclopentadienyltrimethyltin instantly at room temperature to produce respectively π-$C_3H_5Rh(CO)_2$ and π-$C_5H_5Rh(CO)_2$ in virtually quantitative yields.

The oxidative addition of cyclopentadienyltrimethyltin with metal carbonyls has already been reported to form (π-cyclopentadienyl)metal carbonyls.[17,18] We further find that allyltriorganotins undergo reaction with dimeric metal carbonyls to form the corresponding (π-allyl)metal carbonyls as exemplified by equations (5) and (6) below. Such reactions, however, generally require

$$CH_2{=}CH{-}CH_2SnPh_3 + Co_2(CO)_8 \longrightarrow \pi\text{-}C_3H_5Co(CO)_3 + Ph_3SnCo(CO)_4 \quad (5)$$

$$CH_2{=}CH{-}CH_2SnMe_3 + Re_2(CO)_{10} \longrightarrow \pi\text{-}C_3H_5Re(CO)_4 + Me_3SnRe(CO)_5 \quad (6)$$

TABLE 1

Allyltin Reagents

	B.p.	B.p.[a] Lit. b.p.		Analysis			
	°C, mmHg		Yield (%)	Calc. (%)		Found (%)	
Compound				C	H	C	H
$CH_2{=}CH{-}CH_2SnMe_3$	129	[129(760)][b]	69	35·2	6·8	35·1	6·8
$CH_3CH{=}CH{-}CH_2{-}SnMe_3$ $CH_2{=}CH{-}CH(CH^3)SnMe_3$	150	*c*	73	38·4	7·3	38·7	7·4
$CH_2{=}C(CH_3)CH_2SnMe_3$	147	*c*	65	38·4	7·3	38·6	7·3
$(C_6H_5)CH{=}CH{-}CH_2SnMe_3$ $CH{=}CH{-}CH(C_6H_5)SnMe_3$	69(0·03)		70	51·2	6·4	51·4	6·6
$(CH_2{=}CH{-}CH_2)_2SnMe_2$	62(12)		78	41·5	6·9	41·7	6·7
$CH_2{=}CH{-}CH_2SnEt_3$	62(5)	[112(50)][d]	63	43·7	8·1	43·6	8·0
$CH_2{=}CH{-}CH_2SnPr^n{}_3$	91(1)	[103(5)][e]	61	49·8	9·0	49·6	8·9
$CH_2{=}CH{-}CH_2SnBr^n{}_3$	88(0·01)	[155(17)][d]	72	54·3	9·7	54·1	9·5
$CH_2{=}CH{-}CH_2SnPh_3$	73—74[f]	74[g]	80	64·5	5·1	64·5	5·1

[a] Pressure, in mmHg, in parentheses, lit. b.p. in brackets. [b] D. Seyferth and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1957, **79**, 515. [c] H. G. Kuivila and J. A. Verdone, *Tetrahedron Letters*, 1964, 119. [d] W. J. Jones, W. C. Davies, S. T. Bowden, C. Edwards, V. E. Davis, and L. H. Thomas, *J. Chem. Soc.*, 1947, 1446. [e] K. S. Tillyeav and Z. M. Manulkin, *Uzbeksk. Khim. Zhur.*, 1961, **5**, 73. [f] M.p. [g] H. Gilman and J. Eisch, *J. Org. Chem.*, 1955, **20**, 763.

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Table 2

Interactions of σ-bonded enylorganotins with metal carbonyl halides and metal carbonyls

Reactants	Conditions Solvent–Temperature/°C–Time/h	Products	Yield (%)
$CH_2{=}CH{-}CH_2{-}SnMe_3 + Mn(CO)_5Br$	THF–67–4 h	$\pi\text{-}C_3H_5Mn(CO)_4$	82
$CH_2{=}CH{-}CH_2{-}SnMe_3 + Re(CO)_5Br$	THF–67–7 h	$\pi\text{-}C_3H_5Re(CO)_4$	80
$\left.\begin{array}{l}MeCH{=}CH{-}CH_2SnMe_3\\CH_2{=}CH{-}CHMeSnMe_3\end{array}\right\} + Mn(CO)_5Br$	THF–67–4 h	$\pi\text{-}MeCH{\cdot}CH{\cdot}CH_2Mn(CO)_4$	70
$\left.\begin{array}{l}MeCH{=}CH{-}CH_2SnMe_3\\CH_2{=}CH{-}CHMeSnMe_3\end{array}\right\} + Re(CO)_5Br$	THF–67–7 h	$\pi\text{-}MeCH{\cdot}CH{\cdot}CH_2Re(CO)_4$	60
$CH_2{=}CMeCH_2SnMe_3 + Mn(CO)_5Br$	THF–67–4 h	$\pi\text{-}CH_2CMeCH_2Mn(CO)_4$	65
$CH_2{=}CMeCH_2SnMe_3 + Re(CO)_5Br$	THF–67–7 h	$\pi\text{-}CH_2CMeCH_2Re(CO)_4$	60
$\left.\begin{array}{l}PhCH{=}CH{-}CH_2SnMe_3\\CH_2{=}CH{\cdot}CHPhSnMe_3\end{array}\right\} + Mn(CO)_5Br$	THF- 67–4 h	$\pi\text{-}PhCH{\cdot}CH{\cdot}CH_2Mn(CO)_4$	82
$\left.\begin{array}{l}PhCH{=}CHCH_2SnMe_3\\CH_2{=}CH{\cdot}CHPhSnMe_3\end{array}\right\} + Re(CO)_5Br$	THF–67–8 h	$\pi\text{-}C_6H_5CHCHCH_2Re(CO)_4$	65
$CH_2{=}CH{-}CH_2SnMe_3 + Et_4N^+Mn(CO)_4Br_2^-$	THF–67–1 h	$\pi\text{-}C_3H_5Mn(CO)_4$	66
$CH_2{=}CH{-}CH_2SnMe_3 + Mn_2(CO)_8Br_2$	THF–67–3 h	$\pi\text{-}C_3H_5Mn(CO)_4$	70
$(CH_2{=}CH{-}CH_2)_2SnMe_2 + Mn(CO)_5Br$	THF–67–5 h	$\pi\text{-}C_3H_5Mn(CO)_4$	62
$CH_2{=}CH{-}CH_2SnEt_3 + Mn(CO)_5Br$	THF–67–5 h	$\pi\text{-}C_3H_5Mn(CO)_4$	67
$CH_2{=}CH{-}CH_2SnPr^n{}_3 + Mn(CO)_5Br$	THF–67–5 h	$\pi\text{-}C_3H_5Mn(CO)_4$	67
$CH_2{=}CH{-}CH_2SnBu^n{}_3 + Mn(CO)_5Br$	THF–67–5 h	$\pi\text{-}C_3H_5Mn(CO)_4$	59
$CH_2{=}CH{-}CH_2SnPh_3 + Mn(CO)_5Br$	THF–67–5 h	$\pi\text{-}C_3H_5Mn(CO)_4$	73
$CH_2{=}CH{-}CH_2SnMe_3 + \pi\text{-}C_5H_5Mo(CO)_3Cl$	THF–25–120 h	$(\pi\text{-}C_3H_5)(\pi\text{-}C_5H_5)Mo(CO)_2$	60
$CH_2{=}CH{-}CH_2SnMe_3 + \pi\text{-}C_5H_5W(CO)_3Cl$	THF–50–80 h	$(\pi\text{-}C_3H_5)(\pi\text{-}C_5H_5)W(CO)_2$	61
$CH_2{=}CH{-}CH_2SnMe_3 + Fe(CO)_4I_2$	Et_2O–25–2 h	$\pi\text{-}C_3H_5Fe(CO)_3I$	81
$CH_2{=}CH{-}CH_2SnMe_3 + \pi\text{-}C_5H_5Fe(CO)_2Cl$	Et_2O–25–300 h	$(\pi\text{-}C_5H_5)_2Fe$ $\pi\text{-}C_5H_5Fe(CO)_2SnMe_3$ $[\pi\text{-}C_5H_5Fe(CO)_2]_2$	9 *ca.* 1 *ca.* 1
$CH_2{=}CH{-}CH_2SnMe_3 + \pi\text{-}C_5H_5Fe(CO)_2Cl$	Dioxan–100–100 h	$(\pi\text{-}C_5H_5)_2Fe$ $\pi\text{-}C_5H_5Fe(CO)_2SnMe_3$ $[\pi\text{-}C_5H_5Fe(CO)_2]_2$	7 *ca.* 1 *ca.* 15
$CH_2{=}CH{-}CH_2SnMe_3 + [Ru(CO)_3Cl_2]_2$	THF–67–5 h	$\pi\text{-}C_3H_5Ru(CO)_3Cl$ $(\pi\text{-}C_3H_5)_2Ru(CO)_2$	*ca.* 5 10
$CH_2{=}CH{-}CH_2SnMe_3 + \pi\text{-}C_5H_5Ru(CO)_2Br$	THF–67–100 h	$(\pi\text{-}C_3H_5)(\pi\text{-}C_5H_5)Ru(CO)$	*ca.* 2
$CH_2{=}CH{-}CH_2SnMe_3 + \pi\text{-}C_3H_5Ru(CO)_3Br$	THF–67–5 h	$(\pi\text{-}C_3H_5)_2Ru(CO)_2$	83
$CH_2{=}CH{-}CH_2SnMe_3 + Co_2(CO)_8$	Et_2O–35–1 h	$\pi\text{-}C_3H_5Co(CO)_3$ $Me_3SnCo(CO)_4$	*a* 58
$CH_2{=}CH{-}CH_2SnPh_3 + Co_2(CO)_8$	Et_2O–35–2 h	$\pi\text{-}C_3H_5Co(CO)_3$ $Ph_3SnCo(CO)_4$	86 91
$CH_2{=}CH{-}CH_2SnMe_3 + [Rh(CO)_2Cl]_2$	Et_2O–25–0·5 h	$\pi\text{-}C_3H_5Rh(CO)_2$	70
$CH_2{=}CH{-}CH_2SnMe_3 + Mn_2(CO)_{10}$	Diglyme–140–24 h	$\pi\text{-}C_3H_5Mn(CO)_4$ $Me_3SnMn(CO)_5$	2 72
$CH_2{=}CH{-}CH_2SnMe_3 + Re_2(CO)_{10}$	Digylme–150–100 h	$\pi\text{-}C_3H_5Re(CO)_4$ $Me_3SnRe(CO)_5$	37 42
$CH_2{=}CH{-}CH_2SnMe_3 + [\pi\text{-}C_5H_5Fe(CO)_2]_2$	Xylene–130–100 h	$\pi\text{-}C_5H_5Fe(CO)_2SnMe_3$	6
$C_5H_5SnMe_3 + Mn(CO)_5Br$	THF–67–3 h	$\pi\text{-}C_5H_5Mn(CO)_3$	82
$C_5H_5SnMe_3 + Re(CO)_5Br$	THF–67–6 h	$\pi\text{-}C_5H_5Re(CO)_3$	88
$C_5H_5SnMe_3 + \pi\text{-}C_5H_5Mo(CO)_3Cl$	THF–67–2 h	$\pi\text{-}C_5H_5Mo(CO)_3SnMe_3$ $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ $Mo(CO)_6$	19 3 2
$C_5H_5SnMe_3 + \pi\text{-}C_5H_5W(CO)_3Cl$	THF–67–5 h	$\pi\text{-}C_5H_5W(CO)_3SnMe_3$ $[\pi\text{-}C_5H_5W(CO)_3]_2$ $W(CO)_6$	10 2 2
$C_5H_5SnMe_3 + \pi\text{-}C_3H_5(MeCN)_2Mo(CO)_2Cl$	THF–67–0·5 h	$(\pi\text{-}C_3H_5)(\pi\text{-}C_5H_5)Mo(CO)_2$	98
$C_5H_5SnMe_3 + \pi\text{-}C_7H_7Mo(CO)_2I$	THF–25–200 h	$(\pi\text{-}C_7H_7)(\pi\text{-}C_5H_5)Mo(CO)_2$	10
$C_5H_5SnMe_3 + Fe(CO)_4I_2$	Et_2O–25–0·5 h	$(\pi\text{-}C_5H_5)Fe(CO)_2I$	85
$C_5H_5SnMe_3 + [Ru(CO)_3Cl_2]_2$	THF–67–8 h	$(\pi\text{-}C_5H_5Ru(CO)_3Cl$ $[\pi\text{-}C_5H_5Ru(CO)_2]_2$ $\pi\text{-}C_5H_5Ru(CO)_2SnMe_3$	6 3 7
$C_5H_5SnMe_3 + [Ru(CO)_3Cl_2]_2$	MeCN–25–8 h	$\pi\text{-}C_5H_5Ru(CO)_2SnMe_3$	30
$C_5H_5SnMe_3 + C_3H_5Ru(CO)_3Br$	THF–67–5 h	$(\pi\text{-}C_3H_5)(\pi\text{-}C_5H_5)Ru(CO)$ $(\pi\text{-}C_3H_5)_2Ru(CO)_2$ $\pi\text{-}C_5H_5Ru(CO)_2Br$ $[\pi\text{-}C_5H_5Ru(CO)_2]_2$ $\pi\text{-}C_5H_5Ru(CO)_2SnMe_3$	36 20 10 3 2
$C_5H_5SnMe_3 + Me_3SiRu(CO)_4I$	THF–67–5 h	$\pi\text{-}C_5H_5Ru(CO)_2SiMe_3$	49
$C_5H_5SnMe_3 + [Rh(CO)_2Cl]_2$	Et_2O–25–0·5 h	$\pi\text{-}C_5H_5Rh(CO)_2$	90
$MeC_5H_4SnMe_3 + Mn(CO)_5Br$	THF–67–3 h	$\pi\text{-}MeC_5H_4Mn(CO)_3$ $Me_3SnMn(CO)_5$ $Mn_2(CO)_{10}$	40 10 6
Indenyl $SnMe_3 + Mn(CO)_5Br$	THF–67–4 h	$\pi\text{-}C_9H_7Mn(CO)_3$	62
Indenyl $SnMe_3 + Re(CO)_5Br$	THF–67–7 h	$\pi\text{-}C_9H_7Re(CO)_3$	78
Indenyl $SnMe_3 + Co_2(CO)_8$	Et_2O–35–1 h	$\pi\text{-}C_9H_7Co(CO)_2$ $Me_3SnCo(CO)_4$	64 73
Indenyl $SnMe_3 + [Rh(CO)_2Cl]_2$	Et_2O–25–0·5 h	$\pi\text{-}C_9H_7Rh(CO)_2$	70
Indenyl $SnMe_3 + \pi\text{-}C_3H_5(MeCN)_2Mo(CO)_2Cl$	THF–67–1·5 h	$(\pi\text{-}C_3H_5)(\pi\text{-}C_9H_7)Mo(CO)_2$	80
Indenyl $SnMe_3 + \pi\text{-}C_3H_5Ru(CO)_3Br$	THF–67–6 h	$(\pi\text{-}C_3H_5)(\pi\text{-}C_9H_7)Ru(CO)$	77

TABLE 2 (*Continued*)

Reactants	Conditions Solvent–Temperature/°C–Time/h	Products	Yield (%)
Indenyl $SnMe_3$ + $Fe(CO)_4I_2$	Et_2O–25–5 h	π-$C_9H_7Fe(CO)_2I$	28
Fluorenyl $SnMe_3$ + $Mn(CO)_5Br$	THF–67–4 h	π-$C_{13}H_9Mn(CO)_3$	20
		$Me_3SnMn(CO)_5$	31
		$Mn_2(CO)_{10}$	18
Hexadienyl $SnMe_3$ + $Mn(CO)_5Br$	THF–67–8 h	π-$C_6H_9Mn(CO)_4$	25
		π-$MeC_5H_6Mn(CO)_3$	15
		$Me_3SnMn(CO)_5$	2
		$Mn_2(CO)_{10}$	40

[a] Though detected by spectroscopic methods to be present in quantity at the end of the reaction time, π-$C_3H_5Co(CO)_3$ did not survive the subsequent chromatographic separation from $Me_3SnCo(CO)_4$. It could, however, be obtained contaminated with a small amount of $Me_3SnCo(CO)_4$ by fractional distillation.

TABLE 3

Melting point, boiling point, and analytical characterization of the π-enyl products from the reactions in Table 2

Compound	M.p. (b.p.) [a] °C (°C, mmHg)		Analysis Calc. C	Calc. H	Found C	Found H
π-$C_3H_5Mn(CO)_4$ [b]	53	[52—53·5] [1] [55—56] [2]	40·4	2·4	40·2	2·3
π-$CH_3CHCH_2Mn(CO)_4$	(52—54, 2)	[(68, 7)] [2]	43·2	3·15	42·9	3·0
π-$CH_2C(CH_3)CH_2Mn(CO)_4$	(60, 5)	[(50, 2·5)] [2]	43·3	3·15	42·9	3·15
π-$C_6H_5CHCHCH_2Mn(CO)_4$	38—40	[(90, 0·1)] [c]	54·9	3·15	55·0	3·2
π-$C_3H_5Re(CO)_4$ [d]	32·5(51, 1)		24·8	1·5	24·8	1·45
π-$CH_3CHCHCH_2Re(CO)_4$	(53, 0·05)		27·2	2·0	27·3	2·2
π-$CH_2C(CH_3)CH_2Re(CO)_4$	(55, 0·12)		27·2	2·0	27·4	2·05
π-$C_6H_5CHCHCH_2Re(CO)_4$			37·4	2·15	37·6	2·2
(π-C_3H_5)(π-C_5H_5)$Mo(CO)_2$	175—176	[134 (dec.)] [3]	46·5	3·9	46·3	3·9
(π-C_3H_5)(π-C_5H_5)$W(CO)_2$	182—185	[4]	34·7	2·9	34·9	2·9
π-$C_3H_5Fe(CO)_3I$ [e]	95—97° dec.	[85—88] [8] [98] [7]	23·2	1·6	23·3	1·65
(π-C_3H_5)$Ru(CO)_3Cl$ [f]	77—78	[75—77] [12]	27·6	1·9	27·8	1·95
(π-C_3H_5)$_2Ru(CO)_2$ [g]	105—106	[Liquid] [h]	40·2	4·2	40·1	4·0
(π-C_3H_5)$Co(CO)_3$		[(39, 15 mm)] [2]	39·2	2·7	39·5	2·75
(π-C_3H_5)$Rh(CO)_2$	64	[55—60] [i]	30·0	2·5	29·5	2·8
π-$C_5H_5Mn(CO)_3$	77	[77] [j]	47·1	2·45	47·0	2·45
π-$C_5H_5Re(CO)_3$	112·5	[111—114] [k]	28·7	1·5	29·0	1·5
(π-C_7H_7)(π-C_5H_5)$Mo(CO)_2$	106—110	[111—112] [l]	54·5	3·9	54·6	4·2
π-$C_5H_5Fe(CO)_2I$ [m]	119—120	[119—120] [n]	27·6	1·65	27·6	1·65
(π-C_3H_5)(π-C_5H_5)$Ru(CO)$	50	[44—45] [6]	45·9	4·25	45·8	4·3
(π-C_5H_5)$Ru(CO)_2Br$	94·5	[o]	27·8	1·65	28·1	1·75
π-$C_5H_5Ru(CO)_2SiMe_3$	Liquid		40·6	4·75	41·0	4·6
π-$C_5H_5Rh(CO)_2$	Liquid	[−11] [p]	37·5	2·25	37·6	2·3
π-$MeC_5H_4Mn(CO)_3$	Liquid	[1·7—2·0] [q]	49·5	3·2	50·0	3·35
π-$C_9H_7Mn(CO)_3$ [r]	49·5—51	[50—51] [s]	56·6	2·75	56·9	2·75
π-$C_9H_7Re(CO)_3$ [t]	88—89	[89] [u]	37·3	1·8	37·6	1·85
π-$C_9H_7Co(CO)_2$ [v]	54—55·5		57·3	3·05	57·6	3·25
π-$C_9H_7Rh(CO)_2$ [w]	54—55·5		48·1	2·55	48·2	2·6
(π-C_3H_5)(π-C_9H_7)$Mo(CO)_2$	129	[119—121] [x]	54·5	3·9	54·5	4·1
(π-C_3H_5)(π-C_9H_7)$Ru(CO)$ [y]	69		54·7	4·2	54·8	4·3
(π-C_9H_7)$Fe(CO)_2I$ [z]	72—74		37·2	2·0	38·0	1·95
π-$C_{13}H_9Mn(CO)_4$	115—118	[118—119] [s]	63·1	2·95	63·3	3·15
π-$C_6H_9Mn(CO)_4$	Liquid		48·3	3·65	48·8	3·75
π-$C_6H_9Mn(CO)_3$ [aa]	29·5—30·5		49·1	4·1	49·0	4·2

[a] Recorded under nitrogen, literature values in brackets. [b] Calc. Mn, 26·4. Found Mn, 26·4%. [c] W. R. McClellan, U.S.P. 2,990,418 (1961). [d] Calc. Re, 54·9. Found Re, 54·8%. [e] Calc. I, 41·2. Found I, 41·9%. [f] Calc. Cl, 13·6. Found Cl, 13·8%. [g] This compound has been reported previously as a liquid; but in our hands by three different syntheses the product is a white crystalline solid well characterized by analyses, i.r., and n.m.r. spectra. [h] M. Cooke, R. J. Goodfellow, M. Green, and G. Parker, *J. Chem. Soc.* (*A*), 1971, 16. [i] S. O'Brien, *Chem. Comm.*, 1968, 757. [j] T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1955, **1**, 165. [k] R. L. Pruett and E. L. Morehouse, *Chem. and Ind.*, 1958, 980. [l] R. B. King and M. B. Bisnette, *Inorg. Chem.*, 1964, **3**, 785. [m] Calc. I, 41·7. Found I, 42·0%. [n] T. S. Piper and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **2**, 38. [o] E. O. Fischer and A. Vogler, *Z. Naturforsch.*, 1962, **17b**, 421. [p] E. O. Fischer and K. Bittler, *Z. Naturforsh.*, 1961, **16b**, 225. [q] L. T. Reynolds and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1959, **9**, 86. [r] Calc. Mn, 21·6. Found Mn, 21·8%. [s] R. B. King and A. Efraty, *J. Organometallic Chem.*, 1970, **23**, 527. [t] Calc. Re, 48·3. Found Re, 48·2%. [u] E. O. Fischer and W. Fellman, *J. Organometallic Chem.*, 1963, **1**, 191. [v] Calc. Co, 25·6. Found Co, 25·3%. [w] Calc. Rh, 37·6. Found Rh, 38·0%. [x] R. B. King and M. B. Bisnette, *Inorg. Chem.*, 1965, **4**, 475. [y] Calc. Ru, 35·4. Found Ru, 35·4%. [z] Calc. I, 35·8. Found I, 35·5%. [aa] Calc. Mn, 25·0. Found Mn, 25·15%.

much more forcing conditions than the corresponding reactions with metal carbonyl halides, and normally only the more robust (π-allyl)metal carbonyls survive in good yield.

EXPERIMENTAL

Distilled water was flushed with nitrogen before use. Cyclopentadienyltrimethyltin, methylcyclopentadienyltrimethyltin, and indenyltrimethyltin were prepared from dimethylaminotrimethyltin and the appropriate hydrocarbon, according to the published procedures.[19] Fluorenyltrimethyltin was made from fluorenylsodium and trimethyltin chloride. The allyltin reagents (Table 1) were prepared from the requisite organotin halide and a 50% excess of the appropriate allylmagnesium bromide, at 0 °C in diethyl ether. The excess of Grignard reagent was destroyed by the careful addition of saturated ammonium chloride solution. After drying, the ethereal layer was distilled to afford the required product. The proton n.m.r. spectra of the 3-substituted allyltin compounds showed them to be mixtures of the two isomers.

Preparation of Hexadienyltrimethyltins.—A mixture of the bromohexadienes $CH_2{=}CH{\cdot}CH(Br)CH_2CH{=}CH_2$ and $BrCH_2{-}CH{=}CH{\cdot}CH_2CH{=}CH_2$ was prepared from hexa-1,5-diene-3-ol and phosphorus tribromide. This mixture (32·2 g, 0·2 mol) was converted into Grignard reagent by magnesium (36·0 g, 1·5 mol) in diethyl ether (1 l) (0°; 15 h) and to this was added trimethyltin chloride (20·0 g, 0·1 mol) in ether (200 ml) at 0 °C over a period of 4 h. After stirring at 25° for a further 6 h, the excess of Grignard reagent was destroyed by saturated ammonium chloride solution. After water washing and filtration, the ether was distilled off and subsequent low pressure distillation gave the product (16·3 g, 66%) boiling at 39·5—40·5°; 1 mmHg. Analytical data and n.m.r. spectra showed the product to consist of a mixture of the two isomers 3-trimethylstannyl-hexa-1,5-diene and 6-trimethylstannyl-hexa-1,4-diene, along with *ca.* 20% of the hydrocarbon $C_{12}H_{18}$. As both of the organotin isomers would give the same π-allylic product, and the hydrocarbon would not interfere with this reaction the mixture was utilized without further separation.

Reactions of Allyl, Cyclopentadienyl, Indenyl, Fluorenyl, and Related Organotins with Metal Carbonyl Halides and Metal Carbonyls.—Some examples of experiments typifying the very many reactions carried out in this area are outlined below in order to illustrate conditions and isolation procedures. All the reactions together with conditions, products, and yields are listed in Table 2. The analytical characterization, and m.p. of the products are detailed in Table 3. In many cases the reactions of Table 2 yield the same product from a variety of reagents. In these cases only one analysis and m.p. are reported, but for all other cases the analyses and m.p. were also satisfactory.

Interaction of Allyltrimethyltins and the Pentacarbonyl Halides of Manganese and Rhenium.—The allyltrimethyltin (1 mmol) and the pentacarbonyl halide were heated together under reflux in tetrahydrofuran (10 ml), until i.r. monitoring of the reaction mixture showed complete consumption of the pentacarbonyl halide. Water (25 ml) was added to the mixture to precipitate the product, and tetrahydrofuran and the trimethyltin halide were removed by water washing (3 × 10 ml). The residue was taken up in diethyl ether (20 ml) and dried with anhydrous magnesium sulphate. After filtration, ether was removed at 20°; 15 mmHg, and the residue sublimed if a solid, or distilled if a liquid, to afford the pure π-allylic manganese or rhenium tetracarbonyl (Tables 2—4).* In cases where the by-product organotin halide was not easily soluble in water, separation was effected by chromatography in hexane on alumina.

Interaction of Allyltrimethyltin and Tricarbonylchloro-(π-cyclopentadienyl)tungsten.—Allyltrimethyltin (1·03 g, 1 mol) and tricarbonylchloro(π-cyclopentadienyl)tungsten (1·84 g, 1 mol) were heated together under reflux in tetrahydrofuran (20 ml). After 20 h the product was precipitated by the addition of water (50 ml), the residue extracted into ether (20 ml), and the solution dried. Removal of the solvent and chromatography on alumina in benzene–hexane (25 : 75) gave the pure (π-allyl)dicarbonyl(π-cyclopentadienyl)tungsten (1·06 g, 61%) (see Tables 2—4).

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[19] K. Jones and M. F. Lappert, *Proc. Chem. Soc.*, 1964, 22.

* Table 4 has been deposited in Supplementary Publication No. SUP 20729 (8 pp.). For details of the Supplementary Publications scheme see *J. Chem. Soc.* (*A*), 1970, Issue No. 20, Notice to Authors No. 7. Items less than 10 pp. are sent as full size copies.