Journal of Organometallic Chemistry, 113 (1976) 187–200
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

INSERTION REACTIONS OF CARBON DIOXIDE AND CARBON DISULFIDE INTO ALKYL—COPPER BONDS OF ALKYLCOPPER(I) COMPLEXES HAVING TERTIARY PHOSPHINE LIGANDS

AKIRA MIYASHITA and AKIO YAMAMOTO *

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, O okayama, Meguro ku, Tokyo 152 (Japan)

(Received December 8th, 1975)

Summary

Alkylcopper(I) complexes with triphenylphosphine ligands (alkyl = Me, Et, n-Pr, i-Bu) react with carbon dioxide to give carboxylato complexes, $(RCOO)Cu(PPh_3)_2$ and two types of CO_2 adducts, $(RCOO)Cu(CO_2)(PPh_3)_2$ and $Cu_2(CO_2)(PPh_3)_2(C_6H_4PPh_2)_2$. Similar reactions with carbon disulfide yield dithiocarboxylato complexes, $(RCSS)Cu(PPh_3)_2$. Alkylcopper complexes with 1,2-bis(diphenylphosphinoethane), $(RCu)_2(dpe)_3$, also react with carbon dioxide and carbon disulfide to afford insertion products of CO_2 and CS_2 into alkyl—copper bonds. Boiling of $(RCSSCu)_2(dpe)_3$ in CS_2 causes P—C bond cleavage in the dpe ligand and gives $Cu(CS_2)(PPh_2)(dpe)$ together with dithiocarboxylic acid and diphenylvinylphosphine. All the isolated complexes were characterized by elemental analyses, IR and NMR spectroscopy and chemical reactions.

Introduction

Insertion reactions of carbon dioxide into transition metal—carbon bonds have attracted considerable attention, and examples of CO_2 insertions into Ti—phenyl [1], Zr—benzyl [2] and Rh—phenyl [3] bonds have been reported. We report here the insertion of CO_2 into isolated alkylcopper complexes [4] with tertiary phosphine ligands. A part of the results has been reported in preliminary form [5] and the reaction of CO_2 with tricyclohexylphosphine-coordinated alkylcopper complexes have been previously described [6]. Very recently, the reversible reaction of CO_2 with a cyanomethylcopper complex [7], and carboxylation reactions of fluorenyl and phenylethylcopper [8] have been reported.

This report also includes the reactions of alkylcopper complexes with carbon disulfide, an isoelectronic analog of carbon dioxide. The CS_2 insertion reaction into a transition metal—alkyl bond has a few precedents among alkylrhodium [9], alkylmanganese and alkylrhenium complexes [10].

Results and discussion

1. Reactions with carbon dioxide

Preparation of copper(I) carboxylates and their CO_2 adducts. Carbon dioxide is readily inserted into the Cu—C bond of alkylcopper complexes having triphenylphosphine ligands with compositions of $MeCu(PPh_3)_2 \cdot 0.5$ ether and $RCu(PPh_3)_2$ (R = Et, n-Pr, i-Bu) under mild conditions to afford copper(I) carboxylate complexes containing triphenylphosphine (Ia—Ie) and two types of CO_2-coordinated complexes (IIa—IId and III). Tables 1 and 2 summarize analytical data, yields, and physical properties of the complexes isolated. The carboxylate complexes without coordinated CO_2 can be prepared by the reaction of carbon dioxide with alkylcopper complexes at 0°C in diethyl ether or tetrahydrofuran.

$$RCuL_n + CO_2 \xrightarrow[-20 \text{ to } 0^\circ C]{} \underset{(I)}{(RCOO)Cu(PPh_3)_2} \qquad (1)$$

(Ia) $L_n = (PPh_3)_3, (PPh_3)_2 \cdot 0.5\ Et_2O$; R = Me
(Ib) $L_n = (PPh_3)_2$; R = Et
(Ic) $L_n = (PPh_3)_2$; R = n-Pr
(Id) $L_n = (PPh_3)_2$; R = i-Bu

The CO_2 insertion products have been identified as copper(I) carboxylates by comparison with carboxylates obtained independently by reactions of the alkylcopper complexes with the corresponding carboxylic acids. Evolution of 1 mol equivalent of alkane was observed in each case.

$$RCuL_n + R'COOH \xrightarrow[\text{ether}]{} \underset{(I)}{(R'COO)CuL_n} + RH \qquad (2)$$

The melting points, elemental analyses, IR and NMR spectra of the carboxylates prepared by the two routes showed good agreement. Recently, similar acetatocopper(I) complexes containing various ligands including triphenylphosphine have been prepared by Edwards et al. via an independent route [11]; the isolated complexes with the same ligands seem identical to our products.

Alkylcopper complexes having other tertiary phosphine ligands such as diphenylmethylphosphine, tributylphosphine, triethylphosphine and tricyclohexylphosphine react with carbon dioxide to afford their carboxylate complexes.

Prolonged reaction of CO_2 with the alkylcopper complexes containing triphenylphosphine in THF at room temperature caused dissolution of the initially formed complex (I) and gave flaky white crystals of carboxylate complexes containing 1 equivalent of CO_2 coordinated to copper.

The CO_2-coordinated complexes (II) were readily converted into complexes I with loss of CO_2 during their attempted recrystallization from benzene, toluene or THF.

$$\mathrm{RCu(PPh_3)_2 + 2\ CO_2 \xrightarrow[-20\ \mathrm{to}\ 25]{12\ \mathrm{h}} (RCOO)Cu(CO_2)(PPh_3)_2} \qquad (3)$$

(IIa) R = Me
(IIb) R = Et
(IIc) R = n-Pr
(IId) R = i-Bu

When the reaction of $\mathrm{MeCu(PPh_3)_2 \cdot 0.5\ Et_2O}$ with carbon dioxide was carried out in pyridine, a pyridine-coordinated acetatocopper complex $\mathrm{(CH_3COO)Cu(Py)(PPh_3)}$ (Ie) was obtained. Recrystallization of the $\mathrm{CO_2}$-containing complex (IIa) at room temperature from pyridine also gave Ie with the liberation of $\mathrm{CO_2}$.

The $\mathrm{CO_2}$ insertion reaction into the Cu—C bond is considered to proceed through an intermediate $\mathrm{CO_2}$-coordinated alkylcopper complex, but attempts to isolate such an intermediate complex at low temperatures failed, presumably because the insertion reaction of $\mathrm{CO_2}$ takes place rapidly even at low temperatures.

The coordinatively saturated methylcopper complexes with three tertiary phosphine ligands such as $\mathrm{MeCu(PPh_3)_3}$(toluene) and $\mathrm{MeCu(PPh_2Me)_3}$ reacted slowly with $\mathrm{CO_2}$ to give acetato complexes, $\mathrm{(MeCOO)Cu(PPh_3)_3}$ and $\mathrm{(MeCOO)Cu(PPh_2Me)_3}$, but no $\mathrm{CO_2}$-coordinated complexes were obtained.

The isolated complexes I and II show chemical properties expected for the proposed formulations. The carboxylate complexes I and their $\mathrm{CO_2}$-adducts (II) readily react with dry hydrogen chloride in benzene to liberate quantitative amounts of the corresponding carboxylic acids; reactions with methyl iodide and ethyl bromide released methyl and ethyl carboxylates. In these reactions complexes II liberated also 1 mol equivalent of $\mathrm{CO_2}$ per mol equivalent of copper. Pyrolysis of II at 200°C liberated quantitative amounts of $\mathrm{CO_2}$ for the composition of $\mathrm{(RCOO)Cu(CO_2)(PPh_3)_2}$ and acidolysis with $\mathrm{H_2SO_4}$ also released $\mathrm{CO_2}$ quantitatively. The amounts of carboxylic acids and $\mathrm{CO_2}$ liberated in these reactions are included in Tables 1 and 2. These complexes are thermally very stable and the effect of the alkyl chain length on the decomposition temperature was not pronounced.

Another type of $\mathrm{CO_2}$ adduct without carboxylato group was obtained after II was removed from the reaction solution of the alkylcopper complex with $\mathrm{CO_2}$. The complex isolated from the solution contains one molecule of $\mathrm{CO_2}$ per two copper atoms and has an analytical value close to that required by $\mathrm{Cu_2(CO_2)(PPh_3)_4}$.

This complex III differs in its properties from those of I and II. It releases 0.5 equivalent of $\mathrm{CO_2}$ per copper atom on pyrolysis at 200°C, on acidolysis with $\mathrm{H_2SO_4}$ and treatment with methyl iodide. Acidolysis with dry hydrogen chloride in benzene gave no carboxylic acid. The coordinated $\mathrm{CO_2}$ was readily liberated on addition of pyridine, dimethylformamide, acetonitrile and tertiary phosphines.

The molecular weight of complex III, determined by a cryoscopic method in benzene, was 1030, supporting its formulation as a binuclear copper complex. A similar binuclear complex with $\mathrm{CO_2}$ as a bridging ligand has been reported for nickel [12]. Since the complex is diamagnetic, two alternative structures are considered: (i) the copper atoms are zero-valent with spin—spin interaction between

TABLE 1

ANALYTICAL DATA OF COPPER CARBOXYLATES PREPARED BY INSERTION OF CO_2 INTO ALKYLCOPPER CONTAINING TRIPHENYLPHOSPHINE LIGANDS

Number	Formula	M.p. [c] (dec.) (°C)	RCOOH [a] yield (%)	Analysis Found (calcd.) (%)				Yield [b] (%)
				C	H	N	Cu	
Ia	$(CH_3COO)Cu(PPh_3)_2$	185–186	96	70.7 (70.6)	5.1 (5.2)		9.9 (9.8)	68
Ib	$(C_2H_5COO)Cu(PPh_3)_2$	186–188	92	70.2 (70.9)	4.8 (5.4)		9.4 (9.6)	62
Ic	$(n\text{-}C_3H_7COO)Cu(PPh_3)_2$	187–189	87	71.8 (71.2)	5.1 (5.5)		9.3 (9.4)	58
Id	$(i\text{-}C_4H_9COO)Cu(PPh_3)_2$	186–187	90	71.7 (71.5)	5.1 (5.7)		8.9 (9.2)	61
Ie	$(CH_3COO)Cu(PPh_3)(Py)$	175–180	94	63.9 (64.7)	4.7 (5.0)	2.6 (3.0)	13.1 (13.7)	54

[a] The yield of carboxylic acid which was obtained on acidolysis of the carboxylato complex. [b] The yields of the products calculated on the basis of the alkylcopper complexes. [c] Melting (with decomposition) points measured in sealed tubes.

TABLE 2

ANALYTICAL DATA OF COPPER–CARBON DIOXIDE COMPLEXES WITH TRIPHENYLPHOSPHINE LIGANDS

Number	Formula	M.p. (dec.) (°C)	CO_2/Cu [c]	RCOOH [a] yield (%)	Analysis Found (calcd.) (%)			Yield [b] (%)
					C	H	Cu	
IIa	$(CH_3COO)Cu(CO_2)(PPh_3)_2$	151–152	1.01	35	67.7 (67.8)	4.8 (4.7)	9.2 (9.5)	53
IIb	$(C_2H_5COO)Cu(CO_2)(PPh_3)_2$	152–154	0.96	72	68.0 (67.3)	5.0 (4.6)	9.0 (9.3)	62
IIc	$(n\text{-}C_3H_7COO)Cu(CO_2)(PPh_3)_2$	155–158	0.94	84	68.5 (68.6)	5.2 (4.9)	8.8 (8.2)	50
IId	$(i\text{-}C_4H_9COO)Cu(CO_2)(PPh_3)_2$	154–157	1.00	70	68.8 (68.4)	5.4 (5.2)	8.7 (8.2)	45
III	$Cu_2(CO_2)(PPh_3)_2(PPh_2C_6H_4)_2$	150–152	0.46		71.9 (72.7)	5.0 (5.4)	10.4 (10.7)	10

[a, b] See footnotes in Table 1. [c] The amount of CO_2 released on pyrolysis at 200 °C.

them to make the complex diamagnetic; (ii) one of the triphenylphosphine ligands coordinated with each copper atom is *ortho*-metallated. We favor the latter *ortho*-metallated structure, $Cu_2(CO_2)(PPh_3)_2(C_6H_4PPh_2)_2$, since its acidolysis with deuterated sulfuric acid afforded triphenylphosphine in which about one of the three phenyl groups was mono-dueterated as revealed by mass-spectroscopic examination of water produced by degradative oxidation of the triphenylphosphine liberated on acidolysis of III.

NMR and IR spectra of complexes I—III. On reaction of methylcopper complexes with CO_2, the ^1H NMR methyl signal at τ 10.3 ppm disappears and is replaced with a singlet methyl signal of an acetato group at τ 7.65 ppm which is close to the methyl signal of the free acetic acid at τ 7.97 ppm. The NMR spectrum of III shows only triphenylphosphine signals.

Table 3 tabulates the IR absorption bands of the carboxylato group and the coordinated CO_2 molecule. The carboxylate complexes Ia—Id show strong absorption bands of antisymmetric and symmetric stretching vibrations of the carboxylato group in the regions of 1540—1640 and 1410—1420 cm^{-1} and deformation vibration of the carboxylato group near 670 cm^{-1}. The antisymmetric ν(O—C—O) band of the acetato group in Ia appears at lower frequency than that of free acetic acid and is close to that of the acetate anion in $Na(CH_3COO)$ [13] and $(CH_3)_2Sn(CH_3COO)_2$ [14]. With increase of the alkyl chain length of the carboxylato group the antisymmetric ν(O—C—O) band shifts to higher frequency whereas the symmetric ν(O—C—O) and δ(O—C—O) bands showed little change. This tendency is in line with the trend observed in IR shift of the carboxyl absorptions of free carboxylic acids and reflects the inductive effect of the alkyl group. The carboxylato group in $(CH_3COO)Cu(PPh_3)_2$ is probably bonded to copper through two oxygens. Replacement of one of the two triphenylphosphine ligands in $(CH_3COO)Cu(PPh_3)_2$ with pyridine causes a shift of the $\nu(O—C—O_{asym})$ band to a higher frequency. Complex If with three diphenylmethylphosphine ligands also shows the high $\nu(O—C—O_{asym})$ band due to the increase in the basicity of the ligand.

The antisymmetric ν(O—C—O) bands of the carboxylate group in the CO_2-coordinated complexes IIa—IId appear at higher frequencies than those of Ia—Id whereas the symmetric ν(O—C—O) and δ(O—C—O) bands are observed at somewhat lower frequencies than those of Ia—Id and are close to those of the pyridine-coordinated complex Ie. Presumably the CO_2 in type II complexes may be acting as a σ-donor and also may occupy a coordination position to hinder the bidentate coordination of the carboxylato group as in Ia—Id. Either or both effects may be reflected in the carboxylato absorptions bands. The assumption that CO_2 coordination causes the unidentate coordination of the carboxylato group in IIa—IId is compatible with the 18 electron rule.

The CO_2-coordinated carboxylato complexes IIa—IId show characteristic bands near 2600, 1600, 1300 and 820 cm^{-1} which disappear on removal of the coordinated CO_2 by pyrolysis at 150°C. The bands of the carboxylato groups remain after pyrolysis.

The other type of CO_2-adduct (III) shows also bands of the coordinated CO_2 ligand at similar frequencies with those of II except for the absence of the band at 2600 cm^{-1} in complex III. Since III contains one CO_2 molecule per two copper atoms, this band may be related with symmetric vibrations of the coordinated

(continued on p. 198)

TABLE 3

IR SPECTRA [a] OF COPPER(I) CARBOXYLATES AND THEIR CO_2 COMPLEXES

Number	Formula	$\nu(OCO_{asym})$ [c] (cm^{-1})	$\nu(OCO_{sym})$ [c] (cm^{-1})	$\delta(OCO_{sym})$ [c] (cm^{-1})	Others [b]
Ia	$(CH_3COO)Cu(PPh_3)_2$	1550vs	1413s	667s	
Ib	$(C_2H_5COO)Cu(PPh_3)_2$	1512vs	1420s	665(sh)	
Ic	$(n\text{-}C_3H_7COO)Cu(PPh_3)_2$	1600vs	1514m	670(sh)	
Id	$(i\text{-}C_4H_9COO)Cu(PPh_3)_2$	1640vs	1412m	675m	
Ie	$(CH_3COO)Cu(PPh_3)(Py)$	1625vs	1396s	625m	
If	$(CH_3COO)Cu(PPh_2Me)_3$	1625s	1385s	649m	
Ig	$(C_2H_5COOCu)_2(dpe)_3$	1595vs	1382s	642w	
IIa	$(CH_3COO)Cu(CO_2)(PPh_3)_2$	1640s	1393s	622w	2620w, 1600vs, 1302s, 821m
IIb	$(C_2H_5COO)Cu(CO_2)(PPh_3)_2$	1635s	1385s	645w	2600w, 1595vs, 1297s, 815m
IIc	$(n\text{-}C_3H_7COO)Cu(CO_2)(PPh_3)_2$	1638vs	1390s	640w	2600w, 1600vs, 1310s, 825m
IId	$(i\text{-}C_4H_9COO)Cu(CO_2)(PPh_3)_2$	1625s	1408m	660(sh)	2600w, 1605vs, 1325s, 830m
III	$Cu_2(CO_3)(PPh_3)_2(PPh_2C_6H_4)_2$			·	1595s, 1150(sh), 826m

[a] Measured as KBr discs, s, strong, vs, very strong, m, medium; w, weak, (sh), shoulder. [b] Bands disappeared by heating at 150 °C. [c] IR bands of $(CH_3COO)Na$: $\nu(OCO_{asym})$, 1578s, $\nu(OCO_{sym})$, 1414s, $\delta(OCO_{sym})$, 646s.

TABLE 4

ANALYTICAL DATA OF COPPER(I) DITHIOCARBOXYLATES AND CS_2 COMPLEX

Number	Formula	Color	M.p. (dec.)[a] (°C)	Analysis Found (calcd.)			Yield (%)[b]
				C	H	S	
IVa	$(CH_3CSS)Cu(PPh_3)_2$	white orange	180–181	66.9 (67.1)	5.1 (4.9)	9.5 (9.4)	73
IVb	$(C_2H_5CSS)Cu(PPh_3)_2$	brown	185–187	67.8 (67.6)	5.0 (5.1)	9.4 (9.3)	67
IVc	$(n\text{-}C_3H_7CSS)Cu(PPh_3)_2$	brown	169–171	68.0 (67.9)	5.5 (5.3)	9.7 (9.1)	52
Va	$(CH_3CSSCu)_2(dpe)_3$	orange	211–213	64.4 (65.4)	5.6 (5.3)	8.3 (8.5)	65
Vb	$(C_2H_5CSSCu)_2(dpe)_3$	yellow orange	182–185	66.8 (65.8)	5.5 (5.4)	8.2 (8.3)	72
Vc	$(n\text{-}C_3H_7CSSCu)_2(dpe)_3$	white orange	157–159	66.4 (66.2)	5.4 (5.5)	9.0 (8.2)	66
VI	$Cu(PPh_3)(CS_2)(dpe)$	white orange	170–171	64.1 (64.7)	5.4 (4.8)	8.5 (8.8)	35

[a] Melting (with decomposition) points were measured in sealed tubes. [b] Yields are given based on alkylcopper complexes.

CO_2 molecule. The bands ascribed to the coordinated CO_2 disappear on pyrolysis of III with liberation of CO_2.

Insertion of CO_2 into the alkyl—copper bond also takes place with alkylcopper complexes containing bidentate dpe ligands *. $(EtCu)_2(dpe)_3$ reacted with CO_2 to give a propionatocopper complex having a composition close to $(EtCOOCu)_2(dpe)_3$ at 0—20°C. A similar acetatocopper complex with a 2 : 3 composition has been prepared by Edwards et al. [11].

It is known that the dpe ligand in alkyl- and aryl-copper complexes is susceptible to the P—C bond cleavage in solution [4b,15a] **. The fact that the carboxylato complexes were obtained in the reaction of $(RCu)_2(dpe)_3$ with CO_2 suggests that CO_2 insertion into the alkyl—copper bond is a fast reaction and takes place prior to the P—C cleavage reaction of the dpe ligand. In addition to $(EtCOOCu)_2(dpe)_3$, a CO_2-coordinated complex, the composition of which has not been established yet, has been obtained. This complex shows IR bands of the coordinated CO_2 at 2600w, 1610vs, 1352s and 832m in addition to bands of the propionato ligand at 1595vs, 1382s and 642w cm^{-1}.

2. *Reactions with carbon disulfide*

Carbon disulfide is readily inserted into the Cu—alkyl bond of $RCu(PPh_3)_2$ to give dithiocarboxylatocopper(I) complexes.

$$RCu(PPh_3)_2 + CS_2 \xrightarrow[-20 \text{ to } -10^\circ C]{3\text{ h}} (RCSS)Cu(PPh_3)_2 \qquad (4)$$

$$(RCu)_2(dpe)_3 + 2\ CS_2 \xrightarrow[10^\circ C]{4\text{ h}} (RCSS)_2(dpe)_3 \qquad (5)$$

Table 4 summarizes the analytical data and physical properties of the isolated dithiocarboxylato complexes. Reaction of ethylcopper complexes with triphenylphosphine and dpe with dithiopropionic acid led to dithiopropionatocopper complexes with triphenylphosphine and dpe ligands, respectively, with evolution of ethane. The dithiopropionato complexes prepared by two routes were proved to be identical by comparison of m.p.'s elemental analyses, IR and NMR spectra, and chemical properties. $(EtCSS)Cu(PPh_3)_2$ and $(EtCSS)_2Cu(dpe)_3$ released dithiopropionic acid on treatment with hydrogen chloride in CS_2 and gave methyl dithiopropionate on reaction with methyl iodide.

Table 5 shows relevant IR bands and NMR resonances of the dithiocarbonato complexes. As observed in the ν(O—C—O) bands of the carboxylato complexes, the antisymmetric ν(S—C—S) band of the dithiocarboxylato group in (RCSS)-$Cu(PPh_3)_2$ shifts slightly to higher frequency with the increase in the alkyl chain length of the dithiocarboxylato group.

In contrast to the trend in the shift of the symmetric ν(O—C—O) band in the carboxylato complexes the symmetric ν(S—C—S) band shifts to higher frequency with increase of the alkyl chain length. In the dpe-coordinated complexes the trend of the shift of antisymmetric ν(S—C—S) band is reversed from that in the PPh_3-coordinated complexes. The reason for this is not clear. The dpe complexes Va, Vb and Vc isolated from CS_2 solutions show a weak band at 1510

---

* dpe = 1,2-bis(diphenylphosphinoethane).

** Similar reactions involving P—C bond cleavage in PPh_3-coordinated complexes are also known, see e.g. ref. 15b.

TABLE 5

IR AND NMR DATA OF COPPER(I) DITHIOCARBOXYLATES AND AS CS_2 COMPLEX

Number	Formula	IR [a] (cm^{-1})		^1H NMR [b] τ(RCSSCu) (ppm)
		$\nu(CS_{2asym})$	$\nu(CS_{2sym})$	
IVa	$(CH_3CSS)Cu(PPh_3)_2$	1138vs	816vs	7.36(s, CH_3)
IVb	$(C_2H_5CSS)Cu(PPh_3)_2$	1140m	935s	8.82(t, CH_3), 7.22(q, CH_2)
IVc	$(n\text{-}C_3H_7CSS)Cu(PPh_3)_2$	1145m	968s	9.10(t, CH_3), 8.27(sex, CH_2) 7.23(t, CH_2)
Va	$(CH_3CSSCu)_2(dpe)_3$	1140vs	870s	
Vb	$(C_2H_5CSSCu)_2(dpe)_3$	1135m	925s	
Vc	$(n\text{-}C_3H_7CSSCu)_2(dpe)_3$	1130m	950s	
VI	$Cu(PPh_2)(CS_2)(dpe)$	(1025vs, 855m, 540m)		7.92(4H, CH_2 of dpe) 2.92(30 H, Ph in PPh_2 and dpe)

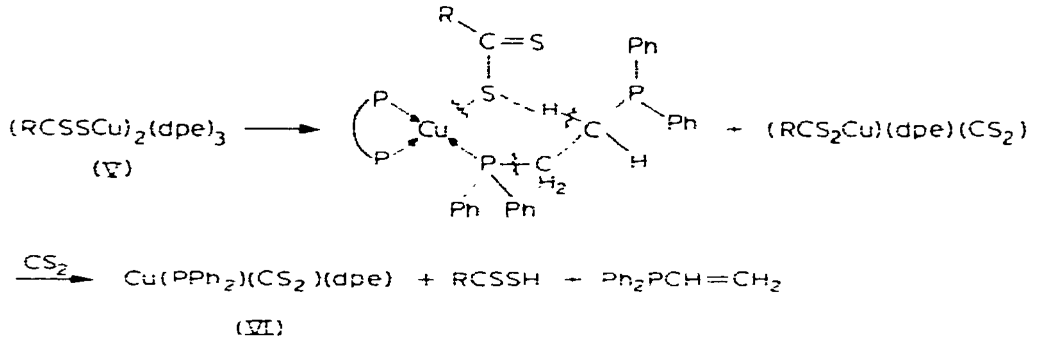
[a] KBr disk, s, strong, vs, very strong; m, medium. [b] CS_2 15% solution, TMS standard; s, singlet; t, triplet; q, quartet; sex, sextet.

cm^{-1} which disappears on thorough vacuum drying. The band may be related with sulfur-bonded CS_2 [9] or solvated CS_2. The PPh_3-coordinated dithiocarboxylato complexes satisfy the inert gas configuration on the assumption that the dithiocarboxylato group is bonded with copper as a bidentate ligand. However, the same assumption applied to the dpe-coordinated complex V leads to a 20 electron configuration around copper if we assume one chelate and the other bridging dpe ligands. Although the question which of the ligands, dpe or RCSS, is monodentate remains open, we favor the monodentate RCSS group because of the similarity of the structure with $(RCu)_2(dpe)_3$ which probably has one chelate and the other bridging dpe ligand per each copper atom, satisfying the 18 electron configuration.

The ^1H NMR spectra of dithiocarboxylato complexes with triphenylphosphine ligands show the presence of the dithiocarboxylato group bonded to copper. The assignments are straightforward and included in Table 5.

In contrast to the carboxylato complexes where the formation of CO_2-coordinated complexes was observed, no CS_2-coordinated dithiocarboxylatocopper(I) complexes were isolated in the reaction of CS_2 with alkylcopper complexes. The interaction of the CO_2 and CS_2 molecules with the carboxylato and dithiocarboxylato complexes depends on two factors. First, the difference in electronegativity between the carboxylato and dithiocarboxylato groups affects the electron density around copper and the less electronegative dithiocarboxylato group would make the copper more electron rich than the carboxylato group, thus interaction with a Lewis base would become weaker. Second, CS_2 is considered to be a stronger electron donor and weaker electron acceptor than CO_2 and as a consequence the interaction of CS_2 with less electronegative dithiocarboxylato complexes would be weaker if electron donation from CS_2 to copper is the main factor in determining the affinity between CS_2 and the copper complex.

Formation of the CS_2-coordinated complex, however, did occur when the dpe-coordinated dithiocarboxylatocopper complexes Va, Vb and Vc were refluxed in carbon disulfide. A complex with a composition of $Cu(CS_2)(PPh_2)(dpe)$ (VI) was isolated from the CS_2 solution. In view of precedents of P—C bond cleavage of the dpe ligand in solution [4b, 15] the reaction is considered to pro-



(6)

ceed as shown in eq. 6. The dithiocarboxylato group in (V) may abstract a hydrogen atom of the bridging dpe ligand thus causing P—C scission which gives the complex with the σ-bonded Ph_2P ligand and diphenylvinylphosphine.

The IR spectrum of VI shows strong absorptions at 1025 and 355 cm^{-1} which are assigned to C=S stretching vibrations and a band of medium intensity at 540 cm^{-1} which is assigned to C—S stretching vibration of CS_2 which is coordinated to copper in a side-on manner [16].

Experimental

All experiments were carried out under deoxygenated nitrogen or argon atmosphere, or in vacuo. Solvents were dried by usual procedures, distilled and stored under argon or nitrogen. Carbon dioxide was used after passing it through $CaCl_2$ and SiO_2 columns. IR spectra were recorded on a Hitachi Model EPI-G3 and ^{1}H NMR spectra were recorded with a Japan Electron Optics Lab. JNM-PS-100 spectrometer with TMS as internal standard. Carbon disulfide was of reagent grade quality and was dried with CaH_2. The alkylcopper(I) complexes $CuR(PPh_3)$ and $(CuR)_2(dpe)_3$ were prepared as previously reported [4,5]. The copper content was determined by iodometry after degrading the sample with sulfuric acid.

Reactions with carbon dioxide

Preparation of acetatobis(triphenylphosphine)copper (Ia). A dry CO_2 stream was bubbled through a THF solution containing methylbis(triphenylphosphine)-copper(I) etherate (3 g), initially at −40° C, with temperature subsequently being raised gradually to 0° C. After a while, the yellow brown color of the solution became colorless, and white crystals were slowly precipitated when the mixture was kept below 0° C. This solid was recrystallized from toluene or THF to give white prisms of complex Ia (2 g), which is diamagnetic and soluble in benzene, toluene and THF, yield 68%. NMR (60 MHz in pyridine): τ 7.65 ppm (s, 3H of CH_3COO^-). cf. CH_3COOH of free acetic acid τ 7.97s ppm.

Preparation of acetato(triphenylphosphine)(pyridine)copper (Ie). To a yellow solution containing 2 g of methylbis(triphenylphosphine)copper etherate in 20 ml of pyridine, CO_2 gas was bubbled initially at −40° C and then at room temperature. Addition of a small amount of n-hexane caused precipitation of white crystals on cooling overnight; yield 0.8 g, 54%. The IR spectrum of the complex (Ie) indicated the bands of coordinated pyridine.

Preparation of propionatobis(triphenylphosphine)copper (Ib) and n-butyratobis(triphenylphosphine)copper (Ic). These complexes were prepared in a similar manner. Into a THF or ether solution of ethylbis(triphenylphosphine)copper (4 g) CO$_2$ was bubbled at —40 C. White crystals were slowly precipitated when the mixture was kept below 0°C. After recrystallization of the solid from THF, white diamagnetic prisms (Ib) were obtained; yield 2.6 g, 62%. The butyrato complex Ic was obtained in a 50% yield as white crystals.

Preparation of acetato(carbon dioxide)bis(triphenylphosphine)copper (IIa). On prolonged bubbling of CO$_2$ into a THF solution of methylbis(triphenylphosphine)copper at room temperature (12 h), the acetato complex Ia which first formed, dissolved again and another copper complex IIa precipitated as flaky white crystals. These were washed repeatedly with dry THF under a CO$_2$ stream, dried in vacuum and characterized as (CH$_3$COO)Cu(CO$_2$)(PPh$_3$)$_2$ (IIa, yield 53%); the product was diamagnetic and had correct elemental analyses. IIa is slightly soluble in benzene, toluene and THF, but attempts to recrystallize it from these solvents resulted in loss of CO$_2$ and recovery of the acetate complex Ia.

Preparation of other carboxylato(carbon dioxide)bis(triphenylphosphine)copper(I) complexes (IIb—IId). Into a THF/ether suspension of ethylbis(triphenylphosphine)copper (4 g), a dry CO$_2$ stream was passed initially at —40°C, with temperature subsequently being raised gradually to room temperature. The resulting colorless solution gradually changed to a white suspension and then CO$_2$ was further bubbled for 10 h. White flaky crystals separated from the colorless solution and were repeatedly washed with dry THF under a CO$_2$ stream, then dried in vacuum and characterized as (C$_2$H$_5$COO)Cu(CO$_2$)(PPh$_3$)$_2$ (IIb, yield 62%); the product was diamagnetic. IIc and IId were prepared in a similar manner in 50 and 45% yields, respectively.

Preparation of μ-(carbon dioxide)bis(triphenylphosphine)bis(o-diphenylphosphinophenyl)dicopper(I) (III). Into a THF solution of methylbis(triphenylphosphine)copper etherate (2.0 g), dry CO$_2$ was passed initially at —40°C. As the temperature was raised gradually to room temperature, white flaky crystals slowly precipitated and then CO$_2$ was further bubbled for 12 h. After removal of the complex which precipitated, white fine crystals were obtained on cooling the solution; they were repeatedly washed with dry ether under a CO$_2$ stream, dried in vacuum and characterized as Cu$_2$(CO$_2$)(PPh$_3$)$_2$(PPh$_2$C$_6$H$_4$)$_2$ (yield 10%). Analytical data are included in Table 2.

For proving the *ortho*-metallated structure the complex was hydrolyzed with D$_2$SO$_4$ diluted with D$_2$O (pH ~ 1). The white powder precipitated was washed three times with D$_2$O and dried in vacuo at 75—60°C. The powder mixed with Cu$_2$O was heated and the water obtained by degration was analyzed by mass spectrometry. The water had a deuterium content of 1.5% (calcd. 3.3%).

Reactions with carbon disulfide

Preparation of dithiocarboxylatobis(triphenylphosphine)copper(I) (IVa—IVc). Carbon disulfide (25 ml) was distilled in vacuo into a reaction vessel containing 1.7 g of CuCH$_3$(PPh$_3$)$_2$ · 0.5 ether (2.7 mmol). The mixture was allowed to react initially at —50°C and then at room temperature for 2—4 h.

Addition of ether to the resultant deep red solution gave white orange needles of CH$_3$CSSCu(PPh$_3$)$_2$ on cooling. The complex was recrystallized from CS$_2$/diethyl ether, washed with ether and vacuum-dried; yield 70%; diamagnetic crystals. IVb and IVc were prepared in a similar manner in yields of 60 and 50%, respectively.

Preparation of dithioacetatobis(diphenylphosphinoethane)-μ-diphenylphosphinoethanedicopper(I) (Va). The light yellow complex $(CuCH_3)_2(dpe)$ (0.5 g) was dissolved in CS_2 (10 ml) at —50°C. With a gradual temperature rise to room temperature, orange crystals were precipitated from the yellow-orange solution. After filtration, the complex was washed with ether and vacuum dried; yield 70%, diamagnetic crystals. Attempted recrystallization from CS_2 led to decomposition and gave $Cu(CS_2)(PPh_2)(dpe)$. $(n\text{-}C_3H\text{-}CSSCu)_2(dpe)_3$ (Vc) was prepared similarly in 65% yield.

Preparation of diphenylphosphino(diphenylphosphinoethane)(carbon disulfide)copper(I) (VI). After CS_2 was added to the yellow orange complex (Va, Vb or Vc) by a trap-to-trap distillation, the reaction mixture was refluxed with stirring till the complex was dissolved. From the resulting dark-red solution which was filtered, white orange crystals were obtained on cooling. They were washed with diethyl ether and vacuum dried; yield 35%, diamagnetic crystals.

Reactions of $CuC_2H_5(PPh_3)_2$ and $(CuC_2H_5)_2(dpe)_3$ with dithiopropionic acid.

Dithiopropionic acid [13] (1 ml), was added to $CuC_2H_5(PPh_3)_2$ (2.5 g) in diethyl ether (50 ml) at —40°C. A white-orange complex precipitated from the resultant reddish-orange solution. Recrystallization from tetrahydrofuran or acetone gave brown crystals, which were washed with ether and vacuum dried, yield 60%. The reaction with the dpe-coordinated complex was carried out similarly.

Reaction of $C_2H_5CSSCu(PPh_3)_2$ and $(C_2H_5CSSCu)_2(dpe)_3$ with hydrogen chloride.

$C_2H_5CSSCu(PPh_3)_2$ was dissolved in CS_2 and dry hydrogen chloride was passed through the solution. The original deep brown color turned to red. The NMR spectrum of the resultant red solution indicated the formation of dithiopropionic acid, C_2H_5CSSH, by comparison with dithiopropionic acid which was prepared by a published method. Formation of dithiopropionic acid was similarly confirmed in the reaction of $(EtCSSCu)_2(dpe)_3$.

Reaction of $C_2H_5CSSCu(PPh_3)_2$ or $(C_2H_5CSSCu)_2(dpe)_3$ with methyl iodide

$C_2H_5CSSCu(PPh_3)_2$ was dissolved in CS_2 in a vacuum system and methyl iodide was added. After reaction for 25 h at room temperature, formation of methyl dithiopropionate, $C_2H_5CSSCH_3$ was confirmed by examining the NMR spectrum of the resultant dark red oily solution, τ (ppm) 8.74 (triplet, 3H in C_2H_5CSS), τ 7.06 (quartet, 2H in C_2H_5CSS) and τ 7.48 (singlet, 3H in SCH_3). $(EtCSSCu)_2(dpe)_3$ reacted in a similar manner with methyl iodide to give methyl dithiopropionate.

References

1 M.E. Vol'pin, Pure Appl. Chem., 30 (1972) 607.

2 C. Zucchini, E. Albizatti and V. Giannini, J. Organometal. Chem., 26 (1971) 357.

3 L.S. Kolomnikov, A.O. Gusev and M.E. Vol'pin, J. Organometal. Chem., 69 (1974) C10.

4 (a) A. Yamamoto, A. Miyashita, T. Yamamoto and S. Ikeda, Bull. Chem. Soc. Japan, 45 (1972) 583. (b) a full paper by A. Miyashita and A. Yamamoto, Bull. Chem. Soc. Japan, submitted.

5 A. Miyashita and A. Yamamoto, J. Organometal. Chem., 49 (1973) C57; Reports Asahi Glass Found. for Contrib. Ind. Techn., 18 (1973) 423.

6 T. Ikariya and A. Yamamoto, J. Organometal. Chem., 72 (1975) 145.

7 T. Tsuda, Y. Chujo and T. Saegusa, Abstr. 23rd Symp. Organometal. Chem. Japan, 1975, p. 37.

8 T. Tsuda, K. Ueda and T. Saegusa, J. Chem. Soc. Chem. Commun., (1974) 380.

9 D. Commereuc, J. Douek and G. Wilkinson, J. Chem. Soc., A, (1970) 1771.

10 E. Lindner, G. Grimmer and H. Weber, Angew. Chem., 82 (1970) 639.

11 D.A. Edwards and R. Richards, J. Chem. Soc. Dalton Trans., (1975) 637 and ref. cited therein.

12 P.W. Jolly, K. Jonas, C. Krüger and Y.H. Tsay, J. Organometal. Chem., 33 (1971) 109.

13 K. Itoh and H.J. Bernstein, Can. J. Chem., 34 (1956) 170.

14 J.D. Donaldson, J.F. Knifton and S.D. Ross, Spectrochim. Acta, 21 (1965) 276.

15 (a) G. van Koten and J.G. Noltes, Chem. Commun., (1972) 452; (b) J.R. Blickensderfer and H.D. Kaesz J. Amer. Chem. Soc., 97 (1975) 2681 and ref. cited therein.

16 I.S. Butler and A.E. Fenster, J. Organometal. Chem., 66 (1974) 161.