Preparation and Properties of Methylcopper-triphenylphosphine Complexes[1]

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Alkyl and aryl copper complexes are considered to be involved in various copper-catalyzed organic reactions.[2] A number of reports have been given on the preparation of alkyl and aryl copper complexes by reactions of copper salts with alkyllithium,[3] alkylzinc,[4] Grignard reagents,[3,5] and tetraalkyllead.[6] Most of the complexes, however, have been prepared *in situ* and the unequivocal isolation of a pure alkyl copper complex free from the alkylating agent does not seem to have been reported so far.

Alkyl copper complexes are thermally unstable. Attempts to stabilize the copper-alkyl bond by addition of ligands such as triphenylphosphine and α,α′-dipyridyl have been unsuccessful.[4,5a] These ligands are claimed to have no stabilizing effects and the methylcopper complexes with these ligands are reported to decompose explosively even at a low temperature.

We wish to report the preparation of moderately stable methylcopper complexes from copper acetylacetonate, dimethylaluminium ethoxide and triphenylphosphine (in a ratio of 1:3:4) below −10C° in toluene and diethyl ether under nitrogen in a similar way to that for the preparation of other alkyltransition metal complexes.[7]

$$\mathrm{Cu(acac)_2 + Al(CH_3)_2OC_2H_5 + PPh_3 \xrightarrow{toluene} CuCH_3(PPh_3)_3\cdot C_6H_5CH_3}\quad (\mathbf{1})$$

$$\mathrm{Cu(acac)_2 + Al(CH_3)_2OC_2H_5 + PPh_3 \xrightarrow{ether} CuCH_3(PPh_3)_2\cdot {}^1/_2(C_2H_5)_2O}\quad (\mathbf{2})$$

Complexes **1** and **2** isolated as light yellow needles and crystalline powder, containing toluene and ether as solvents of crystallization, were characterized by elemental analysis, IR and NMR spectroscopy and chemical reactions.

Found: C, 75.6; H, 6.0; Cu, 6.5; $P(C_6H_5)_3$,[8] 77; $C_6H_5CH_3$,[9] 10.3%; CH_3/Cu, 1.1. Calcd for $CuCH_3\{P(C_6H_5)_3\}_3C_6H_5CH_3$ (**1**): C, 77.7; H, 5.9; Cu, 6.6; $P(C_6H_5)_3$, 82; $C_6H_5CH_3$, 9.6%; CH_3/Cu, 1.0. IR (KBr): 2830, 2780 (C–H of CH_3–Cu); NMR (100 MHz in THF): τ 10.4 (s, 3H, CH_3–Cu), 7.7 (s, 3H, CH_3–C_6H_5), 2.7 (m, 50H, C_6H_5).

Found: C, 72.8; H, 5.8; Cu, 10.0; $P(C_6H_5)_3$,[10] 81—88%; CH_3/Cu, 1.01; $(C_2H_5)_2O$/Cu, 0.43. Calcd for $CuCH_3\{P(C_6H_5)_3\}_2\cdot{}^1/_2(C_2H_5)_2O$ (**2**): C, 73.2; H, 6.0; Cu, 9.9; $P(C_6H_5)_3$, 82.0%; CH_3/Cu, 1.00; $(C_2H_5)_2$ O/Cu, 0.5. NMR: τ 10.3 (s, 3H, CH_3–Cu).

The methyl copper complexes are thermally moderately stable in contrast to the behavior of $CuCH_3(PPh_3)_3$ prepared by Costa *et al.*;[5a] **1** decomposes gradually over 0°C and **2** can be kept at room temperature in the solid state in nitrogen in the dark. These methylcopper complexes are light-sensitive and are decomposed by UV light releasing methane. On alcoholysis and acidolysis **1** and **2** released quantitative amounts of CH_4; the reaction with D_2SO_4 yielded only CH_3D. The possibility of a structure with copper bonded to the *ortho*-carbon of a phenyl group of triphenylphosphine was excluded in view of the absence of deuterium introduced to triphenylphosphine after the acidolysis with D_2SO_4, as proved by mass spectrometric examination of water formed by degradative oxidation of the triphenylphosphine ligands in the presence of copper oxide. On pyrolysis at 85°C **1** gave CH_4 and C_2H_6 in a ratio of 1:2 and **2** released CH_4, C_2H_6, and C_2H_4 in a ratio of 1:4.5:0.5. Reaction of **1** with ethyl iodide gave methane and propane in a ratio of about 1:1; **2** reacted with ethyl iodide yielding methane and propane in a ratio of 3:2 with a trace of butane. Carbon monoxide was inserted into the methyl–copper bond affording acetone.

Vinyl monomers such as acrylonitrile, methacrylonitrile, methyl acrylate, methyl methacrylate and 2-vinyl pyridine were polymerized with **1**. In general complex **2** showed lesser polymerization activities for these monomers.[11]

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1) Presented partly at the Vth International Conference on Organometallic Chemistry, Moscow, 23rd August, 1971.

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8) Triphenylphosphine content of **1** was determined spectrophotometrically as methyltriphenylphosphonium iodide.

9) The amounts of toluene and ether contained in the methyl complexes were determined by gas chromatography of the thermal decomposition products of **1** and **2**.

10) The amount of triphenylphosphine in **2** was determined spectroscopically after hydrolysis of **2** with sulfuric acid and extraction of triphenylphosphine with hexane.

11) Polymerization of acrylonitrile and styrene by methyl- and ethylcopper has been reported by Bawn and Johnson;[6a] Saegusa *et al.* also found the polymerization activity of copper complexes for acrylonitrile, T. Saegusa, Y. Ito, H. Kinoshita, and S. Tomita, This Bulletin, **43**, 877 (1970).