

SYNTHESIS AND THERMAL DECOMPOSITION OF METHYL(TRI-*t*-BUTYLPHOSPHINE)COPPER

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Summary

Methyl(tri-*t*-butylphosphine)copper was obtained from the reaction of $\text{Cu}(\text{acac})_2$ with Me_2AlOEt in the presence of tri-*t*-butylphosphine in diethyl ether. The isolated complex was characterized by means of elemental analysis, ^1H , ^{13}C , ^{31}P NMR and molecular weight determinations. The thermal decomposition of the complex was examined. Methane and ethane were the main gaseous products of the thermolysis, ~96%, the percentage of ethylene and propane averages 4%. The mechanism pathway for the thermolysis of methyl(tri-*t*-butylphosphine)copper is discussed.

Introduction

In our previous report [1] we examined the thermal decomposition of methylcopper and its complex with tricyclohexylphosphine. We assumed that ethane was formed mainly via reductive elimination of two molecules of the complex in a bimolecular or concerted reaction pathway.

The formation of methane proceeds via a hydrogen abstraction by the methyl group both from the methyl group and the ligand, tricyclohexylphosphine.

Until now a number of papers appeared describing the thermal decomposition of the Cu–C bond. Whitesides [2] and Kochi [3] studied the thermal decomposition of alkylcopper derivatives not isolated from the reaction mixture. Alkylcopper, similar to most organotransition metal compounds with hydrogen at β -position, decomposes in two steps via β -elimination of the hydride and then a reaction with a second molecule of the compound. Kochi attributed the autocatalytic decomposition of alkylcopper(I) species to the presence of copper(0) intermediates during decomposition.

When β -elimination is impossible, the direct homolytic cleavage of the Cu–C bond occurs. Neophyl(tri-*n*-butylphosphine)copper [4] and trimethylsilylmethyl-enecopper $(\text{Me}_3\text{SiCH}_2)_4\text{Cu}_4$ [5] decompose mainly by a free radical mechanism. Yamamoto et al. [6] isolated a series of alkylcopper complexes and examined their

decomposition. Examination of the gaseous products of thermolysis led to the conclusion that the thermal decomposition of the alkylcopper complexes having ethyl or longer alkyl chains proceeds via β -elimination.

The first order pathway for the thermolysis of methylcopper complexes in the solid state suggests that the methyl group, "CH₃", liberated from MeCuL by a spontaneous unimolecular process, will rapidly abstract hydrogen from the ligand or another methyl group, or couple with the CH₃ group in another molecule of the complex to give CH₄ and C₂H₆, respectively [7].

In this work the complex of methylcopper with tri-*t*-butylphosphine was prepared and the influence of the ligand on the course of thermolysis and its gaseous products was examined.

Experimental

Materials

All the preparations and procedures were carried out under deoxygenated argon. Solvents were purified by the usual procedures, dried, distilled and stored under argon. Copper diacetylacetonate was either sublimed in vacuo or recrystallized from CHCl₃, then washed with diethyl ether and dried. ¹H NMR spectra were recorded on a 100 MHz Jeol spectrometer. ¹³C NMR and ³¹P NMR spectra were recorded on a 90 MHz Bruker spectrometer. The gases evolved were analyzed using GID gas chromatograph with a Molecular Sieves 13X column for C₁-C₂ hydrocarbons, Poropak Q and Squalan columns for C₁-C₄ hydrocarbons. The phosphines were analysed by GLC using a 10% OV-101 column on Varaport and mass spectrometry. Copper and aluminium contents were determined analytically [8]. Dimethylaluminium monoethoxide was prepared by treating trimethylaluminium with ethyl alcohol in hexane.

A solution of 3.25 g (70.6 mmol) of EtOH in hexane (10wt-%) was added dropwise into the solution of distilled Me₃Al, 5.14 g (71.5 mmol) in 50 cm³ of hexane at -78°C with stirring. The amount of methane evolved was measured volumetrically. When the entire volume of alcohol was added, the temperature was allowed to rise slowly to room temperature. Evaporation of the solvent under reduced pressure was followed by vacuum distillation of Me₂AlOEt. 6.2 g of Me₂AlOEt was obtained, 85% yield. Anal. Found: Al, 26.58. C₄H₁₁AlO calcd.: Al, 26.47%. The ¹H NMR spectrum in benzene showed three signals at the ratio of 6/3/2 at δ -0.41 ppm (s, CH₃-Al), δ 1.14 ppm (t, AlOCH₂CH₃) and at δ 3.67 ppm, (q, AlOCH₂CH₃), respectively.

Tri-*t*-butylphosphine was prepared according to Hoffmann and Schellenbeck [9], b.p. 83-85°C/5 Torr. The ¹H NMR spectrum of P(*t*-Bu)₃ in benzene showed a doublet at δ 1.35 ppm (³J_(PCCH) 10 Hz). The ³¹P NMR spectrum in benzene exhibited a signal at +61.3 ppm, with respect to the external 85% H₃PO₄. The ¹³C NMR spectrum in benzene-*d*₆ showed two doublets at δ 34.38 ppm (¹J_(CP) 33.8 Hz) and at δ 32.58 ppm (²J_(CCP) 13.3 Hz) due to the quaternary and primary carbons of tri-*t*-butylphosphine, respectively.

Synthesis of methyl(*tri-t*-butylphosphine)copper

To an ethereal suspension of copper diacetylacetonate 1.5 g (5.7 mmol) a solution of 1.4 g (6.9 mmol) of tri-*t*-butylphosphine in diethyl ether was added and the

suspension was cooled down to -78°C while stirring. 1.704 g (16.7 mmol) of dimethylaluminium ethoxide in 10 cm^3 of Et_2O was slowly added to the reaction mixture. After the temperature was gradually raised, slow dissolution of $\text{Cu}(\text{acac})_2$ with simultaneous evolution of the gases CH_4 and C_2H_6 was observed at -30 to -25°C . The colourless solution was subsequently warmed up to -5°C over 4 h. On cooling, white crystals which precipitated were filtered off, washed with cooled Et_2O until no aluminium content in the filtrate was determined. The crystalline complex was recrystallized from diethyl ether and dried in vacuo at 0 – 20°C for 2 h. The yield of methyl(tri-*t*-butylphosphine)copper was 52%.

Analysis

Attempts to analyze for copper in the presence of organic compounds of phosphorus were unsuccessful. The sample of $\text{MeCuP}(\text{t-Bu})_3$ was decomposed by addition of sulphuric acid and the volume of methane evolved was measured. The mixture was then heated with the acids $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{HClO}_4$ in the ratio of 2/2/1 till complete degradation of the phosphine took place. The copper content was determined [9].

*Thermolysis of methyl(tri-*t*-butylphosphine)copper*

The Schlenk vessel containing 0.199 g of the solid crystalline $\text{MeCuP}(\text{t-Bu})_3$ was placed in the thermostated bath, the temperature was controlled with an accuracy of $\pm 0.5^{\circ}\text{C}$. The system was connected to a gas burette to measure the volume of the gases evolving during the decomposition. After completion of the thermolysis, the reaction mixture was cooled to room temperature and the volume of gases was found to be 9.6 cm^3 . The composition of the gases evolved was determined by chromatography (CH_4 , 31.2; C_2H_6 64.5; C_2H_4 1.5; C_3H_8 2.8%). After extraction of the thermolysis residue with different solvents such as THF, diethyl ether and benzene, the sample was condensed by evaporation of the solvents. ^1H NMR and ^{31}P NMR spectra of the condensed extracts were recorded in benzene.

Thermolysis of $\text{MeCuP}(\text{t-Bu})_3$ in toluene solution

The solution of 0.275 g of $\text{MeCuP}(\text{t-Bu})_3$ in 2 cm^3 of toluene was placed in a Schlenk tube equipped with reflux condenser. The temperature of the heating bath was raised up to 70 – 75°C and then the solution darkened with a noticeable evolution of gases. The metallic copper slowly precipitated. After 3 h the sample was heated to 80°C and when the evolution of gases stopped, the system was cooled down and the composition of the gases, 9.2 cm^3 , was determined (CH_4 30.0, C_2H_6 66.0, C_2H_4 1.5, C_3H_8 2.5%).

Results

The methyl(tri-*t*-butylphosphine)copper is a white crystalline solid which easily dissolves in common organic solvents such as ethers, aliphatic and aromatic hydrocarbons. It is extremely sensitive towards air and moisture and therefore the microanalysis of C and H were not feasible.

$\text{MeCuP}(\text{t-Bu})_3$ can be kept at room temperature for several hours without noticeable decomposition but when storing a low temperature is required:

The decomposition point of methyl(tri-*t*-butylphosphine)copper is 95 – 97°C .

TABLE 1

COMPOSITION OF GASES EVOLVED DURING THERMAL DECOMPOSITION OF METHYL(TRI-*t*-BUTYLPHOSPHINE)COPPER

Experiment	Temperature (°C)	Yield ^c (%)	Gases			
			CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈
1	99	93	29.5	66.8	1.5	2.2
2	91	90	23.6	73.0	1.1	2.3
3	100	—	25.0	71.9	1.7	1.4
4	84	96.9	31.2	64.5	1.5	2.8
5	87	—	26.1	69.9	1.9	2.1
6 ^a	60–80	72	30.0	66.0	1.5	2.5
7 ^b	60	—	25.9	74.1		

^a Thermal decomposition in the toluene solution of MeCuP(*t*-Bu)₃. ^b Thermal decomposition in the benzene-*d*₆ solution of MeCuP(*t*-Bu)₃. ^c Mol percent of methyl groups bonded to copper decomposed.

Darkening of the sample is accompanied by the appearance of a liquid which probably results from melting of the complex. Anal. Found: Cu, 23.02. CH₃/Cu 1.05/1 C₁₃H₃₀CuP calcd.: Cu, 22.64%. CH₃/Cu 1/1. The ¹H NMR spectrum of CH₃CuP(*t*-Bu)₃ in benzene showed two signals at δ 0.09 ppm (s, 3H) attributed to CH₃Cu protons and at δ 1.45 ppm (d, ³J_(PCCH) 11.5 Hz, 27H) attributed to protons of tri-*t*-butylphosphine. The ¹³C NMR spectrum in benzene-*d*₆ at room temperature exhibited a somewhat broadened resonance at 8.41 ppm corresponding to the CH₃-Cu carbon and two doublets at 36.38 ppm (¹J_(CP) 4.8 Hz) and at 32.12 ppm (²J_(CCP) 6.6 Hz) due to the quaternary and primary carbons of the phosphine, respectively. The ¹H decoupled ³¹P NMR spectrum showed the singlet resonance at +57.2 ppm of the tri-*t*-butylphosphine complexed to methylcopper, with respect to the external H₃PO₄. Molecular weight determinations in benzene showed the complex MeCuP(*t*-Bu)₃ to be monomeric, $M_{(\text{found})}/M_{(\text{calcd.})}$ 1.07.

The composition of the gases evolved during the thermal decomposition of methyl(tri-*t*-butylphosphine)copper is shown in Table 1. Ethane and methane at an approximate 2/1 molar ratio constitute the majority of the gases evolved in the thermolysis of MeCuP(*t*-Bu)₃. The formation of ethylene and propane was also observed.

The decomposition temperature of the solution of the methylcopper complex is lower by 20°C than that of the decomposition point of the solid MeCuP(*t*-Bu)₃ but the composition of the gaseous products after the thermolysis in both cases is essentially the same.

Therefore we assume that the cleavage mechanism of the Cu-C bond in solution and in the solid state is most probably the same. Although MeCuP(*t*-Bu)₃ in benzene has a monomeric structure which was confirmed by the molecular weight determination, the association of the compound on heating followed by its thermal decomposition cannot be excluded. According to literature data [10] many organo-copper compounds exist in the form of multinuclear aggregates with a defined stoichiometry. The coupling of the methyl groups and the H abstraction reactions during the thermolysis of methylcopper complex seem to be facilitated on the surface of the aggregate.

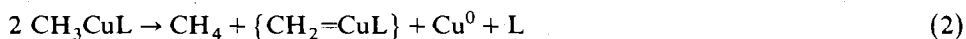
The complexation of methylcopper with tricyclohexylphosphine and tri-*t*-butylphosphine causes an increase in the methane content in the gases evolved; the

ligand, tertiary phosphine is partly the source of hydrogen. The influence of both phosphines on the stability of methylcopper and composition of gases after thermolysis is very similar. On the basis of the results of this work and a previous one [1] we believe that the homolytic cleavage of the Cu-C bond with the formation of short lived radicals, as opposed to free radicals, is most probable, although heterolytic cleavage with the electron pair transfer and further elimination cannot be excluded.

Ethane is formed from a bimolecular coupling of the methyl groups, (eq. 1),



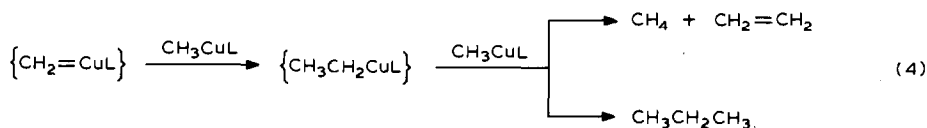
and methane is formed by hydrogen abstraction both from the methyl group of another molecule of $\text{MeCuP}(\text{t-Bu})_3$ (eq. 2)



and the ligand (L = tertiary phosphine) (eq. 3).

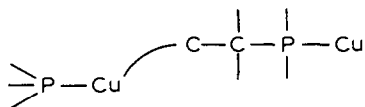


Ethylene and propane formation can be explained by the secondary reactions of the carbenoid species (eq. 4).



In order to isolate the product of reaction 3 the residue, after thermolysis of $\text{MeCuP}(\text{t-Bu})_3$, was extracted several times with benzene, hexane and diethyl ether. Organophosphorus compounds were found in the copper sludge remaining after extraction.

Tri-*t*-butylphosphine was the only product present in the extract, which was confirmed by ^1H NMR, ^{13}C NMR, ^{31}P NMR spectra and GLC analysis of the sample. We think that the presence of organophosphorus derivatives in copper precipitate results from the formation of intermolecular linkages, these interactions may hinder the isolation of the rearrangement product of tri-*t*-butylphosphine:



Polymeric structures consisting of a chain of copper atoms with an organo group bridging two copper atoms were proposed for many alkyl-, alkynyl-, and aryl-copper compounds. On the basis of present information the formation of insoluble $\text{Cu}_x[\text{P}(\text{t-Bu})_2(\text{t-Bu}(-\text{H}))]_y$ species seems very probable.

Depending on the x, y values the polynuclear species remain either in the solid, or in the case of small values of x and y they may transfer to the solution. In some cases, thermolysis of $\text{MeCuP}(\text{t-Bu})_3$ in a solution, the presence of different phosphorus species was detected. The ^{31}P NMR spectra in benzene- d_6 exhibited three resonance peaks at δ 63.2, 61.9 and at 60.1 ppm. The appearance in ^{13}C and ^1H

NMR spectra of many signals in the range of resonance frequencies of t-butyl groups bonded to phosphorus indicates also the formation of a compound, in which the t-butyl groups are in another chemical environment than in the tri-t-butylphosphine.

The presence of the soluble copper species in the extract was also detected.

The GLC analysis and mass spectra of the extract showed that the only volatile compounds are tri-t-butylphosphine and its oxide, resulting from the oxidation of the phosphine exposed to air during GLC analysis.

We propose the formation of $\text{Cu}_x[\text{P}(\text{t-Bu})_2(\text{t-Bu(-H)})]_y$ species during the thermal decomposition of $\text{MeCuP}(\text{t-Bu})_3$ as the result of H abstraction from the ligand by the methyl group of MeCuL (eq. 3).

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References

- 1 S. Pasykiewicz and J. Popławska, *J. Organomet. Chem.*, 282 (1985) 427.
- 2 G.M. Whitesides, E.R. Stredonsky and C.P. Casey, *J. Am. Chem. Soc.*, 92 (1970) 1426.
- 3 R. Wada, M. Tamura and J. Kochi, *J. Am. Chem. Soc.*, 92 (1970) 6656.
- 4 G.M. Whitesides, E.J. Panek and E.R. Stredonsky, *J. Am. Chem. Soc.*, 94 (1974) 232.
- 5 M.F. Lappert and R. Pearce, *J. Chem. Soc. Chem. Commun.*, (1973) 24.
- 6 A. Miyashita and A. Yamamoto, *Bull. Chem. Soc. Japan*, 50 (1977) 1102.
- 7 A. Miyashita, T. Yamamoto and A. Yamamoto, *Bull. Chem. Soc. Japan*, 50 (1977) 1109.
- 8 R. Přibil, *Analytical Applications of EDTA and Related Compounds*, Pergamon Press, Oxford, 1972.
- 9 H. Hoffman and D. Schellenbeck, *Chem. Ber.*, 100 (1967) 692.
- 10 J.G. Noltes and G. van Koten, *Comprehensive Organometallic Chemistry*, Vol. 2, Pergamon Press, Oxford, 1982.