Unsaturated σ-Hydrocarbyl Transition-metal Complexes. Part I. Trimethyltin Acetylides as Sources of Late Transition-metal Derivatives: Metathesis, Oxidative Addition, and Oxidative Cleavage

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The reactions of the tin acetylides $\mathrm{R_3Sn{\cdot}C{:}CPh}$ (R = Me or Et) with some low oxidation state complexes of $\mathrm{Mo^0}$, $\mathrm{Mo^{II}}$, $\mathrm{Co^0}$, $\mathrm{Rh^I}$, $\mathrm{Ir^I}$, and $\mathrm{Pt^0}$ have been investigated. They fall into four classes: metathesis [*e.g.*, with $\mathrm{RhCl(CO)(PPh_3)_2 \longrightarrow Rh(C{:}CPh)(CO)(PPh_3)_2}$]; oxidative addition, with or without neutral ligand elimination [*e.g.*, $\mathrm{Ir(C{:}CPh)(CO)(PPh_3)_2 \longrightarrow Ir(C{:}CPh)_2(SnMe_3)(CO)(PPh_3)_2}$ or $\mathrm{Pt(PPh_3)_3 \longrightarrow Pt(C{:}CPh)(SnMe_3)(PPh_3)_2}$]; metathesis and oxidative addition [*e.g.*, $\mathrm{IrCl(CO)(PPh_3)_2 \longrightarrow Ir(C{:}CPh)_2(SnMe_3)(CO)(PPh_3)_2}$]; and oxidative cleavage [*e.g.*, $\mathrm{\{Mo(\pi\text{-}C_5H_5)(CO)_3\}_2 \longrightarrow Mo(\pi\text{-}C_5H_5)(SnMe_3)(CO)_3}$]. The structures of the compounds are assigned on the basis of spectroscopic data. Complexes having both $\mathrm{SnR_3}$ and acetylide units are regarded as mono-*hapto*-($\mathrm{PhC{:}C{\cdot}M{\cdot}SnR_3}$) rather than bi-*hapto*-($\mathrm{\overline{M{\cdot}CPh{:}C}SnR_3}$). Selected reactions of some of the new Rh, Ir, and Pt acetylides are described.

THIS paper begins a series dealing with transition-metal alkenyls and alkynyls, which collectively we term unsaturated σ-hydrocarbyl complexes; the study is in some way complementary to that on metal carbene complexes.[1] Our interest in both classes stems in part from the recognition that the co-ordinative unsaturation of the ligand opens up the possibility of realising intra- or inter-molecular group transfer reactions. An example of the former process has been demonstrated in another unsaturated ligand system, the ketimide: thus, triphenylphosphine catalyses the tautomerisation of *trans*-$\mathrm{PtH[N{:}C(CF_3)_2](PPh_3)_2}$ into $\mathrm{\overline{PtNHC}(CF_3)_2(PPh_3)_2}$.[2] As for the latter, reactions are envisaged with reagents such as halogens and hydrogen halides, which react both with unsaturated hydrocarbons and with low-valent transition metals. As well as such objectives, which relate to reactivity, others refer to synthesis or bonding. With regard to the former, a key consideration was the availability of certain unsaturated hydrocarbyl tin(IV) complexes as potential precursors; the possibility of $d\pi$–π^* M–C bonding or ionic character in the M–C bond are features relevant to the latter.

The transfer of a ligand from $\mathrm{Sn^{IV}}$ to a transition metal has become a useful synthetic procedure, *e.g.*, $\mathrm{C_5H_5^-}$,[3] $\mathrm{C_3H_5^-}$,[4] or $\mathrm{^-N{:}C(CF_3)_2}$.[5,6] Moreover, trimethyltin acetylides such as $\mathrm{Me_3Sn{\cdot}C{:}CPh}$ are readily available, *e.g.*, from the amide $\mathrm{Me_3Sn{\cdot}NMe_2}$[7] or $\mathrm{Me_3Sn{\cdot}N{:}CR_2}$.[5] This aspect forms a major part of the present paper. Various types of reaction have been discovered and are classified, as shown in Table 1. Additionally, we are concerned with evidence for proposed structures for the new transition-metal acetylides, and with some of their reactions. A preliminary communication has appeared.[8]

As for bonding, we are interested in the electronic effects of carbon ligands, as demonstrated for example by *trans*-influence studies on $\mathrm{Pt^{II}}$ complexes having $\mathrm{Me_3SiCH_2^-}$[9] or carbene[10] ligands. For unsaturated σ-hydrocarbyl complexes, the problem will be discussed in later Parts.[11]

Reactions of Trialkyltin Acetylides with some Transition-metal Complexes.—Transition-metal acetylides have usually been prepared by *metathesis* involving LiX, NaX, or $\mathrm{MgX_2}$ elimination (X = halide).[12] This has now been extended to include chlorotrimethylstannane elimination [equation (1)]. The use of a group IV acetylide is novel except for reports on (i) the $\mathrm{Pt_2Cl_4(C_2H_4)_2}$–$\mathrm{Me_3Si{\cdot}C{:}CPh}$ system, from which chlorotrimethylsilane and ethylene were obtained,[13a] and (ii) the $\mathrm{Co(CO)_2(\pi\text{-}C_5H_5)}$–$\mathrm{Me_3Si{\cdot}C{:}CPh}$ system, which gives π-cyclobutadiene–cobalt derivatives.[13b]

$$\mathrm{LMCl + Me_3Sn{\cdot}C{:}CPh \longrightarrow LM{\cdot}C{:}CPh + Me_3SnCl} \quad (1)$$

Another route to transition-metal acetylides has involved *oxidative addition* reactions, using the addenda $\mathrm{Hg(C{:}CR)_2}$ (R = Ph or $\mathrm{C_5H_{11}}$) or $\mathrm{HC{:}CCO_2Et}$ with $\mathrm{IrCl(CO)(PPh_3)_2}$,[14] and also $\mathrm{BrC{:}CPh}$,[15] $\mathrm{IC{:}CI}$,[15] or HC:CR

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[R = $HOCR^1R^2$,[16] with $Pt(PPh_3)_4$]. Tin compounds, $R_3Sn{\cdot}C{\vdots}CPh$ (R = Me or Et) have now been found to undergo such a reaction (with or without elimination of neutral ligands) [equation (2)] with some d^{10} or d^8 substrates; for Pt^0, Scheme 1; for Rh^I, Scheme 2; and Ir^I, Scheme 3. Attempts to prepare molybdenum acetylides from Mo^0 d^6 precursors, by oxidative addition and concomitant displacement of a labile ligand, were unsuccessful; by contrast with the preparation of $[Mo(C{\vdots}CR)(CO)_5]^-$ from the hexacarbonyl and sodium acetylides,[17] $Me_3SnC{\vdots}CPh$ did not react with (norbornadiene)$Mo(CO)_4$ or $Mo(CO)_6$. For oxidative addition reactions with $Me_3Sn{\cdot}C{\vdots}CPh$ there are, in principle, two possibilities: a two-fragment [equation (2a)] or a single-fragment [equation (2b)] process; although the problem is not yet definitely settled, subsequent reference will assume path (2a). Evidence for mono-*hapto*-(I) rather than di-*hapto*-(II) structures for the adducts is discussed below.

TABLE 1

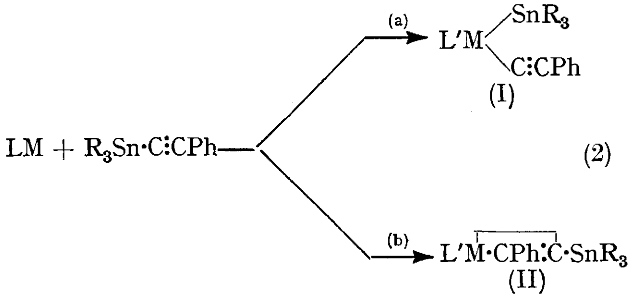
Syntheses of transition-metal acetylides

Reaction type	Reagents	Reaction conditions	Product (yield %)
A	$RhCl(PPh_3)_3 + LiC{\vdots}CPh$	1 : 1·2, THF–ether–benzene, 0°, ½ h	$Rh(C{\vdots}CPh)(PPh_3)_3$ (?) (48)
A	$RhCl(CO)(PPh_3)_2 + LiC{\vdots}CPh$	1 : 1, THF–ether–benzene, 0°, 2 h	(V) (*ca.* 40)
A	$RhCl(CO)(PPh_3)_2 + Me_3SnC{\vdots}CPh$	1 : 4, benzene, reflux, 1½ h	(V) (95)
A	$IrCl(CO)(PPh_3)_2 + LiC{\vdots}CPh$	1 : 1·1, THF–ether–benzene, 20°, ¾ h	(VII; $P = PPh_3$) (52)
B	$RhCl(PPh_3)_3 + Me_3SnC{\vdots}CPh$	1 : 2·5, benzene, 20°, *ca.* 4 h	(IV) (*ca.* 70)
B	$IrCl(CO)(PMe_2Ph)_2 + Me_3SnC{\vdots}CPh$	1 : 2, benzene, 50°, 4 h	(VI; $P = PMe_2Ph$, R = Me) (60)
B	$IrCl(CO)(PPh_3)_2 + Me_3SnC{\vdots}CPh$	1 : 3, benzene, 50°, 5 h	(VI; $P = PPh_3$, R = Me) (48)
B	$IrCl(CO)(PPh_3)_2 + Et_3SnC{\vdots}CPh$	1 : 3·5, benzene, reflux, 1 h	(VI; $P = PPh_3$, R = Et) (*ca.* 20) + (VII; $P = PPh_3$)
C	$Pt(PPh_3)_3 + Me_3SnC{\vdots}CPh$	1 : 2·25, benzene, 20°, ½ h	(III; $P = PPh_3$, R = Me) (*ca.* 95)
C	$Pt(PMePh_2)_4 + Me_3SnC{\vdots}CPh$	1 : 2, benzene, reflux, 1½ h	(III; $P = PMePh_2$, R = Me) (80)
C	$Pt(PPh_3)_4 + Me_3SnC{\vdots}CPh$	1 : 1·1, benzene, 20°, 1 h	(III; $P = PPh_3$, R = Me) (*ca.* 80)
C	$Pt(PPh_3)_4 + Et_3SnC{\vdots}CPh$	1 : 1·25, benzene, 20°, *ca.* 4 h	(III; $P = PPh_3$, R = Et) (60)
C	$Rh(C{\vdots}CPh)(PPh_3)_3 + Me_3SnC{\vdots}CPh$	1 : 3·5, benzene, 20°, 17 h	(IV) †
C	$Ir(C{\vdots}CPh)(CO)(PPh_3)_2 + Me_3SnC{\vdots}CPh$	1 : 2, benzene, 20°, 9 h	(VI; $P = PPh_3$, R = Me)
C	$Mo(CO)_6 + Me_3SnC{\vdots}CPh$	1 : 1, n-hexane, 20°, photolysed, 15 h	No reaction
C	nor-$C_7H_8Mo(CO)_4 + Me_3SnC{\vdots}CPh$	1 : 1, THF, reflux, 4 h	No reaction
D	$[Mo(\pi\text{-}C_5H_5)(CO)_3]_2 + Me_3SnC{\vdots}CPh$	1 : 1, diglyme, reflux, 3 h	$Mo(\pi\text{-}C_5H_5)(SnMe_3)(CO)_3$ (61)
D	$Co_2(CO)_8 + Me_3SnC{\vdots}CPh$	1 : 1, THF, 20°, ½ h	$Co(SnMe_3)(CO)_4$ (24) + $[Co_2(C{\vdots}CPh)(CO)_6]_2$ (?)

Abbreviations

Reaction type: Metathesis, A. Oxidative addition *and* metathesis, B. Oxidative addition, C. Oxidative cleavage, D.

† Identified spectroscopically.



(I)

(II)

(2)

Oxidative cleavage reactions [equation (3)] have been examined using $Me_3Sn{\cdot}C{\vdots}CPh$ and substrates containing metal–metal bonds, $Co_2(CO)_8$ and $[Mo(\pi\text{-}C_5H_5)(CO)_3]_2$. In both cases, the fragment $LM\text{–}SnMe_3$ has been isolated and characterised. Cobalt acetylides are unknown;[18] and it is possible that such a compound would readily rearrange into an acetylenic complex. In the molybdenum experiment, $Mo(\pi\text{-}C_5H_5)(C{\vdots}CPh)(CO)_3$[19] was identified spectroscopically in the reaction mixture.

$$LM{\cdot}ML + R_3Sn{\cdot}C{\vdots}CPh \longrightarrow L'M{\cdot}SnR_3 + L''M{\cdot}C{\vdots}CPh \quad (3)$$

Related oxidative addition reactions are known, for other tin compounds R_3MY. Reactive species include those in which Y = H,[20] Cl,[21] C_5H_5,[3,22] or $CF{\vdots}CF_2$;[11] however, when Y = $CH{\vdots}CH_2$,[11] CH_2Ph,[23] or C_6F_5,[23] there is no addition. The acetylide $Me_3Sn{\cdot}C{\vdots}CPh$ appears to be the most reactive of these addenda. This is probably due to the considerable ionicity of the Sn–C bond and the nucleophilicity of the tin acetylide. The former is related to the stability of the derived anion Y^-; and thus the high reactivity of the perfluorovinyl in contrast to the vinyl compound is explained.[11] The lack of reactivity of Me_3SnCH_2Ph and $Me_3SnC_6F_5$ suggests that the group Y should possess the ability to coordinate to the transition metal *via* unshared electrons or π-bonds in the transition state (note, however, the case of Y = H).

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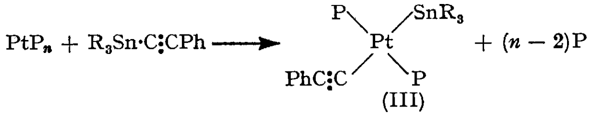
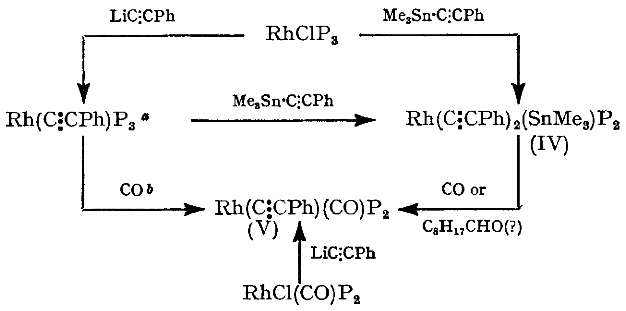
The metathesis or alkynylation reactions were conducted using either LiC:CPh or $Me_3Sn{\cdot}C{:}CPh$. For halogen-containing substrates, [*e.g.* $RhCl(PPh_3)_3$], oxidative addition of $Me_3Sn{\cdot}C{:}CPh$ [equation (2)] occurred *together* with Me_3SnCl elimination [equation (1)]. The analogous reaction of $IrCl(CO)P_2$ ($P = PPh_3$ or PMe_2Ph), when conducted in benzene under reflux, gave an impure product, but milder reaction conditions (50°, 1 h) proved more satisfactory. The oxidative cleavage reaction was found to occur readily for $Co_2(CO)_8$ (THF, 20°, $\frac{1}{2}$ h) but much less readily for $[Mo(\pi\text{-}C_5H_5)(CO)_3]_2$ (diglyme, heating under reflux, 3 h); the reactivity sequence parallels that found for a related complex, $Me_3Sn{\cdot}C_5H_5$.[3,24]



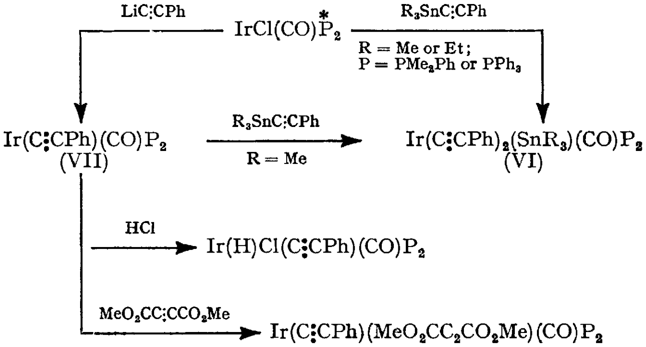
SCHEME 1 Oxidative addition to Pt^0 substrates

($P = PPh_3$, n = 3 or 4;
$P = PPh_2Me$, n = 4;
R = Me or Et)



[a] Not obtained analytically pure. [b] Compound (V) is not obtained pure by this procedure.

SCHEME 2 The chemistry of Rh^I and Rh^{III} acetylides ($P = PPh_3$)



SCHEME 3 The chemistry of Ir^I and Ir^{III} acetylides

* Unless otherwise stated $P = PPh_3$.

Tris(triphenylphosphine)platinum(0) proved to be more reactive towards oxidative addition than the tetrakis-complex. Reactions were faster with $Me_3Sn{\cdot}C{:}CPh$ than $Et_3Sn{\cdot}C{:}CPh$. The latter observation may be due to steric factors; however, the trimethyl derivative is probably more ionic in character. The acetylide reactivity difference accounts for the formation of a significant amount of $Ir(C{:}CPh)(CO)P_2$ (VII) together with $Ir(C{:}CPh)_2(SnEt_3)(CO)P_2$, the analogue of (VI), in the reaction of Vaska's compound with $Et_3Sn{\cdot}C{:}CPh$, but not in the reaction with $Me_3Sn{\cdot}C{:}CPh$ (Scheme 3). The latter reaction affords exclusively (VI), even when a 1 : 1 mol ratio of reactants is used, and unchanged *trans*-chloro(carbonyl)bis(triphenylphosphine)iridium(I) is recovered. Hence the reaction is probably a two-step process: a relatively slow first step of metathesis yielding (VII), followed by a faster oxidative addition thereto of another molecule of tin acetylide to yield the Ir^{III} complex, *e.g.* (VI).

There is an interesting contrast (Scheme 2) in the reactions of phenylethynyltrimethylstannane with chlorocarbonylbis(triphenylphosphine)rhodium(I) [to give (V), the product of metathesis] and chlorotris(triphenylphosphine)rhodium(I) [to give (IV), the product of metathesis *and* oxidative addition]. This suggests that substitution of a triphenylphosphine ligand in Wilkinson's compound by CO inhibits the oxidative addition process, although for the Ir analogue, Vaska's compound, there is such reactivity (*vide supra*). In the context of other oxidative additions (*e.g.* ref. 25), the reactivity order $RhCl(PPh_3)_3 > RhCl(CO)(PPh_3)_2 < IrCl(CO)(PPh_3)_2$ is not uncommon. The reaction of $RhCl(CO)(PPh_3)_2$ with $Me_3Sn{\cdot}C{:}CPh$ to give (V) is the preferred route to the Rh^I acetylide; the reaction of phenylethynyltris(triphenylphosphine)rhodium(I) with carbon monoxide gave a mixture of products.

The Structure of the Rh, Ir, *and* Pt *Acetylides*.—Spectroscopic data for the new compounds are in Table 2. The platinum compounds (III) are pale yellow, reasonably air-stable (>1 day) crystalline solids, which with the exception of the diphenylmethylphosphine derivatives are only sparingly soluble in benzene. Compound (III; R = Me, $P = PPh_3$), is formulated as the product of a two-fragment addition, because there is evidence for a terminal acetylide, ν(C:C) *ca.* 2100 cm^{-1}, and a Me_3Sn group attached to Pt [^1H n.m.r. shows a 1 : 4 : 1 triplet, J(Pt–H) = 16·0 Hz, with additional satellites due to coupling of methyl protons with ^{117}Sn and ^{119}Sn, J(Sn–H) = *ca.* 88 Hz]. The ^{31}P n.m.r. spectrum shows a weak single peak, which implies a *trans*-geometry. The ^1H n.m.r. spectrum of (III; $P = PMePh_2$), exhibits a broad unresolved multiplet due probably to inter- or intra-molecular phosphine exchange.[26]

Compound (IV) is an air-stable (>3 months) complex, deposited as red triclinic crystals from a benzene–n-hexane solution. Upon exposure to air, it slowly decomposed (>1 h) in benzene solution. This compound is so formulated, rather than a di-*hapto*-complex, partly by analogy, and also on the basis of spectra. In the i.r., spectrum, there are absorptions assigned to

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asymmetric and symmetric combinations of terminal acetylide stretching modes. The ^1H n.m.r. spectrum shows a singlet, showing that all the Me groups are magnetically equivalent. An *X*-ray crystal structure determination of the compound is in progress. The chemical properties are consistent with structure (IV) (see below).

The i.r. spectrum of compound (VI; $P = Ph_3P$) reveals a band at 2018 cm^{-1}, consistent with a carbonyl stretching frequency of an Ir^{III} rather than an Ir^{I} species. This, together with i.r. and n.m.r. data similar to those discussed for (IV), supports the mono-*hapto*-assignment.

TABLE 2

Physical data for new acetylides

Compound	Colour	M.p. (t/°C) [c]	Selected i.r. data (cm^{-1}) [d] ν(C:C)	ν(CO)	Selected ^1H n.m.r. data (τ) (Me_3Sn)	Ph	Analytical results Found (%) C	H	Cl	Required (%) C	H	Cl
$Rh(C{:}CPh)(PPh_3)_3$ [a]	Brown		2100br				74·0	5·5		75·2	5·1	
(V)	Yellow	151—154 (d)	2092	1958			69·5 (71·5) †	4·9 (5·1) †		71·4	4·6	
(IV)	Red	140—146	2082sh 2073		9·39 (s) [f]	*ca.* 1·9 (m) 2·95 (m)	67·5	5·3	Trace	65·0	4·9	0·0
(VII; $P = PPh_3$) [b]	Orange-yellow	143—150 (d)	2118	1973			63·5 *	4·4		63·9	4·1	
(VI; $P = PMe_2Ph$, $R = Me$)	Yellow		2120	1995 (2030w)	9·04 (s) [f,g]	2·35 (m) 3·04 (m)	50·8	4·8		50·1	4·8	
(VI; $P = PPh_3$, $R = Me$)	Cream	153—155 (d)	2122	2018	9·19 (s) [f]	*ca.* 2·0 (m) 3·0 (m)	61·7	4·9	Trace	60·5	4·4	0·0
(VI; $P = PPh_3$, $R = Et$)	Yellow						59·5	4·8		61·5	4·8	
$Ni(C{:}CPh)(SnMe_3)(PPh_3)_2$ [a]	Dark green											
(III; $P = PPh_3$, $R = Me$)	Pale yellow	180—182	2100		9·53 (s) [h,i]		57·9	4·8		57·3	4·5	
(III; $P = PMePh_2$, $R = Me$)	Pale yellow	120—122	2110		9·50 (s) [f,j]	2·50 (m) 2·95 (m)	51·6	4·7		51·6	4·7	
(III; $P = PPh_3$, $R = Et$)	Pale yellow	165—167 (d)	2108				58·1	5·0		58·5	4·9	
$IrHCl(C{:}CPh)(CO)(PPh_3)_2$	White	191—192 (d)	2128	2050 [e]			60·2	4·1		61·2	4·1	
$Ir(C{:}CPh)(MeO_2CC_2CO_2Me)(CO)(PPh_3)_2$	Yellow (cream)	50—60 (d)	2112	1980 1745 1680			61·7	4·8		62·0	4·5	

[a] Not obtained analytically pure. [b] See ref. 31. [c] Sealed cap. [d] Nujol mull. [e] ν(IrH) 2225 cm^{-1}. [f] C_6D_6 solvent, used as internal standard. [g] (P–Me) = 8·4 (m) τ. [h] C_6H_6 solvent, used as internal standard. [i] $J(^{195}Pt–H)$ = 16·0 Hz; J(Sn–H) = *ca.* 88 Hz. [j] (P–Me) = 8·23 (m) τ; $J(^{195}Pt–H)$ = 9 Hz.
* See ref. 31. † Analysis figures without parentheses for compound prepared by LiCl elimination, whilst those inside parentheses for compound prepared by Me_3SnCl elimination.

Chemistry of the Rh, Ir, *and* Pt *Acetylides*.—Some experiments were carried out with the platinum compound (III; $P = PPh_3$). Neither methyl nor benzyl chloride proved reactive, although elimination of chlorotrimethylstannane (so often a feature in organotin chemistry; *e.g.* see ref. 27) might have been expected. Likewise, hydrogen chloride, when used in 1 : 1 stoicheiometry in diethyl ether, appeared to be unreactive. However, in a 2HCl : 1(III) reaction in ether, hydridochlorobis(triphenylphosphine)platinum(II) was formed quantitatively; and with excess of gaseous hydrogen chloride, *cis*-$PtCl_2(PPh_3)_2$ was obtained exclusively. The reason for these two latter observations is not clear, since there is no evidence that *trans*-$Pt(H)Cl(PPh_3)_2$ is converted into *cis*-$PtCl_2(PPh_3)_2$ with an excess of hydrogen chloride. In the reactions of *cis*- and *trans*-$Pt(C{:}CPh)_2(PPh_3)_2$ with an excess of hydrogen chloride, *cis*-$PtCl_2(PPh_3)_2$ and *trans*-$PtCl(C{:}CPh)(PPh_3)_2$ were the products obtained respectively.[28] In the latter case, after the replacement of the first acetylide ligand by Cl^-, replacement of the second $\bar{C}{:}CPh$ is inhibited by the low *trans*-influence of the chloride ligand. This implies that the reaction of (III) with hydrogen chloride is unlikely to proceed through a first step involving phenylacetylene elimination; the resulting $PtCl(SnMe_3)(PPh_3)_2$ would not react further with hydrogen chloride since the trimethylstannyl ligand is *trans* to a chloride ligand. The (unsuccessful) reaction of (III) with ammonium hexafluorophosphate was investigated in an attempt to establish a proton transfer, as had been achieved with the same reagent and a Pt^{II} imidoyl complex.[29]

The rhodium compound (IV) was converted into compound (V) by reductive elimination using either carbon monoxide or nonanal. Although at first sight this might appear to support the di-*hapto*-structure for (IV) (the reactions are then simple ligand displacements), there is precedence for similar reactions. Thus, $Rh(H)Cl(GeEt_3)(PPh_3)_2$ is similarly reduced by addition of carbon monoxide or ethylene;[25] it was postulated that the mechanism may proceed *via* predissociation to triethylgermane followed by co-ordination of the neutral ligand to rhodium.

The iridium compound (VII) with hydrogen chloride or acetylene dicarboxylic ester gave 1 : 1 adducts. The former result contrasts with the preparation of $Ir(H)Cl_2(CO)(PPh_3)_2$ from $Ir(C{:}CR)(CO)(PPh_3)_2$ ($R = Me$, Et, or Bu^t), and hydrogen chloride.[30] No reaction was obtained upon heating (VII) with t-butylacetylene, which is consistent with the displacement of $EtC{:}CH$ from $Ir(C{:}CEt)(CO)(PPh_3)_2$ by an excess of $PhC{:}CH$, a more activated acetylene.[30]

EXPERIMENTAL

General Procedures.—Benzene and n-hexane were stored over sodium–potassium alloy and distilled from it before use. Diglyme was distilled from sodium. Diethyl ether and THF were distilled from sodiobenzophenone. Solvents

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[27] K. Jones and M. F. Lappert, 'Organotin Compounds,' ed. A. K. Sawyer, Marcel Dekker, New York, vol. 2, 1971, p. 528.

[28] I. Collamati and A. Furlani, *J. Organometallic Chem.*, 1969, **17**, 457.

[29] P. M. Treichel, J. J. Benedict, R. W. Hess, and J. P. Stenson, *Chem. Comm.*, 1970, 1627.

[30] C. K. Brown, D. Georgiou, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1971, 3120.

[31] R. Nast and L. Dahlenburg, *Chem. Ber.*, 1972, **105**, 1456.

were rigorously degassed under vacuum before use and all reactions were performed under an atmosphere of dry, oxygen-free nitrogen. M.p.s, unless otherwise stated, were determined in sealed evacuated capillaries. Analyses were carried out by Mr. and Mrs. A. G. Olney of the Departmental Microanalytical Laboratory and by Alfred Bernhardt, West Germany. I.r. spectra were recorded using a Perkin-Elmer 457, ^1H n.m.r. spectra using a Varian T60, A60, or HA 100 instrument, and mass spectra were obtained on an A.E.I. MS9 or Hitachi RMU-6 machine.

$RhCl(PPh_3)_3$,[32] $Rh(o\text{-}PPh_2C_6H_4)(PPh_3)_2$,[33] $IrCl(CO)(PPh_3)_2$,[34] $Pt(PPh_3)_3$,[35] $Pt(PPh_3)_4$,[35] $Pt(PMePh_2)_4$,[36] and (norbornadiene)$Mo(CO)_4$ [37] were prepared according to published procedures. Gifts of $Et_3SnC\vdots CPh$ and $Me_3SiC\vdots CPh$ from Mr. B. Josiah, and $[Mo(\pi\text{-}C_5H_5)(CO)_3]_2$, from Dr. S. A. Keppie are gratefully acknowledged. $Me_3SnC\vdots CPh$ was prepared either from $Me_3SnN\vdots CPh_2$ and $PhC\vdots CH$,[5] or from Me_3SnCl and $LiC\vdots CPh$, as described below.

Phenylacetylene (5·5 ml, 5·1 g, 50 mmol) in diethyl ether (20 ml)–THF (20 ml) was added dropwise to a stirred solution of n-butyl-lithium (50 mmol) in n-pentane (33 ml), at −78°. It was allowed to attain room temperature. Trimethyltin chloride (9·95 g, 50 mmol) in Et_2O (20 ml)–THF (20 ml) was added dropwise. The solution was stirred for 1 h at 20° and was then concentrated to *ca.* 60 ml *in vacuo*. Lithium chloride was separated by filtration. Solvent was removed *in vacuo*; the residue gave colourless phenylethynyl(trimethyl)stannane (10·7 g, 81%), b.p. 56—58°/0·1 mmHg (authentic spectra and analyses).

Metathetical Exchange.—Phenylethynyl-lithium with chlorotris(triphenylphosphine)rhodium(I). The lithium reagent (*ca.* 1·2 mmol) in THF–Et_2O [20 ml (3 : 1)] was added dropwise during 45 min to a rapidly stirred solution of the rhodium complex (0·46 g, 1·0 mmol) in benzene (25 ml) at 20°. Stirring was continued for ½ h. Volatiles were removed *in vacuo*. Benzene (15 ml) was added to the residue to give a cloudy solution. The volume of the solvent in the filtrate was reduced to *ca.* 10 ml and n-hexane (40 ml) was added to give, as a brown powder, *phenylethynyltris(triphenylphosphine)rhodium*(I) (0·48 g, 48%).

Phenylethynyl-lithium with trans-*chlorocarbonylbis(triphenylphosphine)rhodium*(I). Addition (dropwise during ½ h) of the lithium reagent (1·0 mmol) in THF–Et_2O (3 : 1, 20 ml) to a stirred yellow slurry of the rhodium complex (0·68 g, 9·97 mmol) in benzene (50 ml) at 20° caused the mixture to become red. The solution was stirred for *ca.* 2 h. Solvent was removed *in vacuo*, whereafter benzene (20 ml) was added. After filtration to remove lithium chloride, the volume of benzene was further reduced and n-hexane was added to give, upon cooling to −30°, a grey-red powder, which was recrystallised (C_6H_6–n-C_6H_{14}) to give the orange-buff powder of *phenylethynylcarbonylbis(triphenylphosphine)rhodium*(I) (*ca.* 40%). A yellow solid (Found: C, 65·1; H, 4·6%) was obtained (on one occasion) by washing the orange-buff solid with Et_2O (5 × 10 ml).

Phenylethynyl(trimethyl)stannane with trans-*chlorocarbonylbis(triphenylphosphine)rhodium*(I). The stannane (0·4 ml, 2·0 mmol) was added to a stirred solution of the rhodium complex (0·35 g, 0·50 mmol) in benzene (30 ml) and the mixture was heated under reflux for 1½ h. The bulk of the benzene was removed *in vacuo* and n-hexane was added to give a bright yellow precipitate, which was washed with n-hexane (2 × 30 ml) and then dried (½ h; 0·001 mmHg). The yellow crystalline product (0·36 g, 95%) was identified as *phenylethynylcarbonylbis(triphenylphosphine)rhodium*(I). This is the preferred procedure (*cf.* $PhC\vdots CLi$, above) for the preparation of $Rh(C\vdots CPh)(CO)(PPh_3)_2$.

Phenylethynyl-lithium with trans-*chlorocarbonylbis(triphenylphosphine)iridium*(I). Phenylethynyl-lithium (1·3 mmol) in Et_2O–THF–n-C_5H_{12} (30 ml, 1 : 1 : 1) was added slowly (¾ h) to a slurry of the iridium compound (0·78 g, 1·0 mmol) in benzene (35 ml) at 20°. The orange solution was stirred for *ca.* ½ h. Solvent was removed *in vacuo*, benzene (*ca.* 20 ml) was added and the solution was filtered. The volume of the filtrate was reduced to *ca.* 5 ml and n-hexane (30 ml) was added. The yellow precipitate was washed with diethyl ether (25 ml), dried (1 h, 0·05 mmHg), and identified as *phenylethynylcarbonylbis(triphenylphosphine)iridium*(I) (0·45 g, 52%).

Oxidative Addition with Metathetical Exchange.—Phenylethynyl(trimethyl)stannane with chlorotris(triphenylphosphine)rhodium(I). The stannane (0·50 ml, 2·5 mmol) was added to a slurry of the rhodium complex (0·92 g, 1·0 mmol) in benzene (50 ml), and the mixture was stirred at 20° for 24 h (reaction complete in *ca.* 4 h). The volume of benzene was reduced to *ca.* 20 ml and the solution was filtered. n-Hexane was then added dropwise to the filtrate to yield deep red crystals of *bis(phenylethynyl)trimethylstannylbis(triphenylphosphine)rhodium*(III) (*ca.* 70%).

Phenylethynyl(trimethyl)stannane with trans-*chlorocarbonylbis(dimethylphenylphosphine)iridium*(I). The iridium compound (0·35 g, 0·65 mmol) was heated (oil-bath temperature 40—50°) with the stannane (0·28 ml, 1·3 mmol) in benzene (15 ml) for 4 h. The volume of solvent was reduced to *ca.* 3 ml and n-hexane (10 ml) was added to give a yellow solid which was recrystallised (C_6H_6–n-C_6H_{14}) to give pale yellow crystals of *bis(phenylethynyl)trimethylstannylcarbonylbis(dimethylphenylphosphine)iridium*(III) (0·34 g, 60%).

Phenylethynyl(trimethyl)stannane with trans-*chlorocarbonylbis(triphenylphosphine)iridum*(I). The stannane (0·60 ml, 3·0 mmol) was added to a stirred solution of the iridium compound (0·78 g, 1·0 mmol) in benzene (40 ml). There was no sign of reaction after 12 h of stirring at 20°, whereafter the mixture was heated (oil-bath temperature, 50°) for 5 h, to give a dark brown-green colour. Most of the benzene was removed *in vacuo* and n-hexane was added dropwise to give cream-yellow crystals of *bis(phenylethynyl)trimethylstannylcarbonylbis(triphenylphosphine)iridium*(III) (0·53 g, 48%).

Phenylethynyl(triethyl)stannane with trans-*chlorocarbonylbis(triphenylphosphine)iridium*(I). The stannane (0·42 ml, *ca.* 1·75 mmol) was added to a stirred solution of the iridium compound (0·39 g, 0·50 mmol) in benzene (30 ml), and the mixture was heated under reflux for 1 h. The volume of benzene was reduced to *ca.* 7 ml and Et_2O–n-C_6H_{14} (30 ml, 1 : 1) was added. A small amount of yellow solid (Found: C, 66·6; H, 4·7%) was deposited at this stage. The liquor was decanted, solvent was removed *in vacuo*, and the residue recrystallised (Et_2O–n-C_6H_{14}) to give *bis(phenyl-*

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[32] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1711.

[33] W. Keim, *J. Organometallic Chem.*, 1968, **14**, 179.

[34] J. P. Collman, C. T. Sears, and M. Kubota, *Inorg. Synth.*, 1968, **11**, 101.

[35] R. Ugo, F. Cariati, and G. La Monica, *Inorg. Synth.*, 1968, **11**, 105.

[36] P. Chini and G. Longoni, *J. Chem. Soc.* (*A*), 1970, 1542.

[37] J. J. Eisch and R. B. King, 'Organometallic Syntheses,' Academic Press, London, 1965, p. 124.

ethynyl)triethylstannylcarbonylbis(triphenylphosphine)iridium(III) (*ca.* 20%).

Oxidative Addition.—Phenylethynyltrimethylstannane with tris(triphenylphosphine)platinum(0). The stannane (0·25 g, *ca.* 0·19 ml, 0·97 mmol) was added to a stirred solution of the platinum complex (0·42 g, *ca.* 0·42 mmol) in benzene (25 ml). The reaction mixture was stirred for 30 min to afford a pale yellow solution. The volume of benzene was reduced to *ca.* 10 ml and n-hexane was added to give pale yellow crystals. Solvent was decanted off, and the solid was washed with n-hexane (2 × 20 ml), and after drying (1 h, 0·001 mmHg) gave *phenylethynyltrimethylstannylbis(triphenylphosphine)platinum*(II) (*ca.* 95%).

Phenylethynyltrimethylstannane with tetrakis(diphenylmethylphosphine)platinum(0). The stannane (0·2 ml, 1·0 mmol) was added to a stirred solution of the platinum complex (0·48 g, 0·48 mmol) in benzene (20 ml). The reaction mixture was heated under reflux for 1½ h. Solvent was removed *in vacuo* to give a yellow oil, which was heated at *ca.* 70°/0·02 mmHg to remove some of the free diphenylmethylphosphine. The residue was dissolved in acetone (5 ml); ethanol (10 ml) was added to give yellow crystals (at −30°). The crystals were washed with n-hexane (25 ml), and after drying (1 h, 0·05 mmHg) gave *phenylethynyltrimethylstannylbis(diphenylmethylphosphine)platinum*(II) (0·33 g, 80%).

Phenylethynyltrimethylstannane with tetrakis(triphenylphosphine)platinum(I). The stannane (0·34 ml, 1·70 mmol) was added to the stirred solution of tetrakis(triphenylphosphine)platinum(0) (1·86 g, *ca.* 1·5 mmol) in benzene (65 ml). The reaction mixture was stirred for *ca.* 15 h, although the reaction appeared to be complete within 1 h. Most of the benzene was removed *in vacuo* (to *ca.* 10 ml); n-hexane (30 ml) was added, giving pale yellow crystals of *phenylethynyltrimethylstannylbis(triphenylphosphine)platinum*(II) (*ca.* 80%).

Phenylethynyltriethylstannane with tetrakis(triphenylphosphine)platinum(0). The stannane (0·10 ml, 0·42 mmol) was added to a slurry of the platinum complex (0·41 g, 0·33 mmol) in benzene (30 ml). The reaction mixture was stirred for *ca.* 15 h at 20°, although after several hours the reaction appeared to be effectively complete, and the solution had become pale yellow-green. Volatiles were removed *in vacuo* and the residue was recrystallised (C_6H_6–n-C_6H_{14}) to afford pale yellow crystals of *phenylethynyltriethylstannylbis(triphenylphosphine)platinum*(II) (0·21 g, 60%).

Phenylethynyltrimethylstannane with phenylethynyltris(triphenylphosphine)rhodium(I). The stannane (0·11 ml, *i.e.*, an excess) was added to a stirred solution of the rhodium complex (0·15 g, *ca.* 0·17 mmol) in benzene (40 ml). The solution was stirred at 20° for 17 h and it gradually became deep red. Solvent was removed *in vacuo* and the oily residue was washed with n-hexane (10 ml). The red-brown solid was identified (i.r.) as bis(phenylethynyl)(trimethylstannyl)bis(triphenylphosphine)rhodium(III).

Phenylethynyltrimethylstannane with o-*phenylenediphenylphosphidobis(triphenylphosphine)rhodium*(I). The stannane (0·13 ml, *ca.* 0·66 mmol) was added to an orange solution of the rhodium complex (0·15 g, *ca.* 0·24 mmol) in benzene (20 ml). The reaction mixture was stirred for 24 h to give a deep red solution (orange meniscus). Most of the benzene was removed *in vacuo* and n-hexane was added to give a flocculent precipitate. Examination (i.r.) of both the insoluble and soluble fractions showed no evidence for bis(phenylethynyl)trimethylstannylbis(triphenylphosphine)rhodium(III).

Phenylethynyltrimethylstannane with trans-*phenylethynylcarbonylbis(triphenylphosphine)iridium*(I). The stannane (0·20 ml, 1·0 mmol) was added to a stirred solution of the iridium compound (0·42 g, 0·5 mmol) in benzene (50 ml). The reaction mixture was stirred for 9 h at 20° to give a brown solution, which was reduced in volume. *n*-Hexane was added to give cream-yellow crystals of *bis(phenylethynyl)trimethylstannylcarbonylbis(triphenylphosphine)iridium*(III).

Phenylethynyltrimethylstannane with bis(triphenylphosphine)nickel(0). The stannane (0·30 ml, 1·5 mmol) was added to a stirred solution of bis(triphenylphosphine)nickel(0)[38] (0·64 g, *ca.* 1·1 mmol) in benzene (25 ml). The reaction mixture was stirred for 20 min at 20° and was then filtered. n-Hexane (20 ml) was added to the filtrate to give dark green crystals, believed to be phenylethynyltrimethylstannylbis(triphenylphosphine)nickel(II) (0·38 g, 41%).

Phenylethynyltrimethylstannane with tetrakis(triphenylphosphine)nickel(0). Similar products were obtained upon addition of the stannane to tetrakis(triphenylphosphine)nickel(0). The pure product, $Ni(C{:}CPh)(SnMe_3)(PPh_3)_2$, was not obtained, due to decomposition on a chromatographic column and the similar solubility of the nickel complex and the other component triphenylphosphine.

Phenylethynyltrimethylstannane with carbonylmolybdenum(0) *complexes*. The stannane (*ca.* 2·5 mmol) in n-hexane (15 ml) or THF (5 ml) was added to a stirred suspension of hexacarbonylmolybdenum(0) (with irradiation for 15 h), or norbornadienetetracarbonylmolybdenum(0) (*ca.* 2·5 mmol) under CO. In the latter reaction, some $Mo(CO)_6$ was identified; otherwise, there was no evidence of reaction.

Oxidative Cleavage.—Phenylethynyltrimethylstannane with bis[π-cyclopentadienyltricarbonylmolybdenum(I)]. The stannane (0·51 g, 0·39 ml, 2 mmol) in benzene (5 ml) was added dropwise to a solution of the molybdenum complex in benzene (15 ml). The solution was heated under reflux for 5 h, but solution i.r. examination indicated no reaction. Most of the benzene was removed *in vacuo*, and toluene was added, whereafter the solution was heated under reflux for 36 h. Most of the solvent was removed; filtration gave a precipitate of unchanged red molybdenum complex (authentic i.r.). n-Hexane was added to the filtrate, the solution was cooled to −78°, and the brown solid obtained was sublimed (50°/0·001 mmHg) to yield yellow π-cyclopentadienyl(trimethylstannyl)tricarbonylmolybdenum(II) (0·1 g, 12·5%) (Found: C, 32·9; H, 3·7. Calc. for $C_{11}H_{14}O_3SnMo$: C, 32·3; H, 3·5%).

The experiment was repeated on a 1 mmol scale using diglyme as solvent. The reaction mixture was heated under reflux for 3 h. Diglyme was removed at *ca.* 20 mmHg over many days. A yellow-green solid collected in the cold trap of the vacuum system with the solvent. A cooled (−78°) probe was inserted into the reaction flask, and π-cyclopentadienyl(trimethylstannyl)tricarbonylmolybdenum(II) (0·19 g, 61%) (Found: C, 32·1; H, 3·4%) was sublimed at 55°/0·001 mmHg.

Phenylethynyltrimethylstannane with octacarbonylcobalt(0). The stannane (0·33 ml, 1·66 mmol) was added to a stirred solution of the carbonyl (0·57 g, 1·66 mmol) in THF (15 ml), with immediate gas evolution, which ceased after *ca.* 10 min. Stirring was continued for 20 min. Most of the solvent was removed at *ca.* 100 mmHg, leaving a dark red solution;

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[38] R. J. De Pasquale, *J. Organometallic Chem.*, 1971, **32**, 381.

this was syringed onto a Florisil chromatographic column, using n-hexane as eluant. Three fractions were collected, concentrated, and cooled to −30°. The third fraction gave colourless crystals, after washing with ice-cold n-hexane, of impure trimethylstannyltetracarbonylcobalt(I) (0·13 g, 24%) (Found: C, 20·8; H, 3·03. Calc. for $C_7H_9CoO_4Sn$: C, 25·1; H, 2·70%) (parent ion at $m/e = 335$). The first fraction gave dark red-brown crystals of $[Co_2(C{\vdots}CPh)(CO)_6]_2$ [39] (*ca.* 5%) (Found: C, 43·1; H, 1·40. Calc. for $C_{28}H_{10}CO_4O_{12}$: C, 43·4; H, 12·9%). The second fraction gave a mixture of the two compounds.

Experiments with the Transition-metal Acetylide Complexes.—*Lack of reaction between phenylethynyltrimethylstannylbis(triphenylphosphine)platinum*(II) *and methyl, benzyl, or hydrogen chloride* (1 *equiv.*) *and ammonium hexafluorophosphate.* Reagents were recovered from the Pt^{II} complex and the following: (i) MeCl bubbled (15 min) through complex in C_6H_6 at 20°; (ii) $PhCH_2Cl$ in C_6H_6, heating under reflux (6 h); (iii) HCl (in Et_2O) and heating under reflux (2 h); and (iv) NH_4PF_6 in MeOH and heating under reflux (½ h).

Phenylethynyltrimethylstannylbis(triphenylphosphine)platinum(II) *with hydrogen chloride* (⩾2 *equiv.*). Hydrogen chloride (4·4 ml of a 0·023M-solution in ether, 0·1 mmol) was added dropwise to a stirred solution of the platinum complex (0·1 g, 0·1 mmol) in benzene (10 ml); the colour was gradually discharged and a white solid was precipitated. The bulk of the solvent was removed and more ether added to give *trans*-hydridochlorobis(triphenylphosphine)platinum (II) (0·08 g, 100%) (Found: C, 57·9; H, 4·4. Calc. for $C_{30}H_{31}ClP_2Pt$: C, 57·2; H, 4·1%) (authentic spectra).

Hydrogen chloride gas was bubbled for 3 min into a solution of the platinum complex (0·28 g, 0·29 mmol) in benzene (20 ml). Within 30 s the yellow colour was discharged and a white precipitate formed. The volume of benzene was reduced to *ca.* 10 ml *in vacuo* and diethyl ether was added to give *cis*-dichlorobis(triphenylphosphine)-platinum(II) (0·18 g, *ca.* 76%) (authentic spectra).

Phenylethynyltris(triphenylphosphine)rhodium(I) *with carbon monoxide.* Carbon monoxide (after passage through a phosphorus pentoxide drying tower) was bubbled for 1 h through a benzene solution of the rhodium acetylide. The volume of benzene was reduced and n-hexane was added to give a buff precipitate [weak ν(C⋮C)] which was discarded. More n-hexane was added to the mother liquor, and the solution was then set aside at room temperature for several days. Dark brown (yellow when crushed) crystals of impure phenylethynylcarbonylbis(triphenylphosphine)rhodium(I) (Found: C, 72·8; H, 5·0%) were gradually deposited.

Reaction of bis(phenylethynyl)trimethylstannylbis(triphenylphosphine)rhodium(III) *with carbon monoxide or nonanal.* Carbon monoxide was bubbled for 2 min through a solution of the rhodium complex in benzene at 20°. The colour of the solution changed from red to yellow-brown. Solvent was removed *in vacuo* and the residue was washed with n-hexane to give the dull yellow powder of phenylethynylcarbonylbis(triphenylphosphine)rhodium(I) (Found: C, 71·5; H, 5·1. $C_{45}H_{35}OP_2Rh$ requires C, 71·4; H, 4·6%); ν(C⋮C), 2092 cm^{-1}; ν(CO), 1957 cm^{-1}; the ^1H n.m.r. spectrum showed absence of a trimethylstannyl group. The phenylethynyltrimethylstannane was not recovered.

The rhodium complex was stirred with a large excess of nonanal in benzene at 20° for 17 h. The reaction mixture was heated under reflux for 15 min to give a yellow solution. Solvent was removed *in vacuo* leaving a yellow oil. An i.r. spectrum of this oil clearly indicated the presence of a rhodium(I) carbonyl species, ν(CO) *ca.* 1960 cm^{-1}.

Lack of reaction between phenylethynylcarbonylbis(triphenylphosphine)iridium(I) *and phenylethynyltrimethylsilane or t-butylacetylene.* A solution of the iridium complex (0·37 g, 0·44 mmol) and the silane (0·2 ml) in benzene (15 ml) was heated under reflux for 1 h. There was no significant reaction (i.r.).

There was no reaction upon heating under reflux a solution of the iridium complex (0·37 g) and t-butylacetylene (0·2 ml) in benzene (15 ml).

Slow Reaction of phenylethynylcarbonylbis(triphenylphosphine)iridium(I) *with diphenylacetylene.* A solution of the iridium complex (0·42 g, 0·5 mmol) and diphenylacetylene (0·26 g, 1·5 mmol) in benzene (10 ml) was stirred for 18 h at 20°. There was no significant reaction (i.r.). The reaction mixture was heated under reflux (1 h), and an i.r. spectrum indicated that some reaction (*ca.* 15%) had taken place, but separated products were not isolated from the complex reaction mixture, apart from the unchanged iridium acetylide.

Reaction of phenylethynylcarbonylbis(triphenylphosphine)-iridium(I) *with hydrogen chloride.* Hydrogen chloride was bubbled for 2 min through a solution of the iridium complex (0·21 g, *ca.* 0·25 mmol) in chloroform (30 ml). The yellow colour of the solution was immediately discharged and a white precipitate was formed. Solvent was removed *in vacuo* to give a white residue which, after being washed with diethyl ether and dried (1 h, 0·05 mmHg), gave hydridochlorophenylethynylcarbonyl(triphenylphosphine)iridium-(III) (*ca.* 100%) (authentic spectra).

In a related reaction, involving hydrogen bromide in methylenedichloride solution, a different, but unidentified yellow crystalline complex was isolated (Found: C, 44·8; H, 3·0%), ν(IrH), 2225 cm^{-1}, ν(CO), 2050 cm^{-1}.

Reaction of phenylethynylcarbonylbis(triphenylphosphine)-iridium(I) *with methyl acetylenedicarboxylate.* A solution of the iridium complex (0·69 g, 0·82 mmol) and ester (0·1 ml, *ca.* 0·82 mmol) in benzene (30 ml) was stirred at 20° for 2 h. Most of the benzene was then removed *in vacuo* and n-hexane (20 ml) was added to give a pale yellow-buff precipitate. This after washing with n-hexane (30 ml) and drying (1 h, 0·01 mmHg), gave the product of oxidative addition, $Ir(C{\vdots}CPh)(MeCO_2C_2CO_2Me)(CO)(PPh_3)_2$.

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[39] A. Ragni, G. Peyronel, and E. F. Trogu, *Atti. Soc. Nat. Mat. Modena*, 1963, **94**, 1 (*Chem. Abs.*, 1965, **63**, 6891b).