

VINYLMETALLICS AS LIGANDS I. THE PREPARATION OF SOME ALKYLVINYLSILANE AND ALKYLVINYL TIN COMPLEXES OF COPPER(I) CHLORIDE

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(Received December 16th, 1970)

SUMMARY

The compounds, $(\text{CH}_3)_3\text{SiCH}=\text{CH}_2 \cdot \text{CuCl}$, $(\text{CH}_3)_3\text{SnCH}=\text{CH}_2 \cdot \text{CuCl}$, $(\text{CH}_3)_2\text{Si}(\text{CH}=\text{CH}_2)_2 \cdot 2 \text{CuCl}$, $(\text{CH}_3)_2\text{Sn}(\text{CH}=\text{CH}_2)_2 \cdot 2 \text{CuCl}$, and $(\text{C}_4\text{H}_9)_2\text{Sn}(\text{CH}=\text{CH}_2)_2 \cdot 2 \text{CuCl}$ are prepared by allowing the neat vinylmetallics to react with copper(I) chloride. The new π -complexes are characterized by elemental analysis and by IR and NMR spectroscopy. A bonding scheme is proposed to explain the unusual stability of these complexes.

INTRODUCTION

The reaction of olefins with copper(I) chloride has been rather extensively investigated¹. Complexes derived from the acyclic alkenes, C_2H_4 , C_3H_6 , and *i*- C_4H_8 , have been reported, but they all have dissociation pressures greater than one atmosphere at temperatures greater than 0°². By using the method of reducing a copper(II) halide with sulfur dioxide in the presence of a cyclic alkene, Doyle and co-workers³ were able to prepare complexes of cyclohexene, cycloheptene, and *cis*-cyclooctene. All complexes were reported to be unstable, and only in the case of the *cis*-cyclooctene.

The acyclic dienes, 1,3-butadiene^{4,5} and isoprene⁴, have also been reported to form rather unstable complexes with copper(I) chloride. On the other hand copper(I) chloride forms more stable complexes with cyclic polyenes, and these compounds have been investigated most thoroughly⁶.

As part of a systematic investigation of the ability of vinylmetallics to function as ligands, we have had occasion to prepare several alkylvinylsilane- and alkylvinyltin-copper(I) chloride complexes. Although the monovinyl complexes show some dissociation at room temperature, the divinyl complexes appear to be among the most stable olefin-copper(I) chloride complexes yet described.

EXPERIMENTAL

General

All reactions were conducted in an atmosphere of pre-purified nitrogen. IR

spectra were obtained on a Beckman IR-10 spectrophotometer. NMR spectra were obtained on a Varian A-60. Carbon and hydrogen analyses were obtained from Galbraith Laboratories, Inc., Knoxville, Tennessee. Copper was determined by the iodometric procedure.

Syntheses

Copper(I) chloride. Copper(I) chloride was prepared as described in the literature⁷ and stored *in vacuo* until needed. (Found: Cu, 64.53. ClCu calcd.: Cu, 64.79%.)

Vinylsilanes and vinyltins. Vinylsilanes⁸ and vinyltins⁹ were prepared according to published procedures and exhibited satisfactory physical constants.

Trimethylvinylsilane-copper(I) chloride. In a typical preparation trimethylvinylsilane (4.8 g, 0.048 mole) was mixed with copper(I) chloride (3.9 g, 0.039 mole) at -78° . The mixture was allowed to warm to room temperature over a period of several hours to give a heterogeneous product. The top of the product was white while the bottom half was dark orange. The white product, crude $(\text{CH}_3)_3\text{SiCH}=\text{CH}_2 \cdot \text{CuCl}$, was then placed in another tube connected through a trap (-78°) to the high vacuum manifold. The entire system was then evacuated, and excess uncomplexed ligand was transferred to the cold trap which was allowed to warm to room temperature. The complex was then allowed to stand *in vacuo* for 24 h in contact with the ligand vapor coming from the trap to reestablish equilibrium conditions. The white product, isolated in 40% yield (3.1 g), decomposed at 120° . (Found: Cu, 32.92. $\text{C}_5\text{H}_{12}\text{ClCuSi}$ calcd.: Cu, 32.07%.)

Trimethylvinyltin-copper(I) chloride. The procedure just described for the preparation of $(\text{CH}_3)_3\text{SiCH}=\text{CH}_2 \cdot \text{CuCl}$ was employed in the preparation of $(\text{CH}_3)_3\text{SnCH}=\text{CH}_2 \cdot \text{CuCl}$. In a typical preparation, begun at -78° , trimethylvinyltin (6.7 g, 0.035 mole) was mixed with copper(I) chloride (2.3 g, 0.023 mole). The white homogeneous product of the reaction, $(\text{CH}_3)_3\text{SnCH}=\text{CH}_2 \cdot \text{CuCl}$, which melts at 54° , is obtained in 70% yield (4.7 g), and is soluble in several organic solvents (tetrahydrofuran, ethanol, dioxane, chloroform). The complex turns orange-brown on more than brief exposure to air. (Found: C, 20.69; H, 4.14; Cu, 21.94. $\text{C}_5\text{H}_{12}\text{ClCuSn}$ calcd.: C, 19.82; H, 4.05; Cu, 22.83%.)

Dimethyldivinylsilane-bis(copper(I) chloride). In a typical preparation dimethyldivinylsilane (5.9 g, 0.050 mole) was mixed with copper(I) chloride (3.6 g, 0.036 mole) at -78° . The stirred mixture was then allowed to warm slowly to room temperature. The white solid which formed was then washed three times with 50 ml portions of pentane and dried *in vacuo* long enough to remove the excess pentane (about 30 min). Yields as high as 80% (3.80 g) were obtained, and the $(\text{CH}_3)_2\text{Si}(\text{CH}=\text{CH}_2)_2 \cdot 2 \text{CuCl}$ which was formed decomposes without melting at 100° . (Found: C, 23.41; H, 3.90; Cu, 40.97. $\text{C}_6\text{H}_{12}\text{Cl}_2\text{Cu}_2\text{Si}$ calcd.: C, 23.21; H, 3.86; Cu, 40.98%.)

Dimethyldivinyln-tin-bis(copper(I) chloride). In a typical preparation dimethyldivinyln-tin (5.1 g, 0.025 mole) was mixed with copper(I) chloride (2.3 g, 0.023 mole) at -78° . The stirred mixture was then allowed to warm to room temperature. Excess ligand was removed under vacuum, and the remaining snow-white crystals of product, $(\text{CH}_3)_2\text{Sn}(\text{CH}=\text{CH}_2)_2 \cdot 2 \text{CuCl}$, were washed twice with 50 ml portions of pentane and then dried *in vacuo*. The product is very stable in dry air and decomposes only after a period of weeks. It decomposes above 120° and is soluble in most organic

solvents tested (tetrahydrofuran, dioxane, chloroform, ethanol). The yield of the product was 3.2 g (62%). (Found: C, 17.82; H, 2.90; Cu, 31.69. $C_6H_{12}Cl_2Cu_2Sn$ calcd.: C, 17.96; H, 2.99; Cu, 31.71%.)

Dibutyldivinyltin-bis(copper(I) chloride). In a typical preparation dibutyldivinyltin (5.8 g, 0.020 mole) was mixed with copper(I) chloride (2.0 g, 0.020 mole) at -78° . The stirred mixture was then allowed to warm to room temperature. The white product was then washed three times with 30 ml portions of pentane and dried *in vacuo*. The complex, $(C_4H_9)_2Sn(CH=CH_2)_2 \cdot 2 CuCl$, which melts at 118° , is soluble in several organic solvents (benzene, chloroform, tetrahydrofuran) and is stable in dry air for months. The yield of product was 4.5 g (92%). (Found: C, 30.19; H, 5.12; Cu, 26.10. $C_{12}H_{24}Cl_2Cu_2Sn$ calcd.: C, 29.71; H, 4.95; Cu, 26.12%.)

RESULTS AND DISCUSSION

Preparations and stabilities

In the preparation of the compounds, $(CH_3)_3SiCH=CH_2 \cdot CuCl$ and $(CH_3)_3SnCH=CH_2 \cdot CuCl$, care had to be exercised to prevent loss of the ligand when the samples were isolated. For this reason the excess ligand was removed from the product by vacuum distilling it into a trap, and then allowing it to stand in the presence of the product in order that any dissociated complex could re-form. The compounds have a considerable vapor pressure at room temperature since excessive pumping [for example-pumping at 0.2 mm for 30 min in the case of $(CH_3)_3SiCH=CH_2 \cdot CuCl$] resulted in their dissociation. Furthermore, the reactions between all of the vinylmetallics studied and copper(I) chloride are noticeably exothermic. To prevent local overheating all reactions were started at -78° .

The behavior of trimethylvinylsilane and trimethylvinyltin toward copper(I) chloride should be contrasted to that of 3,3-dimethyl-1-butene, their carbon analogue. Attempts to prepare $(CH_3)_3CCH=CH_2 \cdot CuCl$ by a procedure similar to that used for the silicon and tin compounds failed. Furthermore, no interaction was detected at 21° through vapor pressure measurements. Consequently, if the reactions are not kinetically controlled, it may be concluded that trimethylvinylsilane and trimethylvinyltin form more stable copper(I) chloride complexes than their carbon analogue.

In contrast to the behavior observed for the monovinyl complexes, the divinyl complexes, $(CH_3)_2Si(CH=CH_2)_2 \cdot 2 CuCl$, $(CH_3)_2Sn(CH=CH_2)_2 \cdot 2 CuCl$, and $(C_4H_9)_2Sn(CH=CH_2)_2 \cdot 2 CuCl$, are stable at room temperature to extended pumping. Furthermore, they are stable for weeks in desiccators over calcium chloride. One sample of $(C_4H_9)_2Sn(CH=CH_2)_2 \cdot 2 CuCl$ was allowed to stand on the laboratory shelf for months in a capped bottle, and very little decomposition was observed.

The complexes of the divinylmetallics were also noted to be stable to washing with hydrocarbon solvents. This behavior should be contrasted to that of the copper(I) complexes of cyclic polyenes which are reported to decompose or dissociate upon extensive washing^{3,10}. The behavior of the divinylmetallic complexes would suggest little dissociation of the complexes in the solid state at room temperature.

Best yields of the divinylmetallic complexes of copper(I) chloride are obtained when excess ligand is used. The observed stoichiometries in the complexes prepared suggest that the divinylmetallic ligands studied do not function as chelating agents toward copper(I) chloride. Neither do they function as monodentate ligands since

no compounds such as $R_2M(CH=CH_2)_2 \cdot CuCl$, in which there is an uncoordinated double bond, were observed.

Most likely, however, the complexes of the divinylmetallics are not monomeric. Rather, they are probably dimerized or polymerized through chloride bridging across copper atoms. However, since all of the divinylmetallic complexes are at least partially soluble in several organic solvents (*e.g.* chloroform), the degree of polymerization is probably not high. Although preliminary molecular weight measurements have been somewhat frustrating, they suggest that the dibutyldivinyltin-bis(copper(I) chloride) complex may be dimeric in solution.

Infrared spectra

The carbon to carbon double bond stretching frequencies for the ligands used and the complexes prepared are tabulated in Table 1. The frequency shift upon coordination, $\Delta\nu$, is observed to be 80 to 90 cm^{-1} .

TABLE 1

DOUBLE BOND STRETCHING FREQUENCIES FOR THE LIGANDS AND COMPLEXES

Compound	$\nu(C=C)$	Compound	$\nu(C=C)$	$\Delta\nu$
$(CH_3)_3SiCH=CH_2^a$	1592	$(CH_3)_3SiCH=CH_2 \cdot CuCl^d$	1508	84
$(CH_3)_2Si(CH=CH_2)_2^b$	1595	$(CH_3)_2Si(CH=CH_2)_2 \cdot 2CuCl^d$	1501	94
$(CH_3)_3SnCH=CH_2^c$	1578	$(CH_3)_3SnCH=CH_2 \cdot CuCl^d$	1497	81
$(CH_3)_2Sn(CH=CH_2)_2^c$	1580	$(CH_3)_2Sn(CH=CH_2)_2 \cdot 2CuCl^c$	1500	80
$(n-C_4H_9)_2Sn(CH=CH_2)_2^c$	1580	$(n-C_4H_9)_2Sn(CH=CH_2)_2 \cdot 2CuCl$	1490	90

^a 25% solution in $CHCl_3$. ^b 25% solution in CCl_4 . ^c Neat film. ^d Nujol mull. ^e KBr pellet.

dination, $\Delta\nu$, is observed to be 80 to 90 cm^{-1} . This shift is greater than that normally observed for olefin-copper(I) chloride complexes, but it is not as large as that usually observed for olefin-platinum complexes¹¹. However, shifts as large as 100 cm^{-1} have been reported for some polyene-copper(I) chloride complexes⁶. No absorption which could be assigned to uncomplexed C=C stretching modes are observed in the spectra of the complexes.

NMR spectra

NMR spectra were obtained for the compounds, $(CH_3)_2Si(CH=CH_2)_2 \cdot 2CuCl$,

TABLE 2

NMR DATA FOR THE DIVINYLMETALLIC COMPLEXES^a

Compound	Center of vinyl multiplet (rel. intensity)	Alkyl resonance (rel. intensity)
$(CH_3)_2Si(CH=CH_2)_2 \cdot 2CuCl$	4.95(1)	9.72(1)
$(CH_3)_2Sn(CH=CH_2)_2 \cdot 2CuCl$	4.75(1)	9.65(1)
$(n-C_4H_9)_2Sn(CH=CH_2)_2 \cdot 2CuCl$	4.78(1)	8.75(3)

^a Spectra obtained in $CDCl_3$ solutions containing tetramethylsilane as internal standard. All chemical shifts are given in units of τ (ppm).

$(\text{CH}_3)_2\text{Sn}(\text{CH}=\text{CH}_2)_2 \cdot 2 \text{CuCl}$, and $(\text{C}_4\text{H}_9)_2\text{Sn}(\text{CH}=\text{CH}_2)_2 \cdot 2 \text{CuCl}$, and the pertinent data are tabulated in Table 2. Each of the compounds has only one vinyl multiplet indicating that the compounds are symmetrical and that there is little decomposition in the deuteriochloroform solutions. Furthermore, the vinyl multiplets of the complexes exhibit the typical upfield shift characteristic of complexed olefins¹². This shift is about 0.9 ppm for the complexes studied. Unfortunately, similar NMR data for olefin-copper(I) chloride complexes are not available for comparison.

Stability of the compounds

There are several factors which might be invoked to explain the unusual stability of vinylmetallic-copper(I) chloride complexes. In the case of the dibutyldivinyltin complex the low volatility of the ligand may contribute to the apparent stability of the complex. However, the other ligands are all somewhat volatile, and it is felt that the explanation for the stability of these compounds possibly lies in the rather unusual bonding which is possible in these complexes.

A large amount of data has been accumulated which indicates the importance of $p_\pi-d_\pi$ bonding in the Group IV vinylmetallic compounds^{13,14}. Even more important, in these systems, because of better energy matching, is $p_\pi-d_\pi$ bonding¹⁵.

The commonly accepted bonding scheme for olefin-transition metal complexes involves two parts, forward coordination and back donation. In forward coordination, electron density flows from the p_π -system of the olefin into empty orbitals of suitable symmetry on the transition metal. The buildup of electron density on the transition metal is compensated by back donation, from suitable occupied d orbitals, into the p_{π^*} orbitals of the olefin. However, in the vinylmetallic ligand the p_{π^*} orbital would be expected to interact rather strongly with an empty d orbital such as $d_{x^2-y^2}$ or d_{z^2} on the Group IV metal. Such an interaction would allow for delocalization of electron density into the Group IV metal from the back bonding of the transition metal. The back bonding electron density would occupy an excited state molecular orbital encompassing three atoms, the Group IV atom and the two carbon atoms of the π -system. On the other hand, a direct $d-d$ orbital interaction between the copper atom and the Group IV atom must also be considered possible since their approach to each other could be very close in the complexes.

We are currently investigating other vinylmetallic-transition metal complexes to determine if enhanced stability is a general feature of the vinylmetallic-transition metal interaction.

ACKNOWLEDGEMENT

The authors are pleased to acknowledge the support of this work by the Robert A. Welch Foundation (Grant No. AI-306).

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