Novel Preparation of σ-Alkynyl Complexes of Transition Metals by Copper(I) Iodide-catalysed Dehydrohalogenation

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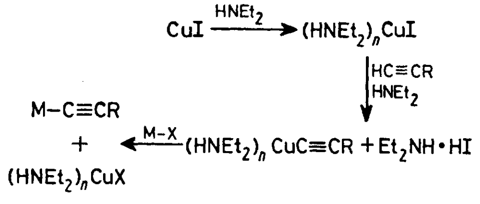
Summary Transition metal alkynyl complexes have been prepared conveniently in high yields under mild conditions by the direct reaction of acetylenes with metal halides in the presence of catalytic amounts of copper(I) iodide in diethylamine.

CONVENTIONALLY σ-alkynyl derivatives of transition metals are prepared either by the reaction of metal halides with an anionic alkynylating agent, such as an alkynyl compound of an alkali metal,[1] magnesium,[1] or copper(I),[2] or by the direct dehydrohalogenation[3] in the reaction between metal halides and active acetylenes having electron-withdrawing substituents. We have now discovered a novel CuI-catalysed dehydrohalogenation as a general method for the preparation of σ-alkynyl complexes of transition metals. This method is especially suitable for the preparation of alkynyl complexes derived from gaseous acetylenes because of its simplicity.



SCHEME. X = Cl, Br, or I

TABLE. Representative CuI-catalysed alkynylation of metal halides: $\mathrm{L}_m\mathrm{MCl}_n + n(\mathrm{HC{\equiv}CR}) \xrightarrow{\mathrm{CuI{-}HNEt_2}} \mathrm{L}_m\mathrm{M(C{\equiv}CR)}_n$

Metal halide	Acetylene	Reaction conditions[a]	Product (yield/%)[b]
$[\mathrm{CpNi(PPh_3)Cl}]$[c]	$\mathrm{HC{\equiv}CH}$	A	$[\mathrm{CpNi(PPh_3)(C{\equiv}CH)}]$[d] (80)
,,	$\mathrm{MeC{\equiv}CH}$	A	$[\mathrm{CpNi(PPh_3)(C{\equiv}CMe)}]$[e] (75)
,,	$\mathrm{Bu^nC{\equiv}CH}$	A	$[\mathrm{CpNi(PPh_3)(C{\equiv}CBu)}]$[e] (72)
trans-$[\mathrm{(PEt_3)_2PdCl_2}]$	$\mathrm{HC{\equiv}CH}$	A	*trans*-$[\mathrm{(PEt_3)_2Pd(C{\equiv}CH)_2}]$[f] (87)
,,	$\mathrm{MeC{\equiv}CH}$	A	*trans*-$[\mathrm{(PEt_3)_2Pd(C{\equiv}CMe)_2}]$[f] (70)
,,	$\mathrm{HC{\equiv}CH_2OH}$	A	*trans*-$[\mathrm{(PEt_3)_2Pd(C{\equiv}CCH_2OH)_2}]$[e] (75)
trans-$[\mathrm{(PMe_3)_2PtCl_2}]$	$\mathrm{HC{\equiv}CH}$	A	*trans*-$[\mathrm{(PMe)_3)_2Pt(C{\equiv}CH)_2}]$[f] (75)
trans-$[\mathrm{(PEt_3)_2PtCl_2}]$	,,	A	*trans*-$[\mathrm{(PEt_3)_2Pt(C{\equiv}CH)_2}]$[g] (90)
cis-$[\mathrm{(PEt_3)_2PtCl_2}]$	,,	B	*trans*-$[\mathrm{(PEt_3)_2Pt(C{\equiv}CH)_2}]$ (7) *cis*-$[\mathrm{(PEt_3)_2Pt(C{\equiv}CH)_2}]$[h] (85)
cis-$[\mathrm{(PBu_3)_2PtCl_2}]$	,,	B	*cis*-$[\mathrm{(PBu_3)_2Pt(C{\equiv}CH)_2}]$[e] (89)
,,	$\mathrm{HC{\equiv}CC{\equiv}CH}$	C	*cis*-$[\mathrm{(PBu_3)_2Pt(C{\equiv}CC{\equiv}CH)_2}]$[e] (90)
trans-$[\mathrm{(PBu_3)_2PtCl_2}]$	,,	A	*trans*-$[\mathrm{(PBu_3)_2Pt(C{\equiv}CC{\equiv}CH)_2}]$[i] (90)

[a] (A) 30 min at room temperature. In the case of *trans*-$[\mathrm{(PMe_3)_2PtCl_2}]$ a solution in 20 ml $\mathrm{CH_2Cl_2}$ must be added dropwise in order to prevent the formation of insoluble *cis*-$[\mathrm{(PMe_3)_2PtCl_2}]$. (B) 1 h at −10 °C. (C) 2 h, from −30 to −10 °C. [b] Based on metal halides. [c] Cp = cyclopentadienyl. [d] H. Yamazaki, T. Nishido, Y. Matsumoto, S. Sumida, and N. Hagihara, *J. Organometallic Chem.*, 1966, **6**, 86. [e] This work. [f] H. Masai, K. Sonogashira, and N. Hagihara, *Bull. Chem. Soc. Japan*, 1971, **44**, 2226. [g] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 4020. [h] Y. Fujikura, Thesis, Osaka University, 1974. [i] Y. Fujikura, K. Sonogashira, and N. Hagihara, *Chem. Letters*, 1975, 1067.

The acetylene (1 or 2 mmol) was either added to or bubbled through an $\mathrm{HNEt_2}$ solution (40 ml) of the metal halide (1 mmol) and CuI (0·01 mmol) under nitrogen. The solvent was evaporated off, water was added to the dry residue, and the mixture was extracted with benzene. Pure complexes were obtained after chromatography on alumina column and recrystallization. Representative examples are summarized in the Table. CuBr and CuCl can also be used as catalysts. All new compounds gave satisfactory elemental analyses and spectral data.

As shown in the Table, *cis-* and *trans*-isomers of bis(trialkylphosphine)dialkynylplatinum(II) can be prepared with retention of configuration at platinum centre of the original halide. For the preparation of thermodynamically less stable *cis*-isomers, a lower reaction temperature is desirable since the *cis–trans* isomerization competes with alkynylation.

Although the exact mechanism of these reactions has not been established, the available data support the process shown in the Scheme.

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[1] M. L. H. Green, 'Organometallic Compounds,' 3rd edn., Vol. 2, eds. G. E. Coates, M. L. H. Green, and K. Wade, Methuen, London, 1968, p. 276.

[2] M. I. Bruce, R. Clark, J. Howard, and P. Woodward, *J. Organometallic Chem.*, 1972, **42**, C 107; O. M. Abu Salah and M. I. Bruce, *J.C.S. Dalton*, 1974, 2302.

[3] P. J. Kim, H. Masai, K. Sonogashira, and N. Hagihara, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 181.