Journal of Organometallic Chemistry, 302 (1986) 269–280
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

REACTIONS OF METHYLCOPPER AND METHYL(TRICYCLOHEXYLPHOSPHINE)COPPER WITH TRIALKYLALUMINIUMS

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(Received September 4th, 1985)

Summary

The reactions of methylcopper and its complexes with tricyclohexyl- and tri-t-butyl-phosphines with trimethylaluminium in 1/1 and 1/2 molar ratios and triethylaluminium in 1/1 molar ratio were studied. On the basis of low temperature ^{31}P NMR investigations ligand exchange between copper and aluminium and the formation of the $Me_3Al \cdot PCy_3$ adduct before decomposition were established. Alkyl group exchange between methylcopper and trialkylaluminium was also observed. The presence of an organoaluminium compound does not influence the reaction temperature and mechanism of the Cu–C σ-bond cleavage. The mechanism of the reaction of $MeCuPCy_3$ with trialkylaluminium is discussed.

Introduction

Until now the reactions of organotransition metal compounds and trialkylaluminiums were not extensively studied. However, there are numerous reports on the reactions of transition metal salts (halides, acetylacetonates) and organoaluminium compounds as components of Ziegler–Natta catalysts [1].

The best characterized catalytic system is $Cp_2TiCl_2/AlR_{3-n}X_n$ ($n = 0, 1, 2$; R = alkyl; X = halide). Sinn et al. [2] studied the reaction of Cp_2TiCl_2 with Me_3Al and noticed that methane evolved and that the organometallic product contained $Ti–CH_2–Al$ units. Tebbe et al. isolated the methylenetitanium complex $Cp_2TiCH_2AlMe_2Cl$ [3], and other methylene titanium derivatives. These compounds indicate olefin metathesis activity and they transfer the methylene unit to ketones and esters to produce olefins and vinyl ethers, respectively. The authors suggest that the role of the organoaluminium compound is to inhibit the rapid decomposition of Cp_2TiMe_2 (Me_3Al dictates the abstraction of the hydrogen from the methyl rather than from the Cp groups). The resulting methylene compound is stabilized by the presence of aluminium.

Grubbs et al. [4] proposed the mechanism for the α-hydrogen abstraction from the $Ti(CH_3)Cl$ unit by alkylaluminium in which the Lewis acidic organoaluminium

0022-328X/86/$03.50

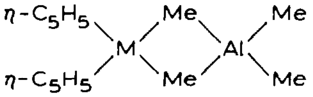
compound activates the titanium methyl group by complexation with chlorine. The resulting aluminate then serves as a strong Lewis base abstracting the α-hydrogen.

Yamamoto [5] and Misbach [6] have investigated the decomposition of alkyl-transition metal compounds by organoaluminium compounds.

Yamamoto examined the reaction of various methyl-transition metal compounds (Ti,Ni,Cr,Fe,Cu) with R_3Al and R_2AlOEt ($R = CH_3$, C_2H_5, n-C_3H_7). On the basis of kinetic measurements the mechanism involving the coordination of R_3Al with the MeM complex and the splitting of the Me–M bond of the binuclear adduct formed was proposed.

Misbach investigated the decomposition of $Me_2Ni \cdot$ bipy in the presence of R_3Al and explained the destabilization of the dimethylnickel complex in terms of displacement of the stabilizing ligand via adduct formation with trialkylaluminium. The unstable $\{Me_2Ni\}$ thus formed decomposed thermally under the reaction conditions. The adduct $Me_2Nibipy \cdot Me_3Al$ was isolated in toluene at −78°C, and a binuclear structure with bridging methyl groups was proposed. The source of hydrogen for methane formation was either the organoaluminium compound or the solvent.

Alkyl groups bridging a transition metal and aluminium are frequently postulated [7] for Ziegler–Natta olefin polymerization catalysts. Recently a few complexes of the $L_nM(\mu\text{-}CH_3)_2AlMe_2$ type which have two bridging methyl groups were prepared and characterized (I).



(I)

(M = Ti, Y [8], Lu [9], η^3-allyl-Ni [10])

The crystal structure of $Cp_2Yb(\mu\text{-}CH_3)_2AlMe_2$ [11] confirmed the postulated structure of binuclear complexes.

We decided to examine the course of the reaction of methylcopper complexes with trimethylaluminium and the role of the organoaluminium component. Therefore, the reactions of free and to PCy_3 complexed trimethylaluminium with methylcopper and its complexes with PCy_3 and $P(t\text{-}Bu)_3$ were investigated. We were also interested in the reaction of an organoaluminium compound containing β-hydrogens in the alkyl group with methylcopper complexes, therefore the reaction of $MeCuPCy_3$ with Et_3Al was also studied.

Results

A toluene solution of 1 equivalent Me_3Al was slowly dropped into a toluene solution of methyl(tricyclohexylphosphine)copper at −78°C. During the addition of the organoaluminium compound a yellow microcrystalline solid precipitated. When the concentration of the reactants was lower than 7×10^{-2} mol/l the yellow solid gradually precipitated after a few hours; a rise of temperature to −40°C favours precipitation from very dilute solutions. No decomposition of the organocopper compound at temperatures under room temperature was found. At room temperature a gradual change in colour of the suspension via green-brown to black was observed. After ca. 20 h a metallic solid was present at the bottom of the flask. In the solution no organocopper compound was found, which indicates complete decomposition of alkylcopper to Cu^0. The composition of gases evolved during the reaction was dėtermined by GC and MS. Due to the great solubility of gases in the reaction mixture it was heated or the pressure in the system reduced to desorb the gases dissolved in the solvent.

All attempts to isolate the yellow precipitate failed. The results obtained (analysis for Cu and Al in the precipitate) were not repeatable; the amount of aluminium in the precipitate varied from 1–3%. It seems probable that the aluminium analysed derives from the organoaluminium compound present in the precipitate.

After decomposition of the organocopper compound, in the reaction of $MeCuPCy_3$ with Me_3Al in a 1/1 molar ratio, only the adduct of trimethylaluminium and tricyclohexylphosphine ($Me_3Al \cdot PCy_3$) was found in the solution above the metallic solid. The hydrolysis of the sample and the determination of the aluminium content gave a CH_3/Al ratio of 2.9.

The ^1H decoupled ^{31}P NMR spectrum exhibits a signal at -6.05 ppm (upfield from external 85% H_3PO_4) corresponding to phosphorus in the $Me_3Al \cdot PCy_3$ adduct (PCy_3 in benzene gives a signal at $+8.86$ ppm).

The ^1H NMR spectrum of the benzene solution of the reaction products of $MeCuP(t\text{-}Bu)_3$ with Me_3Al in a 1/1 molar ratio shows a singlet at δ -0.02 ppm of CH_3-Al protons and the doublet at δ 1.41 ppm (^3J(HCCP) 11.3 Hz) of the t-butyl protons of the $Me_3Al \cdot P(t\text{-}Bu_3)$ adduct.

In order to establish whether the phosphine is transferred to the aluminium component prior to decomposition of the organocopper compound or forms the adduct with trimethylaluminium after Cu–C bond cleavage, the reaction of $MeCuPCy_3$ with Me_3Al was followed by low temperature ^{31}P NMR spectroscopy. Spectral data for methylcopper and trimethylaluminium mixtures are given in Table 1.

In the ^{31}P NMR spectra of an equimolar mixture of $MeCuPCy_3$ with Me_3Al at $-80°C$ an intense signal at -7.2 ppm, corresponding to phosphorus of the adduct $Me_3Al \cdot PCy_3$ can be seen. The weak signal at 13.0 ppm of phosphorus in methyl(tricyclohexylphosphine)copper ($MeCuPCy_3$) is also present. At $-50°C$ a yellow solid precipitates gradually and the appearance of a new signal at 15.1 ppm in the copper-phosphorus resonance range is observed. The three signals described above are present in the spectrum at -50 and $-30°C$, at room temperature the peak of $MeCuPCy_3$ disappears. After decomposition of the Cu–C bond (metallic copper deposits at the bottom of the NMR tube) the ^{31}P NMR spectrum shows only the resonance peak of the $Me_3Al \cdot PCy_3$ phosphorus.

When the reaction of $MeCuPCy_3$ with Me_3Al in a 1/2 molar ratio was monitored by ^{31}P NMR spectroscopy two signals were present at $-80°C$, at $+19.7$ and -7.2 ppm. At $-30°C$ a yellow solid precipitates and a signal of low intensity for $MeCuPCy_3$ at $+14.2$ ppm appears in the ^{31}P NMR spectrum. After completion of the decomposition reaction the signal of the phosphorus in the Al-P region is only present. Although the species responsible for this low field signal at $+19.5$ ppm were not isolated and characterized, the formation of soluble oligomeric structures, $(MeCu)_x(PCy_3)_y$, (where $x > y$) is possible.

During decomposition of the organocopper compound, precipitation of Cu^0 with simultaneous evolution of the gases occurred at room temperature after 20 h. The reagents, reaction conditions and distribution of the gases evolved in the reaction are given in Table 2.

(Continued on p. 274)

TABLE 1

^{1}H-DECOUPLED ^{31}P NMR DATA FOR METHYL(TRICYCLOHEXYLPHOSPHINE)COPPER AND TRIMETHYLALUMINIUM MIXTURES AT VARIOUS TEMPERATURES IN TOLUENE-d_8 (conc. 3×10^{-2} mol/l)

Substrates	Molar ratio	Temperature/chemical shifts (ppm) [a]								Room temperature after decomposition
		−80°C		−50°C		−30°C		Room temp. [b]		
		P–Cu	P–Al	P–Cu	P–Al	P–Cu	P–Al	P–Cu	P–Al	
$MeCuPCy_3 + Me_3Al$	1/1	13.0	−7.2	15.1		15.1		15.1		
					−7.0		−6.7		−6.0	−6.05
				12.1		12.8				
$MeCuPCy_3 + Me_3Al$	1/2	19.7	−7.2	19.5		19.5		20.7		
					−7.2		−7.3		−6.5	−6.5
				13.9		14.2				
$MeCuPCy_3$		12.1 broad		13.5 broad		13.8 broad		14.4 broad		
$Me_3Al\cdot PCy_3$			−7.55		−6.8		−6.65		−6.65	
PCy_3			7.65		7.85		7.75		8.85	

[a] Shifts relative to external 85% H_3PO_4, negative values are shifts upfield from the standard. [b] Spectra performed at room temperature (+18°C) before decomposition.

TABLE 2

THE REACTION OF METHYLCOPPER COMPOUNDS WITH TRIALKYLALUMINIUMS; ROOM TEMPERATURE, 20 h

Exp.	Substrates	Molar ratio	Solvent	Concentr. 10^{-2} mol/l	Gases (%)			
					CH_4	C_2H_6	C_2H_4	C_3H_8
1	$CH_3CuPCy_3 + (CH_3)_3Al$	1/1	toluene	10.5	59.5	40.5		[a]
2	$CH_3CuPCy_3 + (CH_3)_3Al$	1/1	toluene	7.9	25.0	75.0		[b]
3	$CH_3Cu + (CH_3)_3AlPCy_3$	1/1	benzene		58.7	41.7		[a]
4	CH_3Cu		benzene		60.0	40.0		[a]
					26.5	73.0	+	+ [b]
5	$CH_3CuP(t\text{-}Bu)_3 + (CH_3)_3Al$	1/1.3	toluene	26.0	37.6	61.4		[a]
6	$CH_3CuPCy_3 + (C_2H_5)_3Al$	1/1	benzene	10.8	6.5	49.6	43.9	+ [a]
7	$CH_3CuPCy_3 + (C_2H_5)_3AlPCy_3$	1/1	benzene	24.0	27.5 [c]	19.8	44.2	8.5 [a]
8	$CH_3CuPCy_3 + (CH_3)_3Al$	1/2	toluene	8.0	73.0	27.0		[a]
9	$CH_3CuPCy_3 + (CH_3)_3Al$	1/2	benzene-d_6	47.0	24.4	75.6	+	+ [a]
10	$CH_3CuPCy_3 + (CH_3)_3Al$	1/2	toluene-d_8	43.0	13.0 [d]	87.0	+	+ [a]
11	$CH_3Cu + (CH_3)_3Al$	1/1	benzene		78.7	21.3		[a]
12	$CH_3CuPCy_3 + (CH_3)_3AlPCy_3$	1/1	toluene		80.0 [e]	20.0		[a]

[a] Gases evolved from the reaction mixture (atm.pressure). [b] Gases determined after pressure reduction in the system. [c] Reaction temperature 30°C. [d] Reaction temperature 45°C, 1 h, 96% yield. [e] 7 days, decomposition yield 8%.

The volume of the gases evolved was 30–40% of the theoretical value calculated for complete decomposition of the methylcopper complex. After completion of the reaction gas samples were transferred via a syringe to a gas chromatograph. Methane, 60%, and ethane, 40%, were found in the gases evolved. Reduction of the pressure causes desorption of the gases dissolved in the reaction mixture and changes the ratio of methane and ethane to 25 and 75%. The reactions of $MeCuPCy_3$ with Me_3Al in 1/1 molar ratio (Table 2, exp. 1), MeCu + Me_3AlPCy_3 (1/1, Table 2, exp. 3) and MeCu in benzene (Table 2, exp.4) were carried out simultaneously. At room temperature a gradual darkening of the yellow suspensions obtained in the reactions (exp. 1, 3, 4) was observed. The reaction rate and composition of the gases evolved after completion of the reactions are almost the same (methane 60%, ethane 40%). When the reaction of $MeCuPCy_3$ with trimethylaluminium was carried out in a deuterated solvent such as benzene-d_6 or toluene-d_8 the gases evolved did not contain deuterium. After the reaction was complete the metallic precipitate was filtered off and the ^1H and ^{31}P NMR spectra of the filtrate was recorded. Deuterolysis with DCl/D_2O of the filtrate liberated methane (CH_3D, 2.5% CH_2D_2). The aluminium content was determined analytically and from the analysis for Al and the volume of methane evolved the molar ratio CH_3/Al was calculated to be 2.9.

When the toluene solution of the $Me_3Al \cdot PCy_3$ adduct was added to the solution of $MeCuPCy_3$ in toluene (Table 2, exp.12) no precipitation of yellow solid occurred neither at low temperature nor at room temperature. No visible change of the reaction solution and no gas evolution were noticed for 3 days, but small amount of metallic precipitate deposited at the bottom of the reaction vessel after seven days. Methane, 80%, and ethane, 20%, were found in the gases present. The ^1H NMR spectrum of the solution exhibits two singlets corresponding to methyl protons of methylcopper (δ 0.27 ppm) and trimethyaluminium (δ -0.06 ppm) and a multiplet of the cyclohexyl protons (δ 1.59 ppm).

The triethylaluminium-tricyclohexylphosphine adduct was allowed to react with methyl(tricyclohexylphosphine)copper in benzene solution (Table 2, exp. 7). Gradual darkening of the solution and slow precipitation of metallic copper with simultaneous gas evolution occurred after the reaction solution was heated to 30°C; methane, 27.5%, ethane, 19.8%, ethylene, 44.2%, and propane, 8.5%, were the gases found. The ^1H NMR spectrum of the filtrate in benzene shows signals at δ -0.06 (d, J 2 Hz) attributed to CH_3-Al protons, at 0.58 (dq, J 2.2 Hz) attributed to the CH_3CH_2-Al methylene protons and the broad unresolved multiplet of protons of the cyclohexyl rings at 1.66 ppm. The resonance peak of the methyl protons of CH_3CH_2-Al is partly covered by cyclohexyl protons δ 1.14 ppm (t).

The reaction of CD_3CuPCy_3 with $(CH_3)_3Al$ in toluene in a 1/1 molar ratio was studied. From the chromatographic and mass-spectral data the composition of the gases evolved was calculated. d_3- and d_0-isotopes were found both in methane and ethane. The results: CD_3H 28%, CH_4 72% and CH_3CD_3 40%, CH_3CH_3 60% are consistent with the statistical exchange of alkyl groups. Deuterolysis of the filtrate with DCl/D_2O gave CD_4 and CH_3D derived from the methyl groups bonded to aluminium.

When a fourfold excess of perdeuterated trimethylaluminium was added to methyl(tricyclohexylphosphine)copper the gases evolved contained mainly alkanes originating from the organoaluminium compound (eq. 1).

$$CH_3CuPCy_3 + 4(CD_3)_3Al \xrightarrow[\text{toluene}]{} \begin{matrix} CD_3H\ (95\%) \\ CH_4\ (5\%) \end{matrix} + \begin{matrix} CD_3CD_3\ (78\%) \\ CD_3CH_3\ (17\%) \\ CH_3CH_3\ (5\%) \end{matrix} \qquad (1)$$

When the benzene solution of triethylaluminium was added dropwise to a benzene solution of methyl(tricyclohexylphosphine)copper, darkening of the solution and precipitation of metallic copper occurred immediately with simultaneous evolution of the following gases; methane, 6.5%, ethane, 49.6%, ethylene, 43.9, and traces of propane (Table 2, exp. 6, eq. 2).

$$CH_3CuPCy_3 + (C_2H_5)_3Al \xrightarrow{\text{benzene}} CH_4, C_2H_6, C_2H_4, C_3H_8 +$$
$$Cu^0 + (CH_3)_x(C_2H_5)_yAl \cdot PCy_3 \qquad (2)$$

Upon hydrolysis of the filtrate, methane and ethane evolved in a 1/2.6 molar ratio. From that the composition of the organoaluminium compound was calculated as $Me_{0.83}AlEt_{2.17}$.

Discussion

In the studies of the reactions of organotransition metal compounds with organoaluminium compounds published to date the formation of the binary complex $R_xML_y \cdot R'_3Al$ is proposed as the first step of the reaction. Yamamoto explained the activation of the M–R bonds as a result of R'_3Al complexation by an organotransition metal complex and electron withdrawal from the transition metal to the aluminium component. Misbach explained the destabilization of $Me_2Ni \cdot bipy$ in terms of displacement of the stabilizing bipyridyl ligand via the formation of the $Me_3Al \cdot bipy$ adduct.

Ligand exchange reaction

From our studies it appears that methyl(tricyclohexylphosphine)copper does not decompose upon interaction with trialkylaluminium. The results of the ^{31}P NMR studies given in Table 1 indicate that in the first step of the reaction exchange of the tricyclohexylphosphine ligand from copper to aluminium occurs at −80°C.

Besides the strong signal corresponding to the phosphorus in the $Me_3Al \cdot PCy_3$ adduct two signals of low intensity at the P–Cu resonance range are present in the ^{31}P NMR spectrum. We think that the signal lying at lower field than that of phosphorus of $MeCuPCy_3$ corresponds to the phosphine in the oligomeric species $(MeCu)_x(PCy_3)_y$ $(x > y)$.

It seems probable that steric factors hinder direct approach of aluminium to phosphorus and the exchange of tricyclohexylphosphine between copper and aluminium. We believe that a gradual dissociation of $MeCuPCy_3$ (eq.3) is followed by attack of the liberated phosphine on the aluminium atom in the dimeric trimethylaluminium (eq.4).

$$n MeCuPCy_3 \rightleftarrows (MeCu)_n(PCy_3)_{n-1} + PCy_3 \qquad (3)$$

$$1/2[Me_3Al]_2 + PCy_3 \rightarrow Me_3Al \cdot PCy_3 \qquad (4)$$

Soluble, oligomeric species $(MeCu)_x(PCy_3)_y$ (eq.5) existing in equilibrium with $MeCuPCy_3$ and $Me_3Al \cdot PCy_3$ eliminate methylcopper during the ligand exchange reaction.

$$(MeCu)_x(PCy_3)_y \xrightarrow{[Me_3Al]_2} (MeCu)_x \downarrow + yMe_3Al \cdot PCy_3 \qquad (5)$$

If an organoaluminium complex with phosphine, $Me_3Al \cdot PCy_3$, is added to a solution of $MeCuPCy_3$ (Table 2, exp.12) no decomposition of methylcopper is observed at room temperature. The aluminium in the adduct does not abstract the ligand from methyl(tricyclohexylphosphine)copper. The latter compound remains in the solution and it does not decompose thermally at room temperature. When $MeCuPCy_3$ in toluene was left at room temperature traces of metallic precipitate were noticed after 5 days.

If the reaction of $MeCuPCy_3$ and Me_3Al was carried out in THF a decrease in the reaction rate was observed. The rate of the decomposition reaction is dictated by the rate of an electron-donor exchange reaction (eq.6).

$$PCy_3 + Me_3Al \cdot THF \rightleftarrows Me_3Al \cdot PCy_3 + THF \qquad (6)$$

We assume that the role of a Lewis acidic organoaluminium compound is to accept the stabilizing ligand tricyclohexylphosphine from $MeCuPCy_3$ and to form the $Me_3Al \cdot PCy_3$ adduct (eq. 7). The methylcopper $(MeCu)_n$ thus formed decomposes thermally at room temperature.

$$MeCuPCy_3 + Me_3Al \rightarrow \frac{1}{n}(MeCu)_n + Me_3Al \cdot PCy_3 \qquad (7)$$

Thermal decomposition of the methylcopper compound

The yellow solid precipitating from the reaction solution at low temperature undergoes thermal decomposition at room temperature. Since attempts to isolate the solid precipitating from the reaction of $MeCuPCy_3$ and Me_3Al failed, we carried out three experiments in order to explain the role of the organoaluminium compound present in the reaction medium: $MeCuPCy_3 + Me_3Al$ in toluene (Table 2, exp.1), $MeCu + Me_3Al \cdot PCy_3$ (Table 2, exp.3) and thermal decomposition of MeCu in benzene at room temperature (Table 2, exp.4). From the results obtained it appears that the presence of the organoaluminium adduct $Me_3Al \cdot PCy_3$ does not significantly influence the course of the decomposition of organocopper. The methylcopper $(MeCu)_n$ present in the reaction mixture decomposes thermally at room temperature.

As we reported earlier [12] methylcopper decomposes slowly at room temperature with the evolution of methane, ethane, ethylene and propane. The mechanistic pathway for the thermolysis of methylcopper and its complexes with PCy_3 and $P(t\text{-}Bu)_3$ was discussed in our previous papers [12,13].

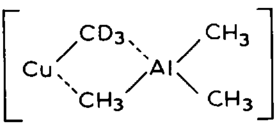
In the reaction of $MeCuPCy_3$ with Me_3Al, followed by the Cu–C bond cleavage, the solvent as well as the organoaluminium compound may be considered as the source of hydrogen for the methane formation. Careful examinations of the gases (GC and MS) evolved in the reaction carried out in benzene-d_6 and toluene-d_8 excluded the solvent as the main source of hydrogen. The isotopic composition of methane, originating from an organoaluminium compound, evolved upon deuterolysis of the post-reaction mixture (CH_3D, 2,5% CH_2D_2), indicates that Me_3Al may be the hydrogen source which appears in methane. The low yield of the reaction towards methane formation makes the isolation of the methylene compound very difficult.

The exchange reaction involving the alkyl groups

When methyl-d_3-(tricyclohexylphosphine)copper was allowed to react with trimethylaluminium, a mixture of CH_4, CD_3H and CH_3CD_3,CH_3CH_3 was obtained. The distribution of the isotopes, the majority of groups derived from an organoaluminium compound, and the formation of the mixed $(CD_3)_x(CH_3)_yAl \cdot PCy_3$ $(x+y = 3)$ compound after decomposition of the organocopper confirm the alkyl exchange reaction.

A high degree of alkyl exchange was observed for the reaction of methyl(tricyclohexylphosphine)copper with fourfold excess of trimethylaluminium-d_9. The methyl groups present in the gases evolved originated mainly from an organoaluminium component, trimethylaluminium-d_9. The distribution of the isotopes was consistent with statistical exchange.

We think that the formation of a binuclear complex with methyl groups bonded both to Cu and Al via electron-deficient bonding $3c$–$2e$ is followed by exchange of the methyl groups between metal atoms. An excess of trimethylaluminium favours the ligand exchange reaction and thus facilitates the formation of the complex between ligand free methylcopper and trimethylaluminium (II).



(II)

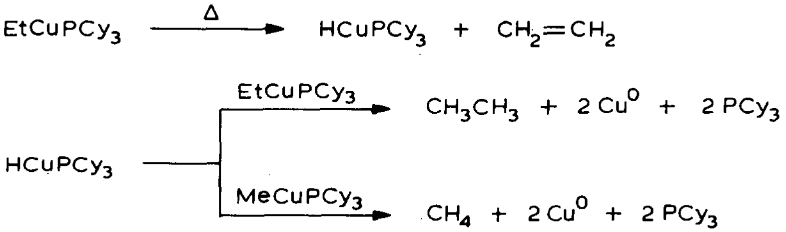
Cleavage of the bridges leads to the elimination of methylcopper with statistically distributed deuterated and nondeuterated methyl groups. The decomposition of methylcopper liberates methane and ethane containing both CD_3 and CH_3 groups. The organoaluminium compound remaining in the solution above the metallic copper contained mixed d_3 and d_0 methyl groups at the aluminium atom.

In the search for further evidence for alkyl group exchange the reaction of methyl (tricyclohexylphosphine)copper with triethylaluminium was studied. The reaction with Et_3Al seemed to be interesting also because of the mechanism of Cu–C σ bond cleavage. It is well-known that organocopper compounds with alkyl substituents containing β-hydrogens are less stable than their methyl analogues [14] and decompose via a β-H-elimination pathway. The addition of triethylaluminium to methyl(tricyclohexylphosphine)copper caused immediate darkening of the solution, precipitation of Cu^0 and gas evolution. Methane, ethane, ethylene and traces of propane were found in the gases and an organoaluminium compound of composition $Et_{2.17}Me_{0.83}Al \cdot PCy_3$ remained in solution after decomposition of the organocopper (Table 2, exp.6). The high yield of the alkyl group exchange, 83% of methyl groups were transferred from copper to aluminium, can be explained by the formation of thermally unstable ethylcopper which decomposed immediately at room temperature facilitating further alkyl exchange. Methylcopper present in the reaction mixture decomposes slowly with the evolution of mainly methane and ethane. Ethane is formed both from thermal decomposition of ethylcopper, as a product of the *β*-elimination reaction, and from the bimolecular coupling of methyl groups during the thermolysis of methylcopper.

If the adduct $Et_3Al \cdot PCy_3$ was added to $MeCuPCy_3$ decomposition of the organocopper occurred slowly at 30°C (Table 2, exp. 7). The distribution of the gases evolved differed significantly from that of the reaction of $MeCuPCy_3$ with Et_3Al.

Yamamoto studied the thermal decomposition of $EtCuPCy_3$ in the solid state; hydrogen, 17%, ethane, 17%, and ethylene, 67%, were found in the gases on thermolysis at 75–80°C [14]. From the studies of the thermolysis of the organocopper complexes in solution it appears that the decomposition temperature of alkylcopper in solution is lower by 40–50°C than that in the solid state.

Ethylcopper, $EtCuPCy_3$, resulting from the alkyl groups exchange reaction decomposes slowly via a *β*-elimination pathway. Copper hydride $HCuPCy_3$ formed in the first step of the reaction may react both with $EtCuPCy_3$ giving ethane and with $MeCuPCy_3$, which is stable at room temperature, giving methane (Scheme 1).



SCHEME 1

The reactions of copper hydride with alkylcopper compounds were studied by Whitesides [15]. Propane is most likely formed during reductive coupling of methyl and ethyl radicals. The insertion of $CH_2{=}CH_2$ into the Cu–C *δ* bond of methylcopper cannot be excluded.

We think that the association of the organocopper compounds with the multinuclear aggregate-clusters occurs and the elimination reactions proceed at the surface of the aggregate. The mixed valence Cu^ICu^0 species formed during the decomposition reaction facilitate further Cu–C *σ* bond cleavage giving vacant coordination sites to which the hydride or the olefin can be transferred in the *β*-hydride elimination step.

Experimental

All the reactions and procedures were carried out under dry, deoxygenated argon. Solvents were purified by the usual procedures, dried, distilled and stored under argon. MeCu, $MeCuPCy_3$ [13] and $MeCuP(t\text{-}Bu)_3$ [14] were prepared as described in the literature. Trimethylaluminium and triethylaluminium (Merck) were distilled prior to use. Tricyclohexylphosphine (Strem Chemicals) was used without prior purification. $Me_3Al\text{-}d_9$ was prepared from CD_3I and Al powder. $MeCuPCy_3\text{-}d_3$ was prepared as described in the literature [13], using $(CD_3)_2AlOEt$ as the methylating agent. ^1H NMR spectra were recorded on a JEOL-100 MHz, and ^{31}P NMR spectra on a JEOL 60FX apparatus.

The gases were analysed with LKB 9000 and LKB 2091 mass spectrometers, and with a Giede gas chromatograph, using Molecular Sieves 13X column for C_1–C_2 hydrocarbons. Porapaq Q and Squalan columns for C_1–C_4 hydrocarbons were used. The copper and aluminium contents were determined analytically after heating the sample with a mixture of inorganic acids (H_2SO_4, HNO_3, $HClO_4$) in order to decompose organophosphorus compounds which disturb the determination of Al and Cu.

Reaction of $MeCuPCy_3$ with Me_3Al at 1/1 and 1/2 molar ratios

In a typical experiment a sample (20–30 mg) of the complex in the solvent (toluene or benzene) in a sealed Schlenk tube was cooled (toluene −78°C, benzene +10°C) and treated with 10% solution of 1 equivalent (2 equivalents) of trimethylaluminium. Immediately a yellow microcrystalline solid precipitated. No changes in the yellow suspension were observed up to room temperature. Slow decomposition, darkening of the suspension, and gas evolution were observed at room temperature. After precipitation of the metallic copper (20 h) a measured volume of the gas was transferred by gas syringe to the gas chromatograph (methane and ethane were found in the gases). Heating the resulting reaction mixture or reduction of the pressure were applied to desorb the gases dissolved in the solution. The clear solution was filtered off from the metallic precipitate, the solid was washed with Et_2O, and the filtrates were combined and evaporated. ^1H NMR and ^{31}P NMR spectra of benzene solutions of the filtrate were performed.

The hydrolysis of the filtrate gave methane and the gas volume was measured. The quantity of aluminium was determined and the CH_3/Al ratio was found to be 2.9. When the filtrate was treated with DCl/D_2O, the gas mixture was analysed by gas chromatography and mass spectroscopy (CH_3D as well as CH_2D_2 were found in the gas).

The reaction of MeCu with Me_3Al or $Me_3Al \cdot PCy_3$

A freshly prepared solution of Me_3Al ($Me_3Al \cdot PCy_3$) was injected into a suspension of MeCu in the solvent (toluene) at low temperature (−78°C) with stirring. The suspension was allowed to warm up to room temperature and further work-up was as described above.

Reaction of $MeCuPCy_3$ with Et_3Al

A benzene solution of Et_3Al was added slowly to a solution of $MeCuPCy_3$ in benzene at room temperature. Simultaneously with the addition of triethylaluminium the darkening of the solution followed on precipitation of the metal (Cu^0) and evolution of gases occurred. The volume of the gases was measured: methane, ethane ethylene and propane were present. The solution decanted from the metallic precipitate was degassed by several freeze-pump-thaw cycles. On acidolysis, methane and ethane evolved (3 mol per 1 mol of Al) and the composition of the organoaluminium compound was calculated, $Me_{0.83}Et_{2.17}Al \cdot PCy_3$.

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