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Preliminary communication

Reactions of trialkyltin acetylides with some low oxidation state transition metal complexes: oxidative addition, oxidative cleavage, and alkynylation

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Compounds having tin-to-transition metal bonds have been the subject of much study[1]. Their formation by (i) an insertion reaction, as shown in Eqn. 1 is known for X = H[2], Cl[3], and C_5H_5[4]; and (ii) a cleavage reaction, as shown in Eqn. 2, is known for X = C_5H_5[5]. We now present data on systems in which X = C≡CPh. The new reactions may be regarded as derived from three basic types (or combinations of these), classified as oxidative addition (Eqn. 1), oxidative cleavage (Eqn. 2), and alkynylation (Eqn. 3). In Eqns. 1–3, M is a transition metal and L, L′, and L″ represent the remaining ligands attached to M. The use of organotins in the sense of Eqn. 3 (*cf.* Grignard reagents) is well-known, *inter alia* for X = allyl, indenyl, or fluorenyl[6]; Me_3Si–C≡CPh has similarly been employed[7]. Only two publications have dealt with the reactions of tin acetylides with transition metal complexes[8]. It is clear that, in general, the organotin acetylides are both more reactive and more versatile than the other derivatives (X = H, Cl, C_5H_5, or C_3H_5). We attribute this to the considerable ionicity of the Sn–C bond and the nucleophilicity of R_3Sn–C≡CPh. A somewhat similar pattern, but with lower reactivity, has also been observed[9] for X = $CF{=}CF_2$ (but not X = $CH{=}CH_2$[9], CH_2Ph[10], or C_6F_5[10]).

$$LM + R_3Sn{-}X \rightarrow L'M\begin{<}SnR_3\\X\end{} \quad (1)$$

$$LM{-}ML + R_3Sn{-}X \rightarrow L'M{-}SnR_3 + L''M{-}X \quad (2)$$

$$LM{-}Cl + R_3Sn{-}X \rightarrow LM{-}X + R_3Sn{-}Cl \quad (3)$$

The new reactions are summarized in Eqns. 4–8, in which P = PPh_3 unless otherwise (Eqn. 4) stated. For Eqns. 4–6, the solvent was benzene (except for reactions with LiCCPh, when THF/Et_2O/C_6H_6 was preferred) at 20–80° for ½–4 h. Some data on the new compounds, which gave satisfactory carbon + hydrogen analyses, are in Table 1. Structural assignments are based on IR and ^1H and ^{31}P NMR spectra, and on reactions. The stereochemistry of some of the new compounds is still uncertain.

TABLE 1

SELECTED DATA ON NEW COMPOUNDS

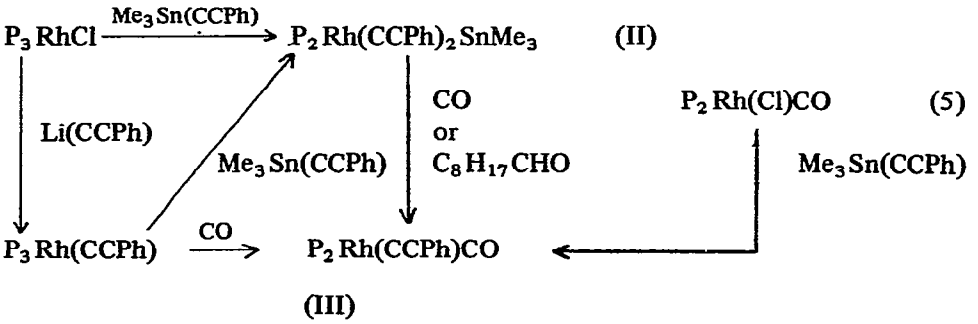
Compound (Yield, %)	M.p. (°) [a]	$\nu(C\equiv C)$ (cm^{-1}) [b]	Compound (Yield, %)	M.p. (°) [a]	$\nu(C\equiv C)$ (cm^{-1}) [b]
(I), P = PPh_3, R = Me (83) [c]	180–182	2100	(III) (90 [f]) [g]	151–154 (d)	2092 [k]
(I), P = PPh_3, R = Et (85) [c]	165–167 (d)	2108	(IV) (50) [h]	153–155 (d)	2122 [l]
(I), P = PPh_2Me, R = Me (79) [c]	120–122	2110	(V) (52) [i]	143–150 (d)	2118 [m]
(II) (40) [d]	140–146	2082(sh), 2073	(V) HCl (ca. 100) [i]	191–192 (d)	2128 [n]
$P_3Rh(CCPh)$ (66) [e]		2100(br)	(V)$MeO_2CC\equiv CCO_2Me$ (73) [g,h]	50–60 (d)	2112 [o]

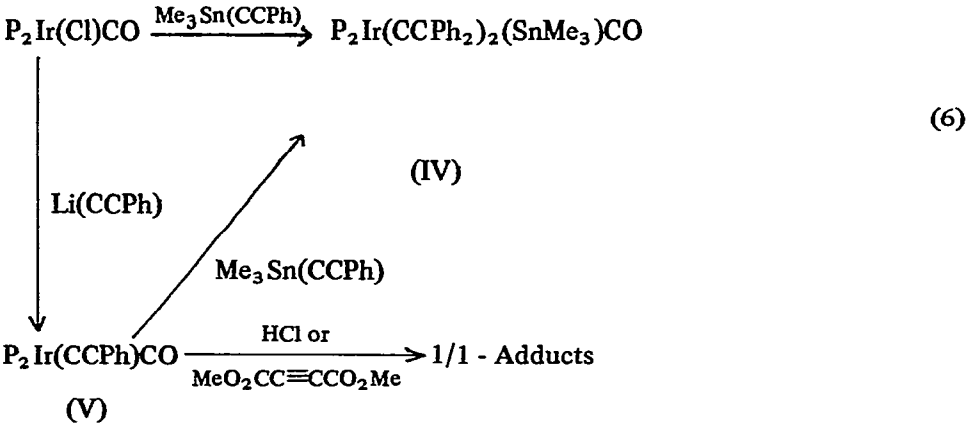
[a] Sealed cap. [b] Nujol mull. [c] Pale yellow. [d] Red. [e] Brown. [f] Yield refers to preparation from $P_2Rh(Cl)CO$; mixture of products obtained from $P_3Rh(CCPh)$ route. [g] Yellow. [h] Cream. [i] Orange-yellow. [j] White. [k] $\nu(CO)$ 1958 cm^{-1}. [l] $\nu(CO)$ 2018 cm^{-1}. [m] $\nu(CO)$ 1973 cm^{-1}. [n] $\nu(IrH)$ 2225, $\nu(CO)$ 2050 cm^{-1}. [o] $\nu(CO)$ 1980 (1745, 1680) cm^{-1}.

$$P_nPt + R_3Sn(CCPh) \rightarrow P_2Pt\begin{matrix}SnR_3\\CCPh\end{matrix} + (n\text{-}2)P \qquad (4)$$

(I)

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





$$[\pi\text{-}C_5H_5Mo(CO)_3]_2 + Me_3Sn(CCPh) \xrightarrow[CO,\ 36\ h]{\text{Diglyme, reflux}} \pi\text{-}C_5H_5Mo(CO)_3SnMe_3 + \text{unidentified products} \qquad (7)$$

$$Co_2(CO)_8 + Me_3Sn(CCPh) \xrightarrow{THF,\ 20^\circ,\ \frac{1}{2}\ h} Me_3Sn\text{–}Co(CO)_4 + \text{unidentified products} \qquad (8)$$

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