Inorganica Chimica Acta, 177 (1990) 35–42

Silyl–, stannyl– and plumbyl–copper compounds containing chelating and monodentate phosphine ligands

Hans-F. Klein*, **J. Montag**, **U. Zucha**

Eduard-Zintl Institut für Anorganische Chemie der Technischen Hochschule Darmstadt, Hochschulstrasse 10, O-6100 Darmstadt (F.R.G.)

Ulrich Flörke and **Hans-J. Haupt**

Anorganische und Analytische Chemie der Universität-GH, Warburger Strasse 100, O-4790 Paderborn (F.R.G.)

(Received May 14, 1990)

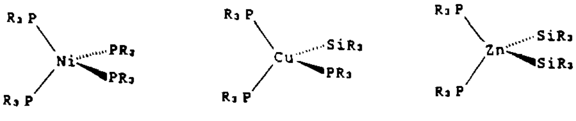
Abstract

Syntheses and properties of metal–metal bonded complexes of the type L_3CuER_3 are described, **1**: $ER_3 = Si(SiMe_3)_3$; 3 $L = CH_3C(CH_2PPh_2)_3 = L^3 =$ triphos. **2**: $ER_3 = SnCl_3$; $L = PMe_3$. **3**: $ER_3 = SnCl_2I$; $L = PMe_3$. **4**: $ER_3 = SnCl_3$; 3 L = triphos. **5**: $ER_3 = SnMe_3$; 3 L = triphos. **6**: $ER_3 = SnPh_3$; $L = PMe_3$. **7**: $ER_3 = SnPh_3$; $L = PPh_3$. **8**: $ER_3 = SnPh_3$; 3 L = triphos. **9**: $ER_3 = PbPh_3$; 3 L = triphos. **10**: $ER_3 = PbMe_3$; 3 L = triphos. Insertion of CS_2 into the CuSi bond of **1** gives $L^3CuS_2CSi(SiMe_3)_3$ (**11**), while **5** affords $L^3CuS_2CSnMe_3 \cdot CS_2$ (**12**). Compound **12** crystallizes in the space group $P2_1/c$ with $a = 15.062(5)$, $b = 13.632(3)$, $c = 22.706(7)$ Å, $\beta = 91.50(2)°$, $V = 4660.5$ Å^3, $Z = 4$. The copper(I) center is coordinated by the chelating phosphine and a monodentate dithiocarboxylate group forming a new SnC bond.

Introduction

There is much current interest in silyl cuprate reagents in organic chemistry [1–5] because of their superior regio- and/or stereoselectivity when compared with silyllithium compounds. In spite of these advances the number of isolated silylcopper compounds has remained small as for their germyl, stannyl and plumbyl homologs. We have investigated isoelectronic and isosteric relations of silyltris(triorganophosphine)copper(I) systems with zerovalent nickel phosphine complexes (Scheme 1), and with disilylbis(phosphine)zinc compounds (subsequent paper).

Using the small trimethylphosphine ligand most attempts to prepare Cu–Si bonds resulted in deposition of elemental copper. However, with chelate phosphines $CH_3C(CH_2PR_2)_3$ a number of silylcopper and some stannylcopper compounds have been prepared. In this paper we describe their syntheses and properties.



Scheme 1. Isoelectronic and isosteric silylmetal compounds.

Experimental

Standard vacuum techniques were used in manipulations of volatile and air-sensitive material. Microanalyses (C, H by combustion) were obtained from Malissa & Reuter, Microanalytical Laboratory, D-5250 Engelskirchen. Melting points (m.p.) and decomposition temperatures were obtained from sealed capillaries under argon and are uncorrected. Starting materials were prepared by literature methods: $P(CH_3)_3$ [6], triphos [7], CuCl(triphos) [8], $CuXL_3$ (X = Cl, I; $L = PMe_3$, PPh_3) [9], $(Me_3Si)_3SiLi \cdot 3$ THF [10], $KSn(C_6H_5)_3$ [11]. Other chemicals (Merck-Schuchardt) were used as purchased. Infrared spectra were recorded on a Perkin-Elmer, type 397, spectrophotometer; ^1H NMR spectra were obtained on Varian EM 360 (60 MHz) and Bruker WM 300 (300 MHz) instruments, where ^{13}C (75.5 MHz) and ^{31}P (121.5 MHz) NMR spectra were also recorded.

---

*Author to whom correspondence should be addressed.

0020-1693/90/$3.50

Preparations

Tris(trimethylsilyl)silyl-1,1,1-tris(diphenylphosphinomethyl)ethane–copper (1)

A suspension of 690 mg CuCl(triphos) (0.95 mmol) and 450 mg $(Me_3Si)_3SiLi \cdot 3$ THF (0.96 mmol) in 35 ml THF are stirred for 1 h at 20 °C to give a yellowish solution that is only a little turbid. The volatiles are removed *in vacuo* and the residue is extracted with 80 ml ether over a glass sinter-disc. Over dry-ice light yellow crystals are precipitated. Drying *in vacuo* produces a powder, decomp. > 120 °C. Yield 675 mg (0.72 mmol, 76%). *Anal.* Calc. for $C_{50}H_{66}CuP_3Si_4$ (935.9): C, 64.17; H, 7.05. Found: C, 63.97; H, 7.13%. ^1H NMR (60 MHz, THF-d_8, 298 K, THF-d_7 as internal reference, $\delta = 1.73$): $\delta(\mathrm{SiC}H_3)$ 0.13 s (27 H); $\delta(\mathrm{CC}H_3)$ 1.31–1.48 m (3 H); $\delta(\mathrm{PC}H_2)$ 2.36–2.58 m (6 H); $\delta(C_6H_5)$ 6.86–7.58 m (30 H).

Trichlorostannyl-tris(trimethylphosphine)copper (2)

500 mg $CuCl(PMe_3)_3$ (1.53 mmol) in 40 ml THF are reacted at 40 °C with 290 mg $SnCl_2$ (1.53 mmol) to give a colourless solution. Over dry-ice white leaflets are deposited. A second crop is obtained by evaporating the mother liquor and combined to give 765 mg (1.48 mmol) of a white powder (97%), decomp. > 95 °C. *Anal.* Calc. for $C_9H_{27}Cl_3CuP_3Sn$ (516.8): C, 20.92; H, 5.27. Found: C, 20.90; H, 5.27%. ^1H NMR (60 MHz, $CDCl_3$, 298 K, $CHCl_3$ as internal reference, $\delta = 7.24$); $\delta(\mathrm{PC}H_3)$ 1.30 d, $^2J(PH)$ 5 Hz. IR (nujol mull, 4000–400 cm^{-1}): 2795w ν_sCH; 1423s $\delta_{as}CH_3$; 1305m, 1285s δsCH_3; 946vs ρ_1CH_3; 844w ρ_2CH_3; 733s $\nu_{as}PC_3$, 669m ν_sPC_3.

Dichloroiodostannyl-tris(trimethylphosphine)copper (3)

420 mg $CuI(PMe_3)_3$ (1.00 mmol) in 30 ml THF are reacted with 190 mg $SnCl_2$ (1.00 mmol) at 20 °C for 2 h to give a clear yellow solution. With 50 ml ether a light yellow product is precipitated. Recrystallization from boiling toluene gives yellow microcrystals. Yield 475 mg (0.78 mmol, 78%); decomp. > 90 °C. *Anal.* Calc. for $C_9H_{27}Cl_2CuIP_3Sn$ (608.3): C, 17.77; H, 4.47. Found: C, 18.03; H, 4.37%. IR (nujol mull, 4000–400 cm^{-1}): 2808w ν_sCH; 1427s, 1416m $\delta_{as}CH_3$; 1313w, 1294s δ_sCH_3; 974s, 952vs ρ_1CH_3; 851w ρ_2CH_3; 736s $\nu_{as}PC_3$, 673w ν_sPC_3.

Trichlorostannyl-1,1,1-tris(diphenylphosphinomethyl)ethane–copper (4)

724 mg CuCl(triphos) (1.00 mmol) and 190 mg $SnCl_2$ (1.00 mmol) in 50 ml THF are reacted at 60 °C to give a colourless solution. After filtration slow cooling to 20 °C affords large colourless crystals. These are dried in a dynamic vacuum for 5 h at 45 °C. When all THF has been released and a constant weight is achieved the crystals are white and no longer transparent. Yield 740 mg (0.81 mmol, 81%), decomp. > 230 °C. *Anal.* Calc. for $C_{41}H_{39}Cl_3CuP_3Sn$ (913.3.): C, 53.92; H, 4.30. Found: C, 54.13; H, 4.50%.

Trimethylstannyl-1,1,1-tris(diphenylphosphinomethyl)ethane–copper (5)

(a) To 1090 mg CuCl(triphos) (1.51 mmol) in 80 ml THF are added 1.1 ml of 1.4 M methyllithium in ether (1.54 mmol) at 20 °C. After 30 min stirring at 30 °C a yellowish solution of $CuCH_3$(triphos) is obtained. At −78 °C 1.00 g $SnH(CH_3)_3$ (6.07 mmol) is condensed *in vacuo* to the mixture that is warmed up to 20 °C. A smooth evolution of gas is finished within 30 min. The volatiles are removed *in vacuo* and the residue is extracted with 80 ml toluene at 30 °C. Upon cooling to −78 °C yellowish crystals are deposited. Recrystallization from THF and drying for 3 h *in vacuo* affords 940 mg (1.10 mmol) light yellow crystals (73% based on copper).

(b) To 913 mg **4** (1.51 mmol) in 75 ml THF are added 2.15 ml of 1.4 M methyllithium in ether (3.00 mmol). After stirring 30 min at 20 °C a yellowish solution is obtained. Work up as above gives 495 mg (0.58 mmol, 58%) pale yellow crystals, decomp. > 100 °C.

Anal. Calc. for $C_{44}H_{48}CuP_3Sn$ (852.0): C, 62.03; H, 5.68. Found: C, 62.20; H, 5.69%. ^1H NMR (60 MHz, THF-d_8, 298 K, THF-d_7 as internal reference, $\delta = 1.73$): $\delta(\mathrm{SnC}H_3)$ 0.25 s + d (15%) (9 H, $^2J(\mathrm{SnH})$ 18 Hz (average for ^{117}Sn and ^{119}Sn); $\delta(\mathrm{CC}H_3)$ 1.50–1.66 m (3 H); $\delta(\mathrm{PC}H_2)$ 2.31–2.56 m (6 H); $\delta(C_6H_5)$ 6.75–7.78 m (30 H). $^{31}P\{^1H\}$ NMR (121.5 MHz, THF-d_8, H_3PO_4 as external reference, $\delta = 0$): $\delta - 15.5$ s.

Triphenylstannyl-tris(trimethylphosphine)copper (6)

600 mg $KSn(C_6H_5)_3$ (1.54 mmol) and 645 mg $CuI(PMe_3)_3$ (1.54 mmol) in 20 ml THF are combined at −78 °C and the mixture is warmed up to 20 °C under stirring. After 10 min the volatiles are removed *in vacuo* and the residue is extracted with 40 ml ether. Reducing the filtrate to 15 ml and cooling over dry-ice gives greenish amber crystals. Yield 540 mg (0.84 mmol, 55% based on copper), decomp. > 80 °C. *Anal.* Calc. for $C_{27}H_{42}CuP_3Sn$ (641.8); C, 50.53; H, 6.60. Found: C, 50.01; H, 6.38%. ^1H NMR (60 MHz, toluene-d_8, 298 K, toluene-d_7 as internal reference, $\delta = 2.03$): $\delta(\mathrm{PC}H_3)$ 0.81 (27 H); $\delta(C_6H_5)$ 7.01–7.96 m (15 H).

Triphenylstannyl-tris(triphenylphosphine)copper (7)

570 mg $KSn(C_6H_5)_3$ (1.32 mmol) and 1150 mg $CuCl(PPh_3)_3$ (1.30 mmol) in 30 ml benzene are kept stirring for 1 h at 30 °C. To the filtrate are added

40 ml pentane. Yield 430 mg (0.36 mmol) of amber precipitate (28% based on copper), decomp. > 161 °C, *Anal.* Calc. for $C_{71}H_{60}CuP_3Sn$ (1200.4) C, 72.04; H, 5.04. Found: C, 72.76; H, 5.21%.

Triphenylstannyl-1,1,1-tris(diphenylphosphinomethyl)ethane–copper (8)

520 mg CuCl(triphos) and 280 mg $KSn(C_6H_5)_3$ (0.72 mmol) in 30 ml THF are kept stirring for 1 h at 20 °C. The volatiles are removed *in vacuo* and the residue is extracted with 15 ml THF at 0 °C. With 60 ml ether microcrystalline material is precipitated, which is dried *in vacuo* for several hours at 20 °C for constant weight. Yield 430 mg (0.41 mmol) white powder (57% based on copper), decomp. > 180 °C. *Anal.* Calc. for $C_{59}H_{54}CuP_3Sn$ (1038.2): C, 68.26; H, 5.24. Found: C, 67.24; H, 5.55%.

Triphenylplumbyl-1,1,1-tris(diphenylphosphinomethyl)ethane–copper (9)

(a) To a stirred suspension of 723 mg CuCl(triphos) (1.00 mmol) in 40 ml THF are added at 20 °C 1.5 ml of 2 M phenyllithium in ether (3.00 mmol). After 15 min the yellow–brown solution is taken to dryness *in vacuo*, the residue is extracted with 100 ml toluene at 30 °C and the filtrate is concentrated to 50 ml. Addition of 50 ml pentane and cooling to −30 °C affords a white solid that is washed with ether and dried *in vacuo* for 5 h at 20 °C. Yield 430 mg (0.38 mmol, 38%) white powder, decomp. > 80 °C.

(b) 877 mg $PbCl(C_6H_5)_3$ (2.00 mmol) and 100 mg lithium sand (excess) in 15 ml THF are vigorously stirred for 4 h at 5 °C. The dark green mixture is filtered onto 1200 mg CuCl(triphos) (1.66 mmol) that are dissolved with a brown colour. The mixture is taken to dryness, the residue is extracted with 60 ml toluene. Work up as above yields 205 mg (0.18 mmol, 11% based on copper) off-white powder, decomp. > 80 °C.

Anal. Calc. for $C_{59}H_{54}CuP_3Pb$ (1126.7): C, 62.89; H, 4.83. Found: C, 62.73; H, 4.94%. ^{1}H NMR (300 MHz, THF-d_8, 298 K, THF-d_7 as internal reference, $\delta = 1.73$): $\delta(\mathrm{CC}H_3)$ 1.56–1.63 m (3 H); $\delta(\mathrm{PC}H_3)$ 2.47–2.59 m (6 H); $\delta(\mathrm{C_6}H_5)$ 7.91–8.02 m (45 H).

Trimethylplumbyl-1,1,1-tris(diphenylphosphinomethyl)ethane–copper (10)

To 723 mg CuCl(triphos) (1.00 mmol) and 278 mg $PbCl_2$ (1.00 mmol) in 50 ml THF at −78 °C are added 2.15 ml of 1.4 M methyllithium in ether (3.00 mmol). The mixture is kept stirring for 20 min at 10 °C, the volatiles are removed and the residue is extracted with 70 ml toluene. Cooling the filtrate to −50 °C gives bunches of needles that are protected from light and carefully dried *in vacuo* to a constant weight. Yield 400 mg (0.43 mmol) off-white crystals (43%), decomp. > 30 °C. *Anal.* Calc. for $C_{44}H_{48}CuP_3Pb$ (940.5): C, 56.19, H, 5.14. Found: C, 56.01; H, 5.41%. ^{1}H NMR (60 MHz, THF-d_8, 298 K, THF-d_7 as internal reference, $\delta = 1.73$): $\delta(\mathrm{PbC}H_3)$ 0.82s + d (22%) (9 H), ^2J(PbH) 24 Hz; $\delta(\mathrm{CC}H_3)$ 1.51–1.73m; $\delta(\mathrm{PC}H_3)$ 2.28–2.60m (6 H); $\delta(\mathrm{C_6}H_5)$ 6.73–7.71m (30 H).

Tris(trimethylsilyl)silyldithiocarboxylato-1,1,1-tris(diphenylphosphinomethyl)ethane–copper (11)

936 mg **1** in 50 ml ether react with 1 ml CS_2 (excess) at −30 °C within a few seconds to give a red solution. The volatiles are removed *in vacuo*, the residue is extracted with 80 ml pentane at 30 °C. Slowly cooling the filtrate to −30 °C affords dark red crystals that are dried *in vacuo*. Yield 860 mg (0.85 mmol, 85%), decomp. > 126 °C. *Anal.* Calc. for $C_{51}H_{65}CuP_3S_2Si_4$ (1012.0): C, 60.53; H, 6.57. Found: C, 59.59; H, 6.53%. ^{1}H NMR (60 MHz, THF-d_8, 298 K, THF-d_7 as internal reference $\delta = 1.73$): $\delta(\mathrm{SiC}H_3)$ 0.36s (27 H), $\delta(\mathrm{CC}H_3)$ 0.86–1.05m (3 H), δ $(\mathrm{PC}H_2)$ 2.41–2.63m (6 H), $\delta(\mathrm{C_6}H_5)$ 7.07–7.90m (30 H).

Trimethylstannyldithiocarboxylato-1,1,1-tris(diphenylphosphinomethyl)ethane–copper·CS$_2$ (12)

426 mg **5** (0.50 mmol) are reacted with 20 ml CS_2 at 30 °C. Upon slow cooling to −30 °C dark red crystals are formed that are isolated and dried *in vacuo* at 20 °C. Yield 475 mg (0.47 mmol, 94%), decomp. > 138°C. *Anal.* Calc. for $C_{46}H_{48}CuP_3S_4Sn$ (1004.3): C, 55.01; H, 4.81%. Found: C, 54.83; H, 4.83. ^{1}H NMR (60 MHz, THF-d_8, 298 K, THF-d_7 as internal reference, $\delta = 1.73$): $\delta(\mathrm{SiC}H_3)$: 0.36s (27 H), $\delta(\mathrm{CC}H_3)$ 0.86–1.05m (3 H), $\delta(\mathrm{PC}H_2)$ 2.41–2.63m (6 H), $\delta(\mathrm{C_6}H_5)$ 7.07–7.90m (30 H).

Methyl-1,1,1-tris(diphenylphosphinomethyl)ethane–copper·LiCl

To 1090 mg CuCl(triphos) (1.51 mmol) in 30 ml THF are added at 20 °C 1.1 ml of 1.4 M methyllithium in ether (1.54 mmol). After stirring 30 min at 40 °C the clear yellowish solution is concentrated to 15 ml and filtered. Addition of 40 ml ether precipitates a light yellow solid that is filtered and washed with ether. Drying *in vacuo* at 20 °C affords 980 mg of a pale yellow powder (1.31 mmol, 87%), decomp. > 80 °C. *Anal.* Calc. for $C_{42}H_{42}ClCuLiP_3$ (745.7): C, 67.65; H, 5.68. Found: C, 67.92; H, 5.81%. IR (nujol mull, 4000–400 cm^{-1}), bands characteristic for $CuCH_3$: 2777m, ν_sCH; 595m(br), νCuC.

X-ray data collection and structure refinement

A crystal of **12** ($0.075 \times 0.125 \times 0.82$ mm) was sealed in a glass capillary under argon. Cell dimensions were obtained on a four circle Nicolet R3m/V diffractometer. $C_{45}H_{48}CuP_3S_2Sn$, M_n 1004.3, monoclinic, space group $P2_1/c$, $Z=4$, $a=15.062(5)$, $b=13.632(3)$, $c=22.706(7)$ Å, $\beta=91.50(2)°$, $V=4660.5$ Å^3, $D_{calc}=1.431$ g cm^{-3}, Mo Kα radiation, $\lambda=71.073$ pm, graphite monochromator, refinement using 25 reflections with $10 \leqslant 2\theta \leqslant 25°$. A total of 6619 intensities was measured ($\omega-2\theta$ scan, scan rate 2.5° min^{-1}), $3 \leqslant 2\theta \leqslant 45°$, $-17 \leqslant h \leqslant 17$, $0 \leqslant k \leqslant 15$, $0 \leqslant l \leqslant 25$, 3 standards, all 400 measured, correction for a 7% loss of intensity using standards. LP correction, numerical absorption correction, min./max. transmissions 0.984/0.990. After merging ($R_{int}=0.0191$) 6118 unique intensities, 2758 with $I > 2.5\sigma(I)$.

The structure was solved by direct and Fourier methods, full-matrix refinement based on F and 198 parameters; Sn, S, P and C7–C9 with anisotropic refinement. Positions of hydrogen atoms were fixed in ideal geometry, phenyl groups were refined as rigid bodies (C–C 139.5, C–H 96.0 pm). Two positions, probably highly disordered solvent (CS_2), with high residual electron density (2.65 and 2.44 e Å^{-3}) in the final difference Fourier synthesis could not be refined. Refinement converged to $R=0.0804$ and $R_w=0.0673$ ($w=1/\sigma^2(F)+0.0001\,F^2$) ($\Delta/\sigma<0.002$). SHELXTL-PLUS programme (Nicolet 1988) including scattering factors was used for structure solution and refinement.

Results

A white suspension of chloro(triphos)copper is reacted with tris(trimethylsilyl)silyl–lithium in THF (eqn. (1)) to give a clear yellow solution

$$CuClL^3 + (Me_3Si)_3SiLi \cdot 3THF \longrightarrow \underset{\mathbf{1}}{Cu[Si(SiMe_3)_3]L^3} + LiCl \qquad (1)$$

$L^3 =$ triphos

From ether at −78 °C small aggregates of pale yellow crystals of a solvate are obtained that lose ether *in vacuo* and appear milky. If rapidly brought to 120 °C **1** is unchanged but decomposes at 80 °C (1 bar argon) within 3 h. When exposed to sunlight in a flask at 25 °C **1** attains a bright yellow colour that is stable in the dark. This material still gives the infrared spectrum (fingerprint) and the ^{1}H NMR spectrum of **1**, while its thermal stability is unchanged. Triphenylsilyl–lithium in a synthesis according to eqn. (1) gives an inseparable mixture of products while triphenylsilane will not react with methyl(triphos)copper prior to decomposition. All attempted syntheses of silylcopper compounds containing monodentate phosphine ligands resulted in deposition of metal. By contrast, a series of new stannyl(phosphine)copper compounds becomes accessible. Starting from a known type [12] of trihalostannyl copper complexes generated by straightforward procedures according to eqns. (2) and (3) an alkylation of SnCl functions was attempted under controlled conditions without competing CuSn bond cleavage.

$$CuX(PMe_3)_3 + SnCl_2 \longrightarrow Cu(SnXCl_2)(PMe_3)_3 \qquad (2)$$

$\mathbf{2}$: X = Cl
$\mathbf{3}$: X = I

$$CuClL^3 + SnCl_2 \longrightarrow Cu(SnCl_3)L^3 \qquad (3)$$

$\mathbf{4}$: $L^3 =$ triphos

The trichlorostannyl complexes **2** and **4** are formed in virtually quantitative yield. The white crystalline materials are soluble in THF, DMSO or chloroform but not in less polar ether, toluene or pentane solvents. The solids are stable in air for more than two days in the dark. Under argon **2** can be heated to 95 °C without decomposition but its THF solution at 20 °C slowly deposits a grey powder that is mostly tin with some elemental copper.

The light yellow crystals of **3** are better soluble in toluene but with rapid decomposition at reflux temperature. When crystallized from THF **4** forms big crystals of a solvate that release THF at 40 °C *in vacuo* within 2 h giving a white powder. This air-stable material does not start decomposing below 230 °C.

Alkylation with three equivalents of methyllithium[*] in THF was successful for **4** while **2** or **3** in THF, toluene or benzene gave irreproducible white or grey mixtures of products.

$$\mathbf{4} + 3LiMe \longrightarrow Cu(SnMe_3)L^3 + 3LiCl \qquad (4)$$

5 58%

$$CuClL^3 + LiMe \xrightarrow[-LiCl]{} CuMeL^3 \xrightarrow[-CH_4]{+Me_3SnH} \mathbf{5}\ 78\% \qquad (5)$$

In a smooth reaction the new complex methyl(triphos)copper with trimethylstannane eliminates methane giving **5** without byproducts and in higher yield.

---

[*] Monomethyl or dimethyl tin intermediates could not be isolated.

From a pale yellow toluene solution off-white crystals are obtained that release solvent *in vacuo*. Larger crystals from THF also lose weight under cracking and eventually become milky. After 3 h at 20 °C *in vacuo* a pale yellow solid of constant weight is obtained that is analytically pure **5**. This powder can be briefly handled in air up to 30 min. Rapid heating to 100 °C under argon does not induce decomposition but this will proceed within 2 weeks at 20 °C in the dark and is accelerated by daylight.

Using triphenyltin–potassium we found the yields of copper–tin bonded compounds to depend essentially on the purity of this reagent. Generated by the method of Corriu and Guerin [11] it gave the highest yields, while the purity of copper(I) halide complexes was in no case a problem.

Thus iodotris(trimethylphosphine)copper according to eqn. (6) at 20 °C in THF smoothly gave the triphenyltin–copper complex **6** for which a triphenylsilyl analog could not be obtained. For other phosphine ligands reaction conditions had to be carefully adjusted.

$$\mathrm{CuI + KSnPh_3 \longrightarrow Cu(SnPh_3)L_3 + KI} \qquad (6)$$

6: L = PMe_3
7: L = PPh_3
8: 3L = triphos

In the synthesis of **7** benzene or toluene were required rather than THF, while **8** could be obtained under both conditions. From a light yellow–green solution in ether at −78 °C small aggregates of amber crystals of **6** with a greenish tinge are grown that are light sensitive but air stable up to one hour. Although stable at 80 °C for short periods under argon **6** decomposes at 20 °C within three weeks. Solutions in THF or samples in daylight start decomposing after one day. Amber microcrystalline **7** under argon melts at 161 °C with some decomposition and can be handled in air for more than 2 h in the dark being only slightly light sensitive. For some weeks **8** is stable to daylight and to oxygen for more than 2 days. Under argon it remains unchanged for several months at 20 °C and is thermally stable up to 180 °C.

The observed increase in stability when going from silylcopper to stannylcopper compounds suggests triorganoplumbylcopper complexes to be accessible. Using triphos as stabilizing ligand this turned out to be possible according to eqn. (7).

$$\mathrm{CuClL^3 + LiPbPh_3 \longrightarrow \underset{\mathbf{9}}{Cu(PbPh_3)L^3} + LiCl} \qquad (7)$$

$$\mathrm{CuClL^3 + PbCl_2 + 3LiR \longrightarrow Cu(PbR_3)L^3 + 3LiCl} \qquad (8)$$

9: R = Ph
10: R = CH_3

The plumbyllithium reagent may be prepared *in situ* either from chlorotriphenyllead and lithium powder or from lead dichloride and three equivalents of phenyllithium (eqn. (8)) giving a 10% yield in either case.

However, if one reacts a mixture of $CuClL^3$ and $PbCl_2$ with phenyllithium according to eqn. (8) the yield is 38%. From toluene solution **9** is precipitated as an off-white solid that is sensitive to light and oxygen. Under argon in the dark decomposition starts at 80 °C or after 4 weeks at 20 °C. The more successful synthesis according to eqn. (8) when conducted with methyllithium at −78 °C affords small yellow–green needles (from toluene) that upon drying give a lighter coloured powder of **10** (43%). Under argon this material may be handled at 30 °C for short periods but even at 0 °C decomposition starts within a few hours. The compound and its THF solution in particular are very light sensitive.

NMR spectra

Compounds **1–10** dissolved in toluene or THF gave proton resonance signals of expected multiplicities in usual positions and intensity ratios consistent with the formula. Some remarkable values of coupling constants were observed for **5** and **10**.

While the Me_3Sn proton resonance at δ 0.25 is well in the range of other metal complexes [13] the distance of $^{117}Sn/^{119}Sn$ satellites is unusual: $^2J(SnH) = 18$ Hz. This value is extremely small, when compared with the lowest reported value $^2J(^{117}SnH) = 35.8$ Hz for $Me_2Sn[Mo(CO)_3C_5H_5]_2$ [14]. The same effect is observed in the ^{207}Pb satellites of the Me_3Pb signal of **10** at δ 0.82: $^2J(PbH) = 24$ Hz. Again this value falls far below that of $Mo(PbMe_3)(C_5H_5)(CO)_3$, $^2J(PbH) = 44.5$ Hz [14], which is the lowest reported for trimethyllead compounds (usual range $^2J(PbH) = 62–155$ Hz).

The $^2J(SnH)$ values have been correlated with the s character of electrons involved in metal–metal bonding [14]. We feel an extrapolation to the observed values in **5** or **10** does not gain physical meaning. While no X-ray diffraction data are available we take the extremely narrow satellites as evidence for the presence of CuSn and CuPb bonds.

Reactions

Metal–metal bonds in complexes **1**, **5–10** cause reactions with chlorinated solvents giving the chloro(phosphine)copper compounds used for their synthesis. Diphenylacetylene could not be inserted into the CuSi or CuSn bonds of **1** or **5**, respectively. Similar reactions did occur with carbon disulfide and carbon dioxide.

CO_2 and CS_2 insertion into Cu–C(alkyl) and Cu–C(aryl) bonds are well documented [15]. A search of the literature suggested that no such reactions have been previously described for CuSi, CuSn or CoPb bonded complexes.

Upon contact with carbon disulfide an ether solution of **1** changes from yellow to red forming an insertion product **11** according to eqn. (9).

$$1 + CS_2 \longrightarrow \underset{\mathbf{11}}{Cu[S_2CSi(SiMe_3)_3]L^3} \qquad (9)$$

From pentane aggregates of dark red crystals are obtained that are stable in light and air. Under argon melting proceeds at 126 °C with decomposition. Analytically pure samples are insoluble in pentane although generated in this solvent. They are easily dissolved in ether, THF, toluene, acetone, dichloromethane or chloroform. In the infrared the dithiocarboxylate group is represented by bands at 1109 ($\nu_{as}CS_2$) and 954 (ν_sCS_2) cm^{-1}.

Solid **5** when dissolved in very little carbon disulfide gives a red solution containing the insertion product according to eqn. (10) as sole species.

$$5 + CS_2 \longrightarrow \underset{\mathbf{12}}{Cu(S_2CSnMe_3)L^3} \qquad (10)$$

Freshly crystallized samples correspond to the formula **12**$\cdot CS_2$, from acetone a corresponding solvate **12**·acetone is obtained. The presence of uncoordinated CS_2 is recognized by infrared bands at 1515 cm^{-1}, CS_2(free), whereas coordinated CS_2 has such absorption bands at 986 and 975 cm^{-1}. In the ^1H NMR both tin satellites are resolved showing the usual coupling $^2J(^{117}SnH) = 52$ Hz and $^2J(^{119}SnH) = 55$ Hz. The increase of this coupling when compared with **5** indicates the absence of a CuSn bond.

Molecular structure of 12

Coordination of the dithiocarboxylate group in **12** can be envisaged in different modes forming either new Sn–C or Cu–C bonds. Correspondingly S-coordinated copper or tin can be expected either with same coordination numbers (monodentate CS_2) or with coordination number 5 (bidentate CS_2) which is possible for both metals. The infrared data are not conclusive on this point. Therefore an X-ray crystal structure determination was undertaken. Figure 1 gives a perspective view of a molecule of **12**.

As a general point the total disorder of uncoordinated CS_2 in the structure is demonstrated by the residual electron density in the difference Fourier map. The chelate phosphine imposes angles on the molecular structure that are close to tetrahedral geometry. In the fourth position only a monodentate dithiocarboxylate group is accommodated: *d*(Cu1S1) 225.8(6) pm. Both C–S distances are equal within experimental error (Table 1) and the C_{3v} Me_3Sn group is attached to this moiety through a long single bond *d*(Sn1C6) 217.7(17) that lies in a plane containing Cu1, S1, C6, S2 and Sn1, i.e. we have an E-configuration Cu1S1 C6Sn1 in the crystal. This could be easily lost through Cu1S1 and S1C6 bond rotation.

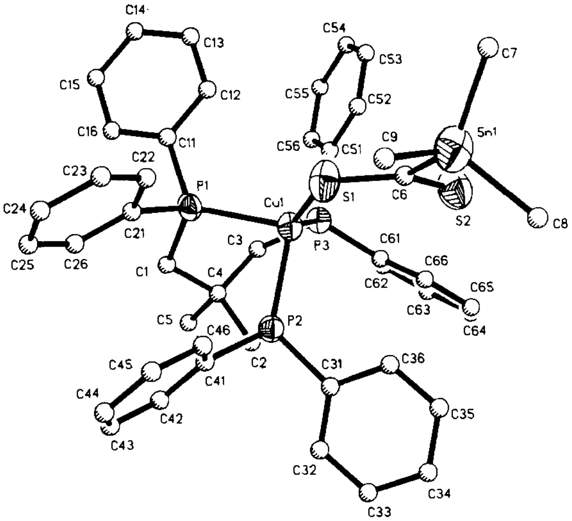


Fig. 1. Perspective view of a molecule of **12**.

Conclusions

Triorganosilicon, tin and lead groups can be attached to copper(I) stabilized by phosphine ligands. Compounds isoelectronic with $Ni(PR_3)_4$ tend to dissociate ligands and for a higher thermal stability need additional assistance through the chelate effect. For tetrahedral geometry around copper(I) triphos is a good choice. Crystalline compounds show an increased solubility in the presence of byproducts that are easily occluded, and also tend to incorporate solvent molecules. Starting from copper halide and lithiumsilyl or stannyl reagents elimination of lithium halide is a general route but is often hampered by impure reagents. The most elegant method is the elimination of methane from methylcopper and tin hydride. Silanes do not give this reaction.

Decomposition temperatures of the light-sensitive compounds are not exactly determined since one may heat the material under argon for short periods well above 30 °C but cannot keep the metastable compounds at 20 °C for longer periods. Only temperatures around −30 °C are safe for several months.

TABLE 1. Important bond distance (pm) and angles (°) in **12**

Sn(1)-)C(6)	2.177 (17)	Sn(1)–C(7)	2.084 (20)
Sn(1)–C(8)	2.109 (19)	Sn(1)–C(9)	2.081 (20)
Cu(1)–P(1)	2.300 (5)	Cu(1)–P(2)	2.286 (5)
Cu(1)–P(3)	2.296 (5)	Cu(1)–S(1)	2.258 (6)
P(1)–C(1)	1.840 (15)	P(1)–C(11)	1.798 (11)
P(1)–C(21)	1.817 (9)	P(2)–C(2)	1.824 (16)
P(2)–C(31)	1.811 (10)	P(2)–C(41)	1.831 (10)
P(3)–C(3)	1.850 (16)	P(3)–C(51)	1.817 (10)
P(3)–C(61)	1.826 (10)	S(1)–C(6)	1.654 (17)
S(2)–C(6)	1.667 (18)	C(1)–C(4)	1.567 (20)
C(2)–C(4)	1.559 (21)	C(3)–C(4)	1.542 (22)
C(4)–C(5)	1.547 (22)		
C(6)–Sn(1)–C(7)	113.4(8)	C(6)–Sn(1)–C(8)	104.5(7)
C(7)–Sn(1)–C(8)	110.3(9)	C(6)–Sn(1)–C(9)	111.3(8)
C(7)–Sn(1)–C(9)	105.2(9)	C(8)–Sn(1)–C(9)	112.4(8)
P(1)–Cu(1)–P(2)	90.5(2)	P(1)–Cu(1)–P(3)	95.2(2)
P(2)–Cu(1)–P(3)	97.7(2)	P(1)–Cu(1)–S(1)	112.9(2)
P(2)–Cu(1)–S(1)	116.3(2)	P(3)–Cu(1)–S(1)	134.4(2)
Cu(1)–P(1)–C(1)	106.9(5)	Cu(1)–P(1)–C(11)	121.1(4)
C(1)–P(1)–C(11)	105.6(6)	Cu(1)–P(1)–C(21)	117.1(4)
C(1)–P(1)–C(21)	104.5(6)	C(11)–P(1)–C(21)	100.1(5)
Cu(1)–P(2)–C(2)	104.1(5)	Cu(1)–P(2)–C(31)	122.2(5)
C(2)–P(2)–C(31)	104.1(6)	Cu(1)–P(2)–C(41)	119.4(4)
C(2)–P(2)–C(41)	104.6(6)	C(31)–P(2)–C(41)	100.4(5)
Cu(1)–P(3)–C(3)	104.0(5)	Cu(1)–P(3)–C(51)	119.7(4)
C(3)–P(3)–C(51)	102.7(6)	Cu(1)–P(3)–C(61)	123.8(4)
C(3)–P(3)–C(61)	104.3(6)	C(51)–P(3)–C(61)	99.7(5)
Cu(1)–S(1)–C(6)	114.7(6)	P(1)–C(1)–C(4)	116.1(10)
P(2)–C(2)–C(4)	117.1(10)	P(3)–C(3)–C(4)	118.4(11)
C(1)–C(4)–C(2)	113.2(12)	C(1)–C(4)–C(3)	111.2(12)
C(2)–C(4)–C(3)	112.8(12)	C(1)–C(4)–C(5)	106.1(12)
C(2)–C(4)–C(5)	106.5(12)	C(3)–C(4)–C(5)	106.4(12)
Sn(1)–C(6)–S(1)	118.1(9)	Sn(1)–C(6)–S(2)	114.3(9)
S(1)–C(6)–S(2)	127.5(11)	P(1)–C(11)–C(12)	118.9(4)
P(1)–C(11)–C(16)	121.0(4)	P(1)–C(21)–C(22)	115.3(4)
P(1)–C(21)–C(26)	124.7(4)	P(2)–C(31)–C(32)	122.6(4)
P(2)–C(31)–C(36)	117.4(4)	P(2)–C(41)–C(42)	125.2(4)
P(2)–C(41)–C(46)	114.8(4)	P(3)–C(51)–C(52)	116.4(3)
P(3)–C(51)–C(56)	123.6(3)	P(3)–C(61)–C(62)	120.7(4)
P(3)–C(61)–C(66)	119.3(4)		

Supplementary material

Hydrogen atom coordinates, anisotropic temperature factors and structure factors listing have been deposited as Supplementary Publication no. CSD 54635. Copies can be obtained through the Fachinformations-Zentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen.

Acknowledgments

Financial support of this work through the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie is gratefully acknowledged.

References

1 J. Fleming, T. W. Newton and F. Roessler, *J. Chem. Soc., Perkin Trans. 1,* (1981) 2527; E. Piers, J. M. Chong and B. A. Keay, *Tetrahedron Lett., 26* (1985) 6265, and refs. therein.

2 B. M. Trost and D. M. T. Chan, *J. Am. Chem. Soc., 104* (1982) 3733.

3 J. G. Smith, S. E. Drozda, S. P. Petraglia, N. R. Quinn, E. M. Rice, B. S. Taylor and M. Viswanathan, *J. Org. Chem., 49* (1984) 4112.

4 H.-M. Chen and J. P. Oliver, *J. Organomet. Chem., 316* (1986) 255.

5 M. Suzuki, H. Koyano and R. Noyori, *J. Org. Chem., 52* (1987) 5583.

6 W. Wolfsberger and H. Schmidbaur, *Synth. React. Inorg. Met.-Org. Chem., 4* (1974) 149.

7 W. Hewertson and H. R. Watson, *J. Chem. Soc.,* (1962) 1490.

8 L. Sacconi and S. Midollini, *J. Chem. Soc., Dalton Trans.*, (1972) 1213; S. Gambarotta, S. Strogolo, C. Floriani, C. Guastini and A. Chiesi-Villa, *Organometallics, 3* (1984) 1444.

9 H. Schmidbaur, J. Adlkofer and K. Schwirten, *Chem. Ber., 105* (1972) 3382; G. Costa, E. Reisenhofer and L. Stefani, *J. Inorg. Nucl. Chem., 27* (1965) 2581; S. J. Lippard and D. A. Ucko, *Inorg. Chem., 7* (1968) 1051; F. H. Jardine, L. Rule and A. G. Vohra, *J. Chem. Soc. A,* (1970) 238.

10 K. H. Pannell and A. R. Bassindale, *J. Organomet. Chem., 229* (1982) 1.

11 R. Corriu and C. Guerin, *J. Organomet. Chem., 197* (1980) C19; *J. Chem. Soc., Chem. Commun.*, (1980) 168.

12 J. A. Dilts and M. P. Johnson, *Inorg. Chem., 5* (1966) 2079; M. Brezeanu and I. Jitaru, *Rev. Roum. Chim., 17* (1972) 1857.

13 J. D. Kennedy and W. McFarlane, in J. Mason (ed.), *Multinuclear NMR*, Plenum, New York, 1987, Ch. 11, p. 305.

14 H. R. H. Patil and W. A. G. Graham, *Inorg. Chem., 5* (1966) 1401.

15 J. F. Normant, G. Cahiez, C. Chuit and J. Villieras, *J. Organomet. Chem., 77* (1974) 281; A. Miyashita and A. Yamamoto, *J. Organomet. Chem., 113* (1976) 187; A. Camus, N. Marsich and G. Pellizer, *J. Organomet. Chem., 259* (1983) 367.