Interaction of Hydridocarbonyltriphenylphosphineiridium(I) Complexes with Alk-1-ynes†

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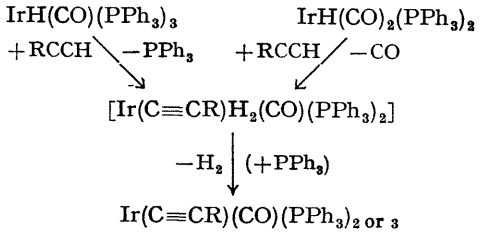
Summary Reaction of aliphatic alk-1-ynes with $IrH(CO)(PPh_3)_3$ or $IrH(CO)_2(PPh_3)_2$ results in loss of hydrogen and formation of novel acetylides $Ir(C{\equiv}CR)(CO)(PPh_3)_{2\text{ or }3}$: the square bistriphenylphosphine species undergo a wide range of oxidative-addition reactions.

THE intermediates in hydroformylation reactions of alkenes[1] and of conjugated dienes and allenes[2] derived from hydridocarbonyltris(triphenylphosphine)rhodium(I), or their considerably more stable analogues obtained from the iridium complexes $IrH(CO)(PPh_3)_3$ or $IrH(CO)_2(PPh_3)_2$ are known.

In studies related to the hydroformylation[3] of acetylenes the interaction of alk-1-ynes with these iridium complexes proceeds with loss of hydrogen and the formation of new iridium(I) acetylide complexes of stoicheiometry $Ir(C{\equiv}CR)(CO)(PPh_3)_{2\text{ or }3}$ ($R = Me$, Et, Bu^n, Bu^t, C_6H_{11}, CH_2OH, *etc.*) (see Scheme). This is in contrast to reactions using various activated acetylenes, where vinyl compounds of formula $Ir(R^1C{=}CHR^1)(R^1C{\equiv}CR^2)(CO)(PPh_3)_2$ were obtained by a hydride-transfer or insertion reaction.[4]

The present reaction with alk-1-ynes proceeds *via* an oxidative addition of $RC{\equiv}CH$ to the metal atom of the square complex produced by dissociation to give a *cis*-dihydrido-complex which then readily loses hydrogen. This reaction is in contrast to the addition of certain activated acetylenes to *trans*-$IrCl(CO)(PPh_3)_2$, to give hydrido-acetylides of iridium(III) of stoicheiometry $Ir(C{\equiv}CR)HCl(CO)(PPh_3)_2$.[5] It is therefore not surprising that, unlike *trans*-$IrCl(CO)(PPh_3)_2$, the square iridium(I) acetylides do not react with molecular hydrogen at 25° and 1 atm.



SCHEME

The new acetylides, $Ir(C{\equiv}CR)(CO)(PPh_3)_3$, are bright yellow, while the square complexes $Ir(C{\equiv}CR)(CO)(PPh_3)_2$, are orange yellow (Table). In solution the species are in

$$Ir(C{\equiv}CR)(CO)(PPh_3)_3 \rightleftarrows Ir(C{\equiv}CR(CO)(PPh_3)_2 + PPh_3 \qquad (1)$$

equilibrium (equation 1). The square complexes are

Representative iridium acetylide complexes[a]

Compound	I.r. spectrum[b]			N.m.r. spectrum[c]
	ν_{CO}	ν_{CC}	Other bands	
$Ir(C{\equiv}CMe)(CO)(PPh_3)_3$	1974s	2132w	—	8·59 (C_6H_6)
$Ir(C{\equiv}CBu^t)(CO)(PPh_3)_2$	1962s	2098w	—	9·24 (C_6H_6)
$Ir(C{\equiv}CEt)(O_2)(CO)(PPh_3)_2$	1998s	2146w	ν_{OO} 832m	7·72(q), 9·21(t) (*J* 7·5 Hz)(C_6H_6)
$Ir(C{\equiv}CMe)(SO_2)(CO)(PPh_3)_2$	2011s	2130w	1190s, 1040s	8·47[d] (C_6H_6)
$Ir(C{\equiv}CMe)(C_6N_4)(CO)(PPh_3)_2$	2058s	2159w	ν_{CN} *ca.* 2230m	8·46[d] ($CDCl_3$)
$Ir(C{\equiv}CMe)[C_2(CO_2Me)_2](CO)(PPh_3)_2$	2004s	2134w	ν_{CC} 1745s, ν_{CO_2Me} 1695s, 1681s	8·11, 8·62[d] (2: 1)($CDCl_3$)
$Ir(C{\equiv}CBu^n)MeI(CO)(PPh_3)_2$	2041s	—	—	—

[a] Good analyses were obtained for new compounds.
[b] Nujol mulls (cm^{-1}).
[c] At 100 MHz, 35° (τ values).
[d] In these compounds and in $Ir(C{\equiv}CMe)(O_2)(CO)(PPh_3)_2$ the methyl signal is a triplet (*J ca.* 2 Hz).

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† No reprints available.

analogues of *trans*-$IrCl(CO)(PPh_3)_2$ and undergo a similarly wide range of oxidative-addition and addition reactions but the acetylides are considerably more soluble in benzene or petroleum. The solid bistriphenylphosphine complexes react rapidly with air or oxygen even in the solid state to give pale cream adducts $Ir(C{\equiv}CR)(O_2)(CO)(PPh_3)_2$, but the tris-complexes are fairly stable to air. The addition of carbon monoxide gives the dicarbonyl $Ir(C{\equiv}CR)(CO)_2(PPh_3)_2$, which can be characterised in solution; there is no evidence of an insertion reaction to give acyl under mild conditions. The complexes also react with SO_2 to give green adducts, with an excess of alk-1-ynes to give orange solutions, and with tetracyanoethylene, dimethyl acetylenedicarboxylate, and methyl iodide to give white crystalline adducts.

We thank the donors of the Petroleum Research Fund of the American Chemical Society for support of this research.

(*Received, November* **13*th*,** 1970; *Com.* **1969.**)

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[1] G. Yagupsky, C. K. Brown, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1970, 1392.

[2] C. K. Brown, W. Mowat, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc.* (*A*), in the press.

[3] F. H. Jardine, J. A. Osborn, J. F. Young, and G. Wilkinson, *Chem. and Ind.*, 1965, 560.

[4] W. H. Baddley and M. S. Fraser, *J. Amer. Chem. Soc.*, 1969, **91**, 3661.

[5] J. P. Collman and J. W. Kang, *J. Amer. Chem. Soc.*, 1967, **89**, 844.