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Preliminary communication

THE FORMATION OF COBALT ACETYLIDES BY DIRECT REACTION AT COBALT(III)

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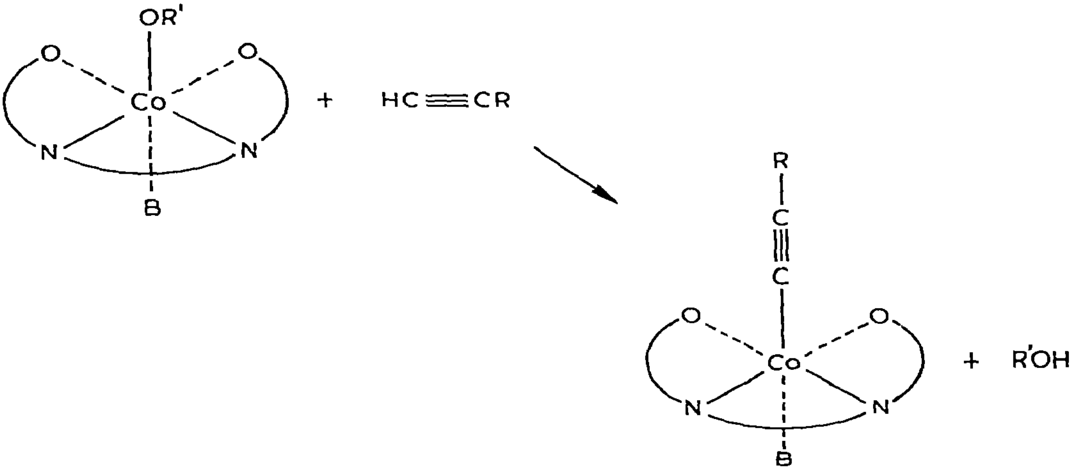
Summary

A new method is described for the preparation of cobalt(III) acetylides, in which monosubstituted alkynes are treated directly with cobalt(III) forms of quadridentate Schiff base compounds in methanol.

Cobalt(III) acetylides, analogous to vitamin B_{12} coenzyme, have been prepared by the conventional method for such species, that is, electrophilic attack of a haloalkyne at a cobalt(I) centre, produced by borohydride reduction [1, 2]. More recently, cobalt—carbon species (substituted alkyls) have been



(I)

(1)

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produced by direct reactions at cobalt(III) of carbon substrates, which have an activated methyl or methylene group [3, 4]. This method also produces cobalt acetylides as in eqn. 1, where O—N—N—O is the dianionic ligand II for R″ = H or Me (abbreviated as salen and salpn, respectively; and B is a readily replaceable sixth ligand, usually H_2O).

In this preliminary study, we have prepared the acetylides listed in Table 1 by treating each of the monosubstituted alkynes listed with the cobalt(III) species under the conditions used for the substituted alkyls [4]. The cobalt(II) Schiff base compound was oxidised in methanol by drawing air through a mixture. The resulting brown solution was filtered and deoxygenated, and then a solution of the alkyne in deoxygenated methanol was added under nitrogen. After the mixture had been stoppered and set aside, crystalline cobalt compounds usually separated out (Table 1).

TABLE 1

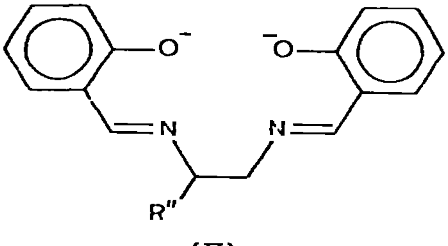
THE CRYSTALLINE SOLIDS ISOLATED FROM THE REACTIONS OF THE TWO DIFFERENT COBALT SPECIES (COLUMNS 2 AND 3) WITH THE ALKYNES TRIED

Alkyne	Product [a,b]	
	Co(salen)	Co(salpn)
$PhC{\equiv}CH$	Acetylide(2128)	Acetylide(2128)
$4\text{-}MeC_6H_4C{\equiv}CH$	Acetylide(2130)	Acetylide(2128)
$4\text{-}BrC_6H_4C{\equiv}CH$	Co^{II}	Impure acetylide
3-Butyn-1-ol	Co^{II}	Co^{II}
3-Butyn-2-one	Olefin (III)	Co^{II}

[a] IR stretching frequencies (cm^{-1}) in parentheses. [b] Acetylide refers to compounds of type I.

The IR spectra were ideal for characterising the formation of the acetylides, and the mass spectra gave "parent ions" of the species I, without axial base B, thus giving unequivocal evidence for the formation of the Co—C bond. Satisfactory analyses have been obtained for all species listed and the characteristic X-ray pattern of each crystalline species has been determined.

Many of the preparations were repeated several times, and, in almost all cases, from at least one of these reactions, variable amounts of $Co_2(salen)_2$ or $Co_2(salpn)_2$ crystallised out. We have not yet identified unequivocally the source of the cobalt(II) in the reaction, but it probably arises from photolytic decomposition of a pre-formed acetylide. Such reactions are fully characterised for the other Co—C species with these Schiff base ligands [4].



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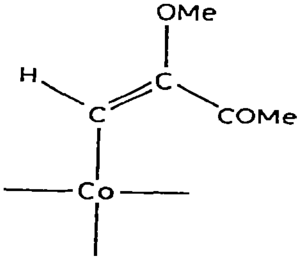

(III)

For 3-butyn-2-one the expected alkynyl species was not obtained (no ν in the IR), and the product gave in its mass spectrum a parent ion 32 *m/e* higher than expected. In this case, methanol has added to the C≡C bond, and the product is formulated as the alkenyl species III (without specification of the particular isomer(s) formed). Such oxidative addition to the acetylide is readily rationalised in terms of the electron-withdrawing character of the cobalt.

Undoubtedly, a great many acetylides will be obtainable by this method, with the major synthetic difficulty being no greater than the choice of a suitable solvent system from which the product will crystallise, and perhaps also, in many cases, protection of the product from photolytic degradation.

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