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PREPARATION AND PROPERTIES OF LIGAND-FREE METHYLCOPPER AND OF COPPER ALKYLS COORDINATED WITH 2,2'-BIPYRIDYL AND TRICYCLOHEXYLPHOSPHINE

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Summary

A series of copper alkyls (methyl, ethyl and n-propyl) with ligands (2,2'-bipyridyl and tricyclohexylphosphine) and copper methyl without ligands has been prepared by the reaction of copper(II) acetylacetonate with dialkylaluminum monoethoxides in the presence or absence of the ligand in diethyl ether under nitrogen at low temperature. The copper alkyls were characterized by elemental analysis, chemical reactions, and by IR and NMR spectra. The ligand-free methylcopper is thermally very unstable and decomposed explosively; the bipyridyl ligand showed little effect on the stability of the copper alkyl. In contrast, the tricyclohexylphosphine-coordinated complexes are thermally very stable. Various reactions of the tricyclohexylphosphine-coordinated copper alkyls toward carbon dioxide, alkyl halides and olefins have been studied.

Introduction

The use of organocopper compounds or copper-based catalysts in organic syntheses has been developing rapidly in the past decade [1]. In most of the organic syntheses copper alkyls prepared in situ are used for convenience. It is desirable, however, to isolate the copper alkyls and to investigate their properties in order to gain a deeper insight into the mechanisms of the copper catalyzed reactions. Simple copper alkyls are generally unstable, although the substitution of the alkyl group with fluorine [2] or a trimethylsilyl group [3] enhances the stability of the copper alkyls. Ligands such as 2,2'-bipyridyl and triphenylphosphine which often serve as the stabilizing ligands for various transition metal alkyls have been stated to have no stabilizing effect on the copper alkyls [4,5]. However, examination of the effect of triphenylphosphine on the stability of the copper alkyls revealed a considerable stabilizing effect of the triphenylphosphine ligand and led to the preparation of $CH_3Cu(PPh_3)_3 \cdot C_6H_5CH_3$ and $CH_3Cu(PPh_3)_2 \cdot \frac{1}{2}(C_2H_5)_2O$ [6]. This finding prompted us to re-investigate the preparation of copper alkyls with ligands containing nitrogen and phosphorus and to compare their properties with those of free methylcopper.

Results and discussion

Copper alkyls were prepared by the reactions of copper(II) acetylacetonate with dialkylaluminum monoethoxide in diethyl ether in the absence or presence of ligand. This method allows an easier separation of the product, compared with other methods employing reactions of copper salts and alkylating agents [7—11], where the complete removal of the salts formed in the reactions often is difficult.

Ligand-free methylcopper(I)

Methylcopper(I) without ligand was obtained as a yellow powder in the reaction employing dimethylaluminum monoethoxide at −5 to −30°. Evolution of methane and ethane in a ratio of 4/1 during the reaction suggests that the reaction proceeds through an intermediate methylcopper(II) which is reduced to methylcopper(I) by splitting of the methyl—copper bond. The methylcopper(I) is unstable and decomposes explosively at room temperature, the explosion being particularly violent in the presence of a small amount of air. The explosive thermal decomposition of the methylcopper in the absence of air released methane, ethane, ethylene and hydrogen in molar ratios of 1/9/1/1 suggesting that the decomposition proceeds partly through hydrogen abstraction from the copper-bonded methyl group and the possible formation of carbene [12]. Slower decomposition on the other hand at 0° during 1 h liberated only ethane, the coupling product of the methyl group.

Reaction of CH_3Cu with triphenylphosphine and tricyclohexylphosphine yielded the known $CH_3Cu(PPh_3)_3 \cdot C_6H_5CH_3$ [6] and $CH_3CuP(C_6H_{11})_3$ (vide infra), respectively, which can be obtained directly by the reaction of copper acetylacetonate and dimethylaluminum monoethoxide in the presence of the tertiary phosphines.

Alkyl(bipyridyl)copper(I)

A series of bipyridyl-coordinated alkylcopper(I) compounds were prepared similarly employing dialkylaluminum monoethoxide with bipyridyl. Methyl(bipyridyl)copper(I) thus prepared seems to be identical with the compound reported by Thiele and Köhler [4] who prepared it by the reaction of copper chloride, dimethylzinc and 2,2′-bipyridyl. The interaction of the bipyridyl ligand with the copper alkyls is weak, and on washing RCu(bipy) with diethyl ether at temperatures above −30° to −40° the coordinated bipyridyl ligand is readily removed, yielding the yellow ligand-free copper alkyls. At −78° the dissociation of the bipyridyl is negligible. In sharp contrast to the marked stabilizing effect of the bipyridyl ligand on the nickel, cobalt and iron alkyls [13], the contribution of the bipyridyl ligand on the stability of the copper alkyl is small. The thermal stabilities of RCu(bipy) decrease in the order of $CH_3 > C_2H_5 > n\text{-}C_3H_7$; the methyl complex can be kept without appreciable decomposition for about 20 min at 20° in the complete absence of air. The composition of the decomposition gas of the methyl copper complex was similar to that of the ligand-free methylcopper, whereas the decomposition of the ethyl and propyl complexes released mainly the disproportionation products of the alkyl groups.

RCu(bipy) compounds react with methyl iodide to produce cross coupling products and initiate the polymerization of acrylonitrile and methyl methacrylate.

Alkyl(tricyclohexylphosphine)copper(I)

In contrast to bipyridyl, tertiary phosphines have a pronounced effect on the stabilities of copper alkyls and the tricyclohexylphosphine-coordinated copper alkyls were prepared as thermally stable, diamagnetic white crystals. The NMR spectrum of $CH_3CuP(C_6H_{11})_3$ in pyridine measured at room temperature shows a peak due to the copper-bonded methyl protons at τ 10.1 ppm (singlet, 3H) and peaks due to the ligand at τ 8.0—9.0 ppm (two multiplets, 33H). The copper-bonded methyl protons have been observed at τ 10.3 for $CH_3Cu(PPh_3)_2 \cdot \frac{1}{2}Et_2O$ [6], 10.6 for $CH_3Cu(PBu_3)$ [14] and 10.9 ppm for $CH_3Cu[P(OCH_3)_3]_3$ [14]*.

Table 1 shows the decomposition temperatures of the series of alkylcopper complexes containing tricyclohexylphosphine and the compositions of the decomposition gases evolved. The thermolysis of the ethyl and propyl complexes releases considerable amounts of olefins and hydrogen suggesting that the decomposition proceeds through a β-elimination pathway, whereas the thermolysis of the methylcopper complex yielded only the coupling product of the methyl group. The copper hydride which may be formed by the β-elimination of the ethyl and propyl complexes seems to be further decomposed in the thermolysis since the treatment of the residue of thermolysis with D_2SO_4 liberated no H_2 or HD. It is noted that the n-propyl complex is somewhat more stable than the ethyl complex, in agreement with Kochi's result [15].

$RCuP(C_6H_{11})_3$ reacted with alkyl halides to give alkanes formed by cross-coupling of the alkyl groups. $CH_3CuP(C_6H_{11})_3$ reacted with methyl iodide to give ethane and a small amount of methane, and with ethyl bromide to give mainly propane and small amounts of methane and ethane. The reaction of $C_2H_5CuP(C_6H_{11})_3$ with methyl iodide released mainly propane, together with a small amount of ethane. These results support the mechanism of cross-coupling for the reaction of copper alkyls prepared in situ with alkyl halides [15].

The phosphine-coordinated copper alkyls react with various vinyl compounds and in some cases the vinyl compounds are polymerized. Acrylonitrile was polymerized rapidly at —30°, methyl methacrylate slowly at room temperature, and methacrylonitrile and styrene were not polymerized. Although a free

TABLE 1

THERMOLYSIS OF $RCuP(C_6H_{11})_3$ IN THE SOLID STATE

R	Decomposition temp. (°C)	Products[a] (molar ratio)				Thermolysis[b] (ΣR%)
		H_2	R(—H)	R(H)	R—R	
CH_3	105—110	0	0	0	1	71
C_2H_5	75—80	1	3—5	1	0	88
n-C_3H_7	85—90	7—8	20	1	0	77

[a] R(—H) = olefin; R(H) = alkane, R—R = coupling product. [b] ΣR = R(—H) + R(H) + 2R—R.

* These complexes have been prepared in situ from cuprous iodide and methyllithium in the presence of ligand.

radical mechanism has been proposed for the polymerization of vinyl monomers initiated by copper and silver alkyls prepared in situ [16], the polymerization activities of our isolated copper alkyls for various vinyl monomers are not compatible with the free radical polymerization and may be better accounted for by a coordination mechanism [17].

The tricyclohexylphosphine-coordinated methylcopper complex reacted with carbon dioxide to give a CO_2 insertion product, $CH_3COOCuP(C_6H_{11})_3$, and its adduct $CH_3COOCu(CO_2)P(C_6H_{11})_3$. A similar reaction has been observed with $CH_3Cu(PPh_3)_2 \cdot \frac{1}{2}Et_2O$ [18]. The CO_2 adduct loses on pyrolysis at 150° an almost theoretical amount of CO_2 to give $CH_3COOCuP(C_6H_{11})_3$. On treatment of the CO_2 adduct with HCl in benzene, the formation of acetic acid and CO_2 was detected, and the reaction with methyl iodide produced methyl acetate. When $CH_3COOCu(CO_2)P(C_6H_{11})_3$ is heated at 150° its IR spectrum loses the intense bands at 1610 and 1380 and medium bands at 2600, 1420, 830 and 650 cm^{-1}. These bands may be associated with the coordinated CO_2. The silver-CO_2 adduct $C_6H_5AgCO_2$ [19] shows strong bands at 1496, 1326 and 828, and a rhodium—CO_2 adduct, $Rh_2(CO)_2(CO_2)(PPh_3)_3(C_6H_6)$ [20], has bands due to the coordinated CO_2 ligand at 1498, 1368 and 813 cm^{-1}. The intense bands remaining in the thermolysis residue of $CH_3COOCu(CO_2)P(C_6H_{11})_3$ at 1600 and 1365 cm^{-1} can be assigned to ν(OCO) stretching vibrations of the acetate ligand. An analogous spectral change has been observed during the heating of $CH_3COOCu(CO_2)(PPh_3)_2$ to give $CH_3COOCu(PPh_3)_2$.

Experimental

All reactions and handling of air-sensitive compounds were carried out under nitrogen or in vacuum.

Analysis

Microanalyses of carbon and hydrogen were performed by Mr. T. Saito of our laboratory by using a Yanagimoto CHN Autocorder, Type MF-2 and the copper content was analysed on a macroscopic scale. Bipyridyl content in the complexes were determined spectrophotometrically by observation of the absorbance of bipyridyl extracted from the complex with n-hexane after gradual thermolysis in hexane.

Materials

Nitrogen gas was dried and deoxygenated by passing through columns containing $CaCl_2$, P_2O_5 and activated copper. Solvents were purified and dried by the usual procedures and stored under nitrogen.

Preparation of alkylcopper complexes

Methylcopper. To an ether suspension of copper(II) acetylacetonate (5 mmol) cooled at −40° was added dimethylaluminum monoethoxide (15 mmol) with stirring. The reaction mixture was stirred for 3 to 4 h at −10 to −5°. The yellow microcrystalline powder which precipitated was washed carefully at −40° with ether. The compound thus obtained was dried below −10° in vacuum for 5 h. The compound was scarcely soluble in ether, benzene, and toluene and slightly soluble in pyridine, dimethylformamide and triethylamine.

Since the compound has a tendency to explode in the dry state, it was usually handled in the form of suspensions in ether or hexane. Alcoholysis of the compound yielded a quantitative amount of methane and thermolysis in n-hexane at room temperature yielded ethane and methane, from the amounts of which a CH_3/Cu ratio of 1.01 was deduced.

RCu(bipy). To a mixture of copper(II) acetylacetonate (5 mmol) and bipyridyl (30 mmol) cooled at −78° in diethyl ether was added dimethylaluminum monoethoxide (15 mmol) with stirring. The reaction mixture was stirred for 10 h at −55 to −30°. The light brown complex which precipitated was filtered and then washed four times at −78° with cooled ether and finally with cooled ether containing some bipyridyl. The addition of a small amount of bipyridyl was necessary to suppress the dissociation of bipyridyl from the complex. The complex is slightly soluble in pyridine and dimethylformamide, but is insoluble in almost all other organic solvents. The analysis of CH_3Cu(bipy) is shown below as an example. CH_3/Cu, 0.99; bipy/Cu, 1.01; [CH_3 = (C_1 content + C_2 content × 2) as deduced from the thermolysis product analysed by gas chromatography]. In the case of preparations of the ethyl and n-propyl complexes the experiments were carried out similarly except that the reaction temperatures for the preparation of ethyl and n-propyl complex were at −65 to −40°, and at −70 to −60°, respectively. Analyses of these complexes are as follows. C_2H_5-Cu(bipy): C_2H_5/Cu, 0.81; (bipy)/Cu, 1.00; (C_2H_5 = C_2 content + C_4 content × 2). C_3H_7Cu(bipy): C_3H_7/Cu, 0.70; (bipy)/Cu, 0.96; (C_3H_7 = C_3 content).

Acidolysis of these complexes yielded quantitative amounts of alkanes. Yields of these alkyl(bipyridyl)copper compounds averaged about 60%. Since the complexes tend to explode on contact with a trace of air, they should be prepared in small quantities.

$RCuP(C_6H_{11})_3$. The preparation of a series of copper alkyls coordinated with tricyclohexylphosphine was carried out in a similar way to that of the bipyridyl complexes. As a typical example the preparation of $CH_3CuP(C_6H_{11})_3$ complex is described below. Copper(II) acetylacetonate (5 mmol) and tricyclohexylphosphine (5.5 mmol) and dimethylaluminum monoethoxide (15 mmol) were mixed in diethyl ether at −50°. At −30° the mixture gradually changed from a blue suspension to a colorless solution. The colorless clear solution was further stirred for 5 h at −20 to −10° and then was cooled at −78° to give white crystals. The white crystals were filtered and washed with cooled ether and then were recrystallized from diethyl ether. The complex thus obtained was dried at 10° in vacuum (yield 70%). The white complex is very sensitive to air and moisture. The complex is soluble in diethyl ether, tetrahydrofuran, acetone, toluene, benzene, pyridine, and other solvents. The ethyl and n-propyl complexes were prepared in a similar way in about 70% yield. The solutions of the ethyl and n-propyl complexes are more sensitive to air than the methyl complex. Table 2 summarizes the analytical data of tricyclohexylphosphine coordinated complexes.

Reaction of carbon dioxide with $CH_3CuP(C_6H_{11})_3$

A dry CO_2 stream was bubbled through a diethyl ether solution of $CH_3CuP(C_6H_{11})_3$ at 0° for 2 to 3 h. Gradual precipitation of white crystals was observed. After some time these were filtered, washed with cooled ether at low

TABLE 2

ANALYTICAL DATA FOR TRICYCLOHEXYLPHOSPHINE COMPLEXES[a]

	Analysis found (calcd.) (%)			Acidolysis (RH%)[c]	
	C[b]	H[b]	Cu		
$CuCH_3P(C_6H_{11})_3$	64.1 (63.6)	10.2 (10.1)	17.8 (17.7)	CH_4	106
$CuC_2H_5P(C_6H_{11})_3$	63.5 (64.4)	10.1 (10.2)	16.9 (17.0)	C_2H_6	105
$Cu(n\text{-}C_3H_7)P(C_6H_{11})_3$	63.8 (65.2)	10.5 (10.4)	15.8 (16.4)	C_3H_8	85
$Cu(CH_3COO)(CO_2)P(C_6H_{11})_3$	55.8 (56.4)	8.63 (8.06)	14.5 (14.2)		

[a] All compounds are white. [b] Microanalysis was difficult due to the extreme air-sensitivity of the sample. [c] The amount of alkane (RH) evolved on acidolysis.

temperature and dried in vacuum. The product was characterized by IR spectroscopy and chemical reactions. The complex liberated acetic acid when treated with HCl as identified by gas chromatography.

On pyrolysis at 150° the complex released an almost quantitative amount of CO_2 for the composition of $CH_3COO(CO_2)P(C_6H_{11})_3$. Analytical data are also included in Table 2.

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References

1 (a) M. Fieser and L. Fieser, Reagents for Organic Synthesis, Wiley Interscience, New York, 1972, Vol.1, p.155; Vol.2, p.82, 351, 400; Vol.3, p.63;
(b) J.F. Normant, Synthesis, (1972) 63;
(c) T. Saegusa, T. Tsuda and Y. Ito, Kogyo Kagaku Zasshi, 72 (1969) 1627, Chem. Abstr., 72 (1970) 289;
(d) R.G.R. Bacon and H.A.O. Hill, Quart. Rev., 19 (1965) 95.
2 (a) V.C.R. McLoughlin and J. Thrower, Tetrahedron, 25 (1969) 5921;
(b) P.L. Coe and N.E. Milner, J. Organometal. Chem., 39 (1972) 395; J. Burdon, P.L. Coe, C.R. Marsh and J.C. Tatlow, J. Chem. Soc., Perkin I, (1972) 639.
(c) W.T. Miller and R.J. Burnard, J. Amer. Chem. Soc., 90 (1968) 7367.
3 M.F. Lappert and R. Pearce, J. Chem. Soc., Chem. Commun., (1973) 24.
4 K.-H. Thiele and J. Köhler, J. Organometal. Chem., 12 (1968) 225.
5 G. Costa, G. Pellizer and F. Rubessa, J. Inorg. Nucl. Chem., 26 (1964) 961.
6 A. Yamamoto, A. Miyashita, T. Yamamoto and S. Ikeda, Bull. Chem. Soc. Japan, 45 (1972) 1583.
7 (a) H. Gilman and L.A. Woods, J. Amer. Chem. Soc., 65 (1943) 435;
(b) C.E.H. Bawn and F.J. Whitby, Disc. Faraday Soc., 7 (1947) 228;
(c) G. Costa, A. Camus and E. Pauluzzi, Gazz. Chim. Ital., 86 (1956) 997.
8 A. Camus and N. Marsich, J. Organometal. Chem., 14 (1968) 441.
9 G. Wilkinson and T.S. Piper, J. Inorg. Nucl. Chem., 2 (1956) 32.
10 G. Costa, G. DeAlti, L. Stefani and G. Boscarato, Ann. Chim., 52 (1962) 289.
11 A. Cairncross and W.A. Sheppard, J. Amer. Chem. Soc., 93 (1971) 247.
12 L.S. Pu and A. Yamamoto, J. Chem. Soc., Chem. Commun., (1973) in press.
13 A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida and A. Misono, J. Amer. Chem. Soc., 87 (1965) 4652; ibid, 90 (1968) 1878; T. Saito, Y. Uchida, A. Misono, A. Yamamoto, K. Morifuji and S. Ikeda, J. Organometal. Chem., 6 (1966) 572; J. Amer. Chem. Soc., 88 (1966) 5198.
14 H.O. House and W.F. Fischer, Jr., J. Org. Chem., 33 (1968) 949.

15 M. Tamura and J.K. Kochi, J. Organometal. Chem., 42 (1972) 205.
16 C.E.H. Bawn and R. Johnson, J. Chem. Soc., (1960) 3923; C.E.H. Bacon and E.J. Whitby, J. Chem. Soc., (1960) 3926; C.E.H. Bawn and R. Johnson, J. Chem. Soc., (1960) 4162; C.E.H. Bawn, W.H. Janes and A.M. North, J. Polym. Sci., 58 (1962) 335.
17 See for example: A. Yamamoto and S. Ikeda, in S. Okamura and M. Takayanagi (Eds.), Progress in Polymer Science, Japan, Vol.3, Kodansha Ltd., Tokyo, 1972, p.49—96, and refs. therein; T. Yamamoto, A. Yamamoto and S. Ikeda, Bull. Chem. Soc. Japan, 45 (1972) 1111.
18 A. Miyashita and A. Yamamoto, J. Organometal. Chem., 49 (1973) C57.
19 C.D.M. Beverwijk and G.J.M. Van der Kerk, J. Organometal. Chem., 49 (1973) C57.
20 Y. Iwashita and A. Hayata, J. Amer. Chem. Soc., 91 (1969) 2525.