

Preparation and Properties of Methylcopper-triphenylphosphine Complexes¹⁾

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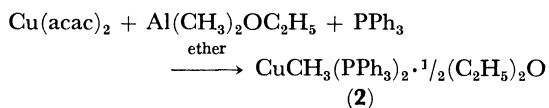
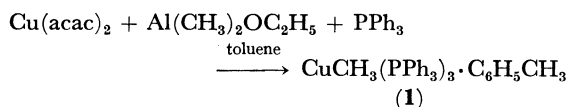
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Alkyl and aryl copper complexes are considered to be involved in various copper-catalyzed organic reactions.²⁾ A number of reports have been given on the preparation of alkyl and aryl copper complexes by reactions of copper salts with alkyllithium,³⁾ 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, dimethylaluminum ethoxide and triphenylphosphine (in a ratio of 1:3:4) below -10°C in toluene and diethyl ether under nitrogen in a similar way to that for the preparation of other alkyltransition metal complexes.⁷⁾



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

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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; $\text{P}(\text{C}_6\text{H}_5)_3$,⁸⁾ 77; $\text{C}_6\text{H}_5\text{CH}_3$,⁹⁾ 10.3%; CH_3/Cu , 1.1. Calcd for $\text{CuCH}_3\{\text{P}(\text{C}_6\text{H}_5)_3\}_3\text{C}_6\text{H}_5\text{CH}_3$ (**1**): C, 77.7; H, 5.9; Cu, 6.6; $\text{P}(\text{C}_6\text{H}_5)_3$, 82; $\text{C}_6\text{H}_5\text{CH}_3$, 9.6%; CH_3/Cu , 1.0. IR (KBr): 2830, 2780 (C-H of $\text{CH}_3\text{-Cu}$); NMR (100 MHz in THF): τ 10.4 (s, 3H, $\text{CH}_3\text{-Cu}$), 7.7 (s, 3H, $\text{CH}_3\text{-C}_6\text{H}_5$), 2.7 (m, 50H, C_6H_5).

Found: C, 72.8; H, 5.8; Cu, 10.0; $\text{P}(\text{C}_6\text{H}_5)_3$,¹⁰⁾ 81–88%; CH_3/Cu , 1.01; $(\text{C}_2\text{H}_5)_2\text{O}/\text{Cu}$, 0.43. Calcd for $\text{CuCH}_3\{\text{P}(\text{C}_6\text{H}_5)_3\}_2 \cdot \frac{1}{2}(\text{C}_2\text{H}_5)_2\text{O}$ (**2**): C, 73.2; H, 6.0; Cu, 9.9; $\text{P}(\text{C}_6\text{H}_5)_3$, 82.0%; CH_3/Cu , 1.00; $(\text{C}_2\text{H}_5)_2\text{O}/\text{Cu}$, 0.5. NMR: τ 10.3 (s, 3H, $\text{CH}_3\text{-Cu}$).

The methyl copper complexes are thermally moderately stable in contrast to the behavior of $\text{CuCH}_3\text{-(PPh}_3)_3$ 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⁾

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).