Inorganica Chimica Acta, 177 (1990) 43–46

Silylzinc and stannylzinc compounds containing monodentate phosphine ligands

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

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

(Received May 14, 1990)

Abstract

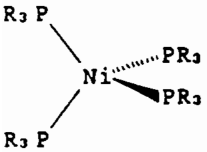
Syntheses and properties of metal–metal bonded complexes of the type $ZnX(ER_3)L_2$ are described, **1**: $X=ER_3=SiPh_3$, $L=PMe_3$; **2**: $X=ER_3=SiPh_3$, $L=PPh_3$; **3**: $X=Cl$, $ER_3=SiPh_3$, $L=PMe_3$; **4a**: $X=Cl$, $ER_3=Si(SiMe_3)_3$; **4b**: $X=I$, $ER_3=Si(SiMe_3)_3$; **5**: $X=ER_3=SnCl_3$, $L=PMe_3$; **6**: $X=ER_3=SnPh_3$, $L=PMe_3$. Syntheses of starting materials ZnX_2L_2 ($X=Cl$, I; $L=PMe_3$, PPh_3) are also described.

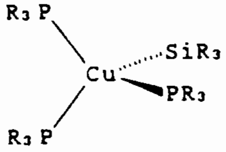
Introduction

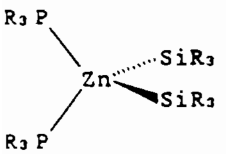
Silylzinc compounds have been synthesized since 1963 but the number of isolated and characterized examples is limited. Ligand-free compounds $Zn(SiR_3)_2$ ($R=Ph$ [1], Me [2], C_6F_5 [3]) in the solid are believed to be composed of linear molecules as demonstrated by the structure of $Zn[Si(SiMe_3)_3]_2$ [4]. With less steric crowding addition of donor ligands should cause bending of the SiZnSi unit without much activation as has been observed with $Zn(SiF_3)_2$ and pyridine [5] or with germylzinc complexes $Zn(GePh_3)_2 \cdot D$ ($D=THF$, NH_3), $Zn(GePh_3)_2 \cdot 2D$ ($D=THF$ [6], $2D=$bpy, tmeda [7], DMF, HMPT [8]).

Stannylzinc compounds usually contain hard donor ligands. Examples are $Zn(SnMePh_2)_2$ (tmeda) [9]; $Zn(SiPh_3)_2L^2$ ($L^2=$bpy, DME) [7, 10]; $ZnCl(SnPh_3)L^2$ ($L^2=$DME, tmeda) [9]; but $[ZnCl(SnPh_3)]_2$ [9, 11] as an exception contains chloride bridges.

Extending the concept of isoelectronic complexes from copper [12] to zinc we describe the synthesis of some 18 electron silylzinc and stannylzinc compounds containing two phosphine donors.







Experimental

Techniques and methods of synthesis and characterization of air-sensitive material have been described in the preceding paper [12]. Anhydrous zinc halides (Merck-Schuchardt) and lithium sand (Metallgesellschaft) were used as purchased. Literature procedures were followed in the synthesis of $Zn(SiPh_3)_2$ [1], Si_2Ph_6 [14], $(Me_3Si)_3SiLi \cdot 3THF$ [15] and $KSnPh_3$ [16].

Dichlorobis(trimethylphosphine)zinc [13]

4.4 g anhydrous zinc chloride (32.3 mmol) in 100 ml THF containing 5.0 g trimethylphosphine (65.7 mmol) are kept stirring at 60 °C for 10 min. The clear solution is filtered through a glass sinter-disc while warm. Slow cooling to 20 °C gives large colourless crystals that are dried *in vacuo*. Yield 8.1 g (28.1 mmol, 87%), decomp. > 121 °C.

Anal. Calc. for $C_6H_{18}Cl_2P_2Zn$ (288.4): C, 24.98; H, 6.29. Found: C, 24.31; H 6.13%. IR (nujol mull, 2000–400 cm^{-1}): 1432m, 1418s, 1401s $\delta_{as}CH_3$; 1283 s δ_sCH_3; 964vs, 952vs, ρ_1CH_3; 851m ρ_2CH_3; 747s $\nu_{as}PC_3$; 720 w ν_sPC_3. ^1H NMR (60 MHz, $CDCl_3$, $CHCl_3$ internal reference $\delta=7.24$): δCH_3 1.32 d, $^2J(PH)=8$ Hz.

0020-1693/90/$3.50

Diiodobis(trimethylphosphine)zinc

10.58 g ZnI_2 (33.15 mmol) in 75 ml THF containing 5.1 g trimethylphosphine (67.04 mmol) are kept stirring at 30 °C for 8 min. The volatiles are removed *in vacuo* and the white residue is dissolved in 80 ml benzene at 60 °C. The filtered solution upon cooling to 10 °C gives colourless crystals. From the mother liquor another crop is obtained by adding 100 ml pentane. Yield 14.35 g (30.45 mmol, 92%), decomp. > 130 °C.

Anal. Calc. for $C_6H_{18}I_2P_2Zn$ (471.4): C, 15.29; H, 3.85. Found: C, 15.26; H, 3.69%. IR (nujol mull, 2000–400 cm^{-1}): 1417s $\delta_{as}CH_3$; 1286s δ_sCH_3; 961vs, 950vs ρ_1CH_3; 847w ρ_2CH_3; 747s $\nu_{as}PC_3$; 724w ν_sPC_3.

Diiodobis(triphenylphosphine)zinc

2.40 g ZnI_2 (7.52 mmol) in 150 ml THF containing 4.20 g triphenylphosphine (16.01 mmol) are kept stirring at 30 °C for 20 min. The volatiles are removed *in vacuo* and the residue is dissolved in 400 ml toluene at 112 °C. Cooling to 0 °C gives aggregates of colourless crystals. Yield 5.4 g (6.40 mmol, 85%), m.p. 255–256 °C.

Anal. Calc. for $C_{36}H_{30}I_2P_2Zn$ (843.8): C, 51.31; H, 3.58. Found: C, 50.95; H, 3.45%. IR (nujol mull, 2000–400 cm^{-1}): 1586w, 1570w, 1478s, 1432s, 1329w, 1317m, 1310m, 1189m, 1179m, 1157m, 1122w, 1093s, 1063m, 1025m, 998m, 989m, 927m, 920w, 851m, 755s, 742vs, 727m, 707s, 697vs, 615w, 538m, 522vs, 511s, 496s, 483s, 441m, 424w (without assignment).

Bis(triphenylsilyl)bis(trimethylphosphine)zinc (1)

(a) 340 mg $Zn(SiPh_3)_2$ (0.58 mmol) are dissolved in 100 ml ether containing 200 mg trimethylphosphine (2.63 mmol) at 20 °C. The clear solution is concentrated *in vacuo* to 20 ml precipitating a microcrystalline white solid that is dried *in vacuo*. Yield 260 mg white powder (0.35 mmol, 61%).

(b) 1 g hexaphenyldisilane (1.93 mmol) in 50 ml THF is reacted with 100 mg lithium sand at 20 °C for 1 h to give a greenish dark solution that after filtering looks yellow–brown. The volatiles are removed *in vacuo* and to the brown residue of $LiSiPh_3$ are added 500 mg $ZnCl_2(PMc_3)_2$ (1.73 mmol) at −70 °C. A total of 100 ml ether is condensed onto the mixture that is warmed up under stirring to 20 °C. After 1 h workup proceeds as under (a). Yield 380 mg (0.52 mmol, 30%), decomp. > 104 °C.

Anal. Calc. for $C_{42}H_{48}P_2Si_2Zn$ (736.3): C, 68.51; H, 6.57. Found: C, 67.98; H, 6.48%. ^1H NMR (60 MHz, toluene-D_8, toluene-D_7 as internal reference $\delta = 2.03$): δCH_3 0.56 d (18 H), $^2J(PH) = 5$ Hz; δC_6H_5 (3-H, 4-H) 6.90–7.28 m (18 H); δC_6H_5 (2-H) 7.43–7.80 m (12 H).

Bis(triphenylsilyl)bis(triphenylphosphine)zinc (2)

510 mg $Zn(SiPh_3)_2$ (0.78 mmol) and 460 mg triphenylphosphine (1.75 mmol) in 90 ml ether are reacted at 20 °C for 15 min. After filtration the colourless solution is concentrated to 15 ml *in vacuo* precipitating a light amber solid that is washed with pentane and dried *in vacuo*. Yield 268 mg (0.24 mmol, 31%), decomp. > 160 °C.

Anal. Calc. for $C_{72}H_{60}P_2Si_2Zn$ (1108.8): C, 78.00; H, 5.45. Found: C, 77.58; H, 5.50%. IR (nujol mull, 2000–400 cm^{-1}): 1577w, 1558w, 1473s, 1430s, 1320w, 1303w, 1252w, 1178w, 1163w, 1151w, 1087s, 1064w, 1025m, 999m, 741s, 726m, 701vs, 677m, 620w, 542m, 512s, 504s, 491s, 429w.

Chloro(triphenylsilyl)bis(trimethylphosphine)zinc (3)

70 mg $ZnCl_2(PMe_3)_2$ (0.24 mmol) and 160 mg **1** (0.22 mmol) in 30 ml toluene are kept stirring at 20 °C for 5 h. After filtering a white solid is precipitated by 30 ml pentane. Yield 85 mg (0.17 mmol, 75%), decomp. > 65 °C.

Anal. Calc. for $C_{24}H_{33}ClP_2SiZn$ (512.4): C, 56.26; H, 6.49. Found: C, 56.51; 6.44%. ^1H NMR (60 MHz, C_6D_6, toluene-CH_3 as internal reference $\delta = 2.32$): δCH_3 0.92 d (18 H), $^2J(PH) = 6$ Hz; δC_6H_5 (3-H, 4-H) 7.27–7.62 m (9 H); δC_6H_5 (2-H) 8.02–8.30 m (6 H).

Chloro[tris(trimethylsilyl)silyl]bis(trimethylphosphine)zinc (4a)

350 mg $ZnCl_2(PMe_3)_2$ (1.21 mmol) in 30 ml ether are reacted with 570 mg $(Me_3Si)_3SiLi \cdot 3THF$ (1.21 mmol) at 30 °C for 3 h. The mixture is taken to dryness *in vacuo* and the residue is taken up with 25 ml pentane. By filtration a clear colourless solution is obtained that upon cooling to −78 °C yields small bunches of colourless needles that are dried *in vacuo*. Yield 380 mg (0.76 mmol, 63%), decomp. > 85 °C.

Anal. Calc. for $C_{15}H_{45}ClP_2Si_4Zn$ (500.6): C, 35.99; H, 9.06. Found C, 36.23; H, 9.45%. ^1H NMR (60 MHz, C_6D_6, C_6D_5H as internal reference $\delta = 7.15$): $\delta SiCH_3$ 0.40 s (27 H); δPCH_3 0.84 d (18 H), $^2J(PH) = 5.3$ Hz.

Iodo[tris(trimethylsilyl)silyl]bis(trimethylphosphine)zinc (4b)

680 mg $ZnI_2(PMe_3)_2$ (1.44 mmol) in 40 ml ether are reacted with 680 mg $(Me_3Si)_3SiLi \cdot 3THF$ (1.44 mmol) at 20 °C for 15 h. The mixture is taken to dryness and the residue is taken up with 80 ml pentane as above. From 40 ml solution colourless leaflets are obtained. Yield 715 mg (1.21 mmol, 84%), decomp. > 85 °C.

Anal. Calc. for $C_{15}H_{45}IP_2Si_4Zn$ (592.1): C, 30.43; H, 7.66.Found: C, 30.67; H, 8.12%. ^1H NMR (60

MHz, toluene-D_8, $C_6D_5CHD_2$ as internal reference $\delta = 2.03$): $\delta SiCH_3$ 0.36 s (27 H); δPCH_3 0.90 d (18 H), $^2J(PH) = 5.5$ Hz.

Bis(trichlorostannyl)bis(trimethylphosphine)zinc (5)

490 mg $ZnCl_2(PMe_3)_2$ (1.70 mmol) and 644 mg (3.4 mmol) $SnCl_2$ in 90 ml isopropyl alcohol are kept stirring at 80 °C for 20 min. After filtering the colourless solution upon slow cooling to 20 °C deposits a flaky white solid that is dried *in vacuo* for 3 h. Yield 950 mg white powder (1.42 mmol, 84%), decomp. > 105 °C.

Anal. Calc. for $C_6H_{18}Cl_6P_2Sn_2Zn$ (667.6): C, 10.79; H, 2.72. Found: C, 11.65; H, 3.04%. IR (nujol mull, 2000–400 cm^{-1}): 1417m, 1404m $\delta_{as}CH_3$; 1312m, 1297s δ_sCH_3; 1007s, 961vs ρ_1CH_3; 787s $\nu_{as}PC_3$; 724m ν_sPC_3.

Bis(triphenylstannyl)bis(trimethylphosphine)zinc (6)

(a) 205 mg $ZnCl_2(PMe_3)_2$ (0.71 mmol) in 50 ml ether are reacted with 555 mg $KSnPh_3$ (1.43 mmol) at 10 °C for 24 h. The mixture is taken to dryness and the residue is extracted with 15 ml benzene. Addition of 30 ml pentane to the filtrate precipitates a white solid that is recrystallized from little toluene. Yield 200 mg white microcrystals (0.22 mmol, 31%).

(b) To 1080 mg $ZnCl_2(PMe_3)_2$ (3.74 mmol) and 20 ml ether at 20 °C are added 5.4 ml of 1.4 M $LiCH_3$ in ether (7.56 mmol) by a syringe. After 2 h at 20 °C the volatiles (containing $Zn(CH_3)_2 \cdot 2PMe_3$ and ether) are condensed upon 2630 mg $SnHPh_3$ (7.48 mmol). From this solution within 5 days aggregates of small crystals are obtained that are recrystallized from toluene. Yield 2100 mg white microcrystals (2.29 mmol, 61%), decomp. > 130 °C.

Anal. Calc. for $C_{42}H_{48}P_2Sn_2Zn$ (917.6): C, 54.98; H, 5.20. Found: C, 55.66, H, 5.25%. ^1H NMR (60 MHz, THF-D_8, THF-D_7 as internal reference, $\delta = 1.73$): δPCH_3 1.17 d (18 H), $^2J(PH) = 5$ Hz; δC_6H_5 6.93–7.76 m (30 H). ^{31}P NMR (121.5 MHz, THF-D_8, H_3PO_4 external reference $\delta = 0$) 293 K: $\delta -36.92$ s; 258 K: $\delta -35.97$ s+d (broad), $^2J(^{117,119}SnP) = 289$ Hz; 193 K: $\delta -34.14$ s+d+d, $^2J(^{117}SnP) = 274$ Hz, $^2J(^{119}SnP) = 287$ Hz. ^{119}Sn NMR (93.3 MHz, THF-D_8, Me_4Sn external reference, $\delta = 0$) 203 K: $\delta -87.7$ t, $^2J(PSn) = 286$ Hz.

Results

Ligand-free silylzinc or stannylzinc compounds rapidly react with oxygen or water and are often light-sensitive. $Zn(SiPh_3)_2$ is stabilized by trimethylphosphine according to eqn. (1).

$$\mathrm{Zn(SiPh_3)_2 + 2L \longrightarrow Zn(SiPh_3)_2L_2} \qquad (1)$$

1: L = PMe_3 (61%)
2: L = PPh_3 (31%)

On evaporating the ether solution **1** is obtained as white powder that is only slightly soluble in fresh ether and remains dissolved at −78 °C for more than six weeks. It is insoluble in pentane but freely miscible with benzene or toluene. THF solutions are rapidly decomposed at 20 °C. The white powder is stable in light and may be safely handled in air for 1 h. Under argon **1** is thermally stable up to 104 °C.

Adding triphenylphosphine according to eqn. (1) gives a light amber solid that is only slightly sensitive to air and moisture and little affected by daylight. Decomposition under argon starts above 160 °C. Solubility in toluene or chloroform is sufficient but is slight in ether or pentane.

1 transfers silyl groups according to eqn. (2) if toluene is the reaction medium and **3** is precipitated by added pentane.

$$\mathrm{1 + ZnCl_2L_2 \longrightarrow 2ZnCl(SiPh_3)L_2} \qquad (2)$$

L = PMe_3 **3** (75%)

When compared with **1** solid **3** is less stable thermally but otherwise displays similar properties.

With $(Me_3Si)_3SiLi \cdot 3THF$ stepwise and clean silylation reactions are achieved in syntheses according to eqn. (3)

$$\mathrm{ZnX_2L_2 + (Me_3Si)_3Li \cdot 3THF \longrightarrow ZnX[Si(SiMe_3)_3]L_2}$$

L = PMe_3
4a: X = Cl (63%)
4b: X = I (84%)

In a 1:2 ratio the reaction yields ligand-free $Zn[Si(SiMe_3)_3]_2$ [4] containing two bulky silyl ligands that prevent phosphine coordination. Like **3** the monosilyl complexes **4a** and **4b** are thermally less stable (decomposition with loss of phosphine starting at 110 and 85 °C, respectively) than the ligand-free disilylzinc compound [4] (decomposition above 190 °C).

Fingerprint infrared bands of $Si(SiMe_3)_3$ and PMe_3 groups (each local C_{3v} symmetry) are given in Table 1.

In an attempted synthesis of $Zn(SiMe_3)_2(PMe_3)_2$ according to eqn. (4) variable amounts of phosphine were collected with the solvent and separated with iodomethane as tetramethylphosphonium iodide.

$$\mathrm{ZnCl_2L_2 + 2LiSiMe_3 \longrightarrow}$$
$$\mathrm{Zn(SiMe_3)_2L_2 \rightleftharpoons Zn(SiMe_3)_2 + 2L} \qquad (4)$$

TABLE 1. Infrared bands (nujol mull, 2000–400 cm^{-1}) of tris(trimethylsilyl)silyl and trimethylphosphine (L) ligands for **4a**, **4b** and $Zn(silyl)_2$ [4]

4a	**4b**	Zn-(silyl)$_2$	Assignment
1438m	1430m	1436s	
1420m	1420m	1427m	$\delta_{as}CH_3$
1394m		1416m	
		1398m	
1306w	1305w	1305m	
1257m	1251m	1252m	$\delta_s SiCH_3$
1241vs	1235s	1238s	
	1285m	1289m	$\delta_s PCH_3$
	987s		$\rho_1 PCH_3$
	952s	958s	
	863s		
834vs	832vs	830vs	$\rho_1 SiCH_3$
738m	737m	736s	$\nu_{as}PC_3$
686s	679m	680s	$\nu_{as}SiC_3$, $\nu_s PC_3$
612s	621m	620s	$\nu_s SiC_3$

The disilylzinc complex decomposed at −20 °C displaying exactly the sensitivity to air, moisture, and heat that was described for the ligand-free compound [2].

Conclusions

Phosphine stabilization in tetrahedral zinc complexes ZnX_2L_2 is evident for X = halide and becomes less effective as the number of silyl groups ($X = SiR_3$) is increased. Replacing SiR_3 by SnR_3 supports the coordination of phosphine ligands at the zinc center. The effect appears to be dominantly steric in nature as in $Ni(PR_3)_4$ complexes [17].

Acknowledgements

Financial support of this work through the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie is gratefully acknowledged. We thank Paul Pregosin, ETH Zürich, for ^{31}P and ^{119}Sn NMR spectroscopic measurements.

References

1 E. Wiberg, O. Stecher, H.-J. Andrascheck, L. Kreuzbichler and E. Staude, *Angew. Chem., 75* (1963) 516.

2 L. Rösch and G. Altnau, *Angew. Chem., 91* (1979) 62; *Angew. Chem., Int. Ed. Engl., 18* (1979) 60.

3 M. N. Bochkarev, L. P. Maiorova, S. P. Korneva and L. N. Bochkarev, *J. Organomet. Chem., 73* (1974) 229.

4 J. Arnold, T. D. Tilley, A. L. Rheingold and S. J. Geib, *Inorg. Chem., 26* (1987) 2106.

5 M. A. Guerra, T. R. Bierschenk and R. J. Lagow, *J. Am. Chem. Soc., 108* (1986) 4103; T. R. Bierschenk, M. A. Guerra, T. J. Juhlke, R. J. Lagow and S. B. Larson, *J. Am. Chem. Soc., 109* (1987) 4855.

6 E. Amberger, W. Stoeger and R. Hönigschmid-Grossich, *Angew. Chem., 78* (1966) 549; E. Amberger and W. Stoeger, *J. Organomet. Chem., 18* (1969) 83.

7 F. J. A. des Tombes, G. J. M. van der Kerk, N. M. J. C. Creemers, N. A. D. Carey and J. G. Noltes, *J. Organomet. Chem., 44* (1972) 247.

8 V. T. Bychkow, N. S. Vyazankin and G. A. Vostokov, *Zh. Obshch. Khim., 43* (1973) 793; *Chem. Abstr., 79* (1973) 53490x.

9 F. J. A. des Tombes, G. J. M. van der Kerk and J. G. Noltes, *J. Organomet. Chem., 43* (1972) 323.

10 F. J. A. des Tombes, G. J. M. van der Kerk, J. G. Noltes and H. M. J. C. Creemers, *Chem. Commun.*, (1966) 914.

11 F. J. A. des Tombes, G. J. M. van der Kerk and J. G. Noltes, *J. Organomet. Chem., 13* (1968) P9.

12 H. F. Klein, J. Montag, U. Zucha, U. Flörke and H. J. Haupt, *Inorg. Chim. Acta, 177* (1990) 35; U. Zucha, *Doctoral Thesis*, Technische Hochschule, Darmstadt, 1989.

13 K. Dey and H. Werner, *Chem. Ber., 112* (1979) 823.

14 W. Schlenk, J. Renning, and G. Racky, *Chem. Ber., 94* (1911) 1178.

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

16 R. Corriu and C. Guerin, *J. Organomet. Chem., 197* (1980) C 19; R. Coriu and C. Guerin, *J. Chem. Soc., Chem. Commun.*, (1980) 168.

17 C. A. Tolman, *Chem. Rev., 77* (1977) 313.