Journal of Organometallic Chemistry, 255 (1983) C31—C33
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

INSERTION OF FORMALDEHYDE INTO A COPPER—CARBON BOND

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(Received July 4th, 1983)

Summary

Upon mixing equimolar amounts of mesitylcopper(I), CuAr, Ar = 2,4,6-trimethylphenyl and polymeric formaldehyde in THF in the presence of PPh_3 the formaldehyde quickly dissolves. Gas-chromatographic analysis of the products after hydrolytic workup reveals the presence of mesityl alcohol, $ArCH_2OH$ (60% yield), the expected product of direct insertion of formaldehyde into a mesityl—copper bond. When the reaction is carried on for several days, 2,4,6-trimethylbenzyl formate and methyl formate are the main products.

Free formaldehyde has been suggested to be formed as a reactive intermediate in CO hydrogenation catalysed by transition metal complexes [1]. Its incorporation into organic fragments may play a key role in the formation of multicarbon organic products. While insertion of formaldehyde into a pre-existing metal—oxygen and metal—hydrogen bond has been reported [2], to the best of our knowledge, there is no example of formaldehyde insertion into a metal—carbon bond.

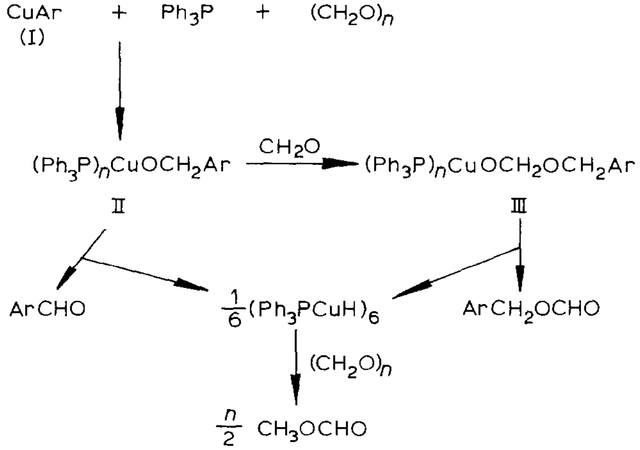
The recent discovery [3,4] of the stable, isolable arylcopper(I) derivative, mesitylcopper(I) I, CuAr, has led us to observation of the insertion of formaldehyde into a copper—carbon bond. A THF suspension of polymeric formaldehyde quickly reacts with I in the presence of an excess of PPh_3 to give a light yellow solution. Gas-chromatographic analysis of the products after hydrolysis revealed the presence of mesitylic alcohol, $ArCH_2OH$ (60% yield) and a small amount of mesityl aldehyde, ArCHO, the expected products derived from the copper(I) alkoxide (II) formed via insertion of formaldehyde into the copper—carbon bond (eq.1).

0022-328X/83/$03.00

$$\underset{\text{(I)}}{\mathrm{ArCu}} + n\,\mathrm{PPh_3} + \frac{1}{n}\,(\mathrm{CH_2O})_n \rightarrow \underset{\text{(II)}}{(\mathrm{PPh_3})_n\mathrm{CuOCH_2Ar}} \qquad (1)$$

If the reaction is continued for several days, 2,4,6-trimethylbenzyl formate, $ArCH_2OCHO$, and methyl formate are the main products; mesityl aldehyde is absent, and only traces of mesityl alcohol can be detected after hydrolytic workup. When the reaction was carried out in the presence of an excess of polymeric formaldehyde, a stoichiometric amount of $ArCH_2OCHO$ and up to 4 mmol of methyl formate per mmole of mesitylcopper(I) were obtained. The reported reactions were not observed in the absence of PPh_3.

Metal-promoted disproportionation of aldehydes, the Tishchenko reaction [5], was reported to take place in the presence of t-BuOCu(PR_3) [6] and $(HCuP)_6$ (P = p-tolyl$_3$P) [7]. Insertion of the aldehydic C=O group into the copper—oxygen bond [6] or copper—hydrogen [7] bond was suggested as the initial step. We suggest, taking account of the identity and the sequence of the organic products formed, that in our system insertion into Cu—H and Cu—O bonds follows insertion into the Cu—C bond (Scheme 1).



SCHEME 1

Formation of copper(I)-hydride complexes by a β-hydride shift from intermediates such as II and III is not uncommon in copper(I)-alkoxide chemistry [8].

A typical experiment was as follows: 2.0 mmol of CuAr and equimolar amounts of $(CH_2O)_n$ were mixed under nitrogen with a twofold excess of PPh_3 in 5 ml of THF. After 30 min the formaldehyde had completely dissolved and the IR spectrum of the solution showed a strong absorption at 1726 cm^{-1} (ν(CO) formate esters). The composition of the products at various times was determined by hydrolysis, elution on a silica gel column, followed by a gas-chromatographic analysis/mass-spectral analysis with a Hewlett—Packard 5995A Gas Chromatograph/Mass Spectrometer.

Acknowledgements. We thank CNR, Roma, for financial support.

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