Alkylation (or Arylation) of Olefins with Organocobalt Compounds in the Presence of Palladium Salts

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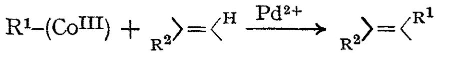
Summary Organic derivatives of cobalt chelates including methylcobalamine alkylate (or arylate) mono- and di-substituted ethylenes in the presence of bivalent palladium salts at 20—50°; under the same conditions an allylcobalt compound transfers its organic ligand to palladium(II) affording a stable π-allylpalladium complex.

THE ability of organocobalt compounds to form carbon–carbon bonds is of interest in the study both of biochemical mechanisms involving organocobamides and of vitamin B_{12} models.[1,2] The availability of some stable, non-toxic simple and substituted alkylcobalt complexes[3,4] makes their application in organic syntheses attractive, but little progress has yet been made in this field. Recently Schrauzer and Sibert[5] showed that methyl(pyridinato)cobaloxime reacts with carbon dioxide in presence of dithiols in aprotic media to give acetic acid in low yield. If the Co–C bonds are to be involved in syntheses it seems reasonable to use heavy metal compounds since the lowest alkyl-cobalamines and -cobaloximes readily exchange their organic ligand with mercury salts.[6–8] We have thus found that organocobalt compounds alkylate and arylate olefins under mild

Organocobalt compound	Olefin	Molar ratio $[R(Co^{III}) : olefin : Li_2PdCl_4]$	Temperature	Product	Yield (%)[c]
$MeCo(dmg)_2,H_2O$	Styrene	1:4:2	20—25°	Propenylbenzene[a]	64
$MeCo(dmg)_2.py$	„	1:4:3	„	„	76
„	Hex-1-ene	1:4:2	„	Hept-2-ene	32
„	Oct-1-ene	1:2:1	„	Non-2-ene	20
„	Cyclohexene	1:2:1	„	1-Methylcyclohexene	1
„	Vinyl acetate	1:2:1	„	Propenyl acetate	20
„	Methyl acrylate	1:1:1	„	Methyl crotonate	7
$MeCo(salen),H_2O$	Styrene	1:4:2[c]	„	Propenylbenzene	41
Methylcobalamine	„	1:4:3		„	24
$PhCo(dmg\ _2,py$	„	1:4:2	50°	*trans*-stilbene	4

[a] Identified by g.l.c. on Apiezon L, Reoplex-400, and Carbowax 20 M. [b] Identified by means of g.l.c., t.l.c. on alumina, and u.v. spectra. [c] NaOAc (2 mol.) added. [d] Based on g.l.c. analyses.

conditions in the presence of palladium salts. The organic



$$R^1\text{-}(\mathrm{Co^{III}}) + {}_{R^2}\!\!>\!=\!<^{H} \xrightarrow{Pd^{2+}} {}_{R^2}\!\!>\!=\!<^{R^1} \qquad (1)$$

derivatives of cobaloximes, RCo(dmg),B and bis(salicylidenato)ethylenediaminecobalt RCo(salen),B (B = H_2O or py) as well as methylcobalamine were used as alkylating (or arylating) agents. Various polar solvents (Me_2CO, tetrahydrofuran, MeCN, or $HCONMe_2$) can be used, but the best results were obtained in methanol (Table).

Transfer of the alkyl or aryl portion to the double bond probably proceeds *via* formation of a labile σ-organopalladium compound [equation (2)]. The latter then reacts with

$$\mathrm{R\text{-}(Co^{III}) + PdCl_2 \longrightarrow R\text{-}PdCl} \qquad (2)$$

olefin, as assumed by Heck[9] who used non-transition metal organic derivatives in combination with palladium salts as alkylating and arylating agents. When a stable organopalladium compound might be expected to be formed [*i.e.* in the reaction of allyl(pyridinato)cobaloxime and lithium chloropalladate] under the same conditions (room temp.; MeOH), bis-(π-allylpalladium chloride) was actually isolated.

$CH{=}CH\text{-}CH_2Co(dmg)_2,py$ (0·5 mmol) and Li_2PdCl_4 (1·5 mmol) in MeOH (10 ml) were stirred for 10—12 h at room temperature. Solid was filtered off, and the filtrate was poured into water and extracted with chloroform. The chloroform solution was dried ($CaCl_2$) and evaporated *in vacuo*. The product had m.p., i.r., n.m.r., and visible spectra which were similar to those for bis-(π-allylpalladium chloride).[10,11] The transfer of organic ligands from similar cobalt complexes to organic substrates by means of other transition metal compounds is under investigation.

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