Inorganica Chimica Acta, 26 (1978) L25–L26
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Complexes of t-Butyl(trimethylsilyl- and germyl)-phosphines with Silver Bromide: Unexpected Kinetic Stability of the Ag–P Bond

W.-W. DU MONT

Institut für Anorganische und Analytische Chemie der Technischen Universität Berlin, D-1000 Berlin 12, Germany

Received November 26, 1977

In the course of our work on the coordination chemistry of phosphine-stabilized and phosphino-substituted divalent germanium and tin compounds [1, 2] we were interested in the question if covalent and coordinative Ge(II)–P and Sn(II)–P bonds are stable even when the lone pairs of electrons at P, Ge or Sn are used for coordination with silver halides. Curiously very little also is known about reactions of Si(IV)-, Ge(IV)- and Sn(IV)-phosphines with group IA halides [3, 4]. Therefore we studied the interaction of a couple of phosphines of the type $Me_3E–P(CMe_3)_2$ (E = C, Si, Ge, Sn) with silver halides [5]. Silver chloride predominantly cleaves the P–E bonds of organometalphosphines yielding organometalchlorides and silver phosphides, whereas silver iodide tends to form quite stable 1:1 complexes that are only sparingly soluble in common inert solvents, preventing us from collecting any significant cryoscopic and NMR spectroscopic data:

$$Me_3E{-}P(CMe_3)_2 + AgCl \xrightarrow[20\ ^\circ C]{toluene} Me_3ECl + AgP(CMe_3)_2$$

E = Si, Ge

$$Me_3EP(CMe_3)_2 + AgBr \xrightarrow[20\ ^\circ C]{toluene} 1/4\ [(Me_3C)_2(Me_3E)PAgBr]_4$$

E = Si, Ge

Silver bromide gives fairly soluble 1:1 complexes with di-tert-butyl(trimethylsilyl)phosphine and di-tert-butyl(trimethylgermyl)phosphine [6], no trimethylbromosilane or -germane elimination from these complexes being observed in solution or in the solid state. Both compounds are thermally less stable than the tri-tert-butylphosphine silver bromide complex or the di-tert-butyl(trimethylsilyl)phosphine silver iodide complex; with moisture cleavage of the P–Si or P–Ge bonds occurs and the di-tert-butylphosphine silver bromide complex is obtained. To our surprise the silylphosphine and the germylphosphine silver bromide complexes gave fairly well resolved room temperature phosphorus NMR spectra with two sets of doublets arising from $^1J(^{31}P^{107}Ag)$ and $^1J(^{31}P^{109}Ag)$, as does the tri-tert-butylphosphine complex. Alkyl- and arylphosphine and -phosphite silver complexes are generally kinetically labile at room temperature and phosphorus–silver coupling constants were observed only at quite low temperatures, as shown by Muetterties and Alegranti few years ago. No P–Ag couplings were observed in the room temperature NMR spectra of trimethylphosphine silver halide complexes [7, 8]. The proton NMR spectra of the $(Me_3C)_2(Me_3E)PAgBr$ complexes (E = C, Si, Ge) show doublet signals arising from $^3J(HCCP)$ and $^3J(HCEP)$ with coupling constants somewhat larger than those of the non-coordinated ligands (Table I).

Monomeric or dimeric structures with coordination number 2 or 3 at silver [9] favouring high AgP bond s-character and large AgP NMR coupling constants are inconsistent with our cryoscopic molecular weight determinations of the complexes in benzene. From our data the well-known cubane-like tetrameric structure should be predominant in solution, equilibria with rapid Ag–P bond breaking are excluded since $^1J(PAg)$ is observed at ambient concentration [10].

In presence of excess ligand or for instance in the mixture $(Me_3C)_2(Me_3Ge)PAgBr/(Me_3C)_3P$ rapid competition of both ligands for coordination with AgBr is indicated by coalescence of the $\{^1H\}$ ^{31}P NMR multiplets at room temperature; there was no evidence for the formation of a stable 2:1 adduct (Table I). The kinetic stability of the complexes in absence of excess ligand should be due to the steric requirements of the bulky ligands at phosphorus. The large difference of the ^{31}P coordination shift (AgBr complexes 1–5 ppm, $t\text{-}Bu_3PAgCl$ 34 ppm) and $^{31}P–^{107}Ag$ coupling constants (AgBr complexes J = 471–541 Hz, $t\text{-}Bu_3PAgCl$ 686 Hz) between the AgBr complexes and $t\text{-}Bu_3PAgCl$ [9] might indicate structural differences, too. From $Me_3Sn\text{-}P(CMe_3)_2$ and AgBr we got a fairly soluble material showing two broad signals in ^{31}P NMR and two sets of doublets (with $^3J(HCSnP)$ and $^3J(HCCP)$) in ^1H NMR, but after 48 h at −15 °C significant amounts of Me_3SnBr were present in the product; obviously the tendency of formation of $Me_3E–X$ is one crucial point for the stability of Si(IV)-, Ge(IV)- and Sn(IV)-phosphine silver halide complexes.

Acknowledgment

I wish to thank the *Deutsche Forschungsgemeinschaft*, Bonn–Bad Godesberg, for financial support, *Prof. Dr. H. Schumann*, TU Berlin for the friendly support of my work, and *Dr. H.-J. Kroth* for recording the ^{31}P NMR spectra.

TABLE I. ^{1}H-NMR and ^{31}P-NMR Spectroscopic Data and Analyses.[a]

Compound	$\delta(H_3C{-}E)$ (ppm)	$^{3}J(HP)$ (Hz)	$\delta(H_3C{-}C)$ (ppm)	$^{3}J(HP)$ (Hz)	$\delta(P)$ (ppm)	$^{1}J(^{107/109}Ag^{31}P)$ (Hz)	C% Calcd	C% Found	H% Calcd	H% Found
$Me_3GeP(t\text{-}Bu)_2AgBr$	0.13^{d}	4.0	0.93^{d}	14.0	15.7 2^{d}	491/562	29.32	29.46	6.04	5.64[c]
$Me_3GeP(t\text{-}Bu)_2$	0.46^{d}	2.6	1.29^{d}	11.0	14.3 s					
$Me_3SiP(t\text{-}Bu)_2AgBr$	0.03^{d}	4.5	0.90^{d}	13.6	2.0 2^{d}	471/544	32.53	31.92	6.70	6.60[c]
$Me_3SiP(t\text{-}Bu)_2AgI$							29.15	29.09	6.01	5.97[c]
$Me_3SiP(t\text{-}Bu)_2$	^{d}	3.3	^{d}	11.0	−3.1 s					
$P(t\text{-}Bu)_3AgBr$[b]			1.5^{d}	12.4	66.5 2^{d}	541/624	36.95	36.83	6.98	6.92[d]
$P(t\text{-}Bu)_3$			^{d}	9.8	62.5 s					
$Me_3GeP(t\text{-}Bu)_2AgBr$	0.6^{d}	3.2	1.4^{d}	13.1	15 s					
$/P(t\text{-}Bu)_3$			1.45^{d}	12.1	65 s					
$P(t\text{-}Bu)_3AgCl$[b]			1.1^{d}	13.2	86.3 2^{d}	686/791				

[a] Varian EM 360 (60 MHz for 1-H), Bruker SXP (36.44 MHz for 31-P); chemical shifts in ppm tow. TMS, resp. 85% H_3PO_4; pos. sign corr. downfield shift; coupling constants in Hz. Solutions in $C_6H_5CH_3/C_6D_6$ or CD_2Cl_2. [b] *Cf.* ref. [5]. [c] Therm. dec. above 110 °C. [d] M.p. > 250 °C.

References

1 W.-W. du Mont, *J. Organomet. Chem., 131,* C37 (1977).

2 W.-W. du Mont and B. Neudert, *Chem. Ber.,* in press.

3 G. M. Kosolapoff and L. Maier, "Organic Phosphorus Compounds", Vol. 1, Wiley–Interscience, New York (1972).

4 E. H. Brooks, F. Glockling, and K. A. Hooton, *J. Chem. Soc.,* 4283 (1965).

5 Tri-tert-butylphospine silver halide complexes have been prepared very recently: H. Schmidbaur, pers. comm.; W.-W. du Mont, unpubl. results; R. W. Goel, th Int. Conf. Coord. Chem. Sao Paulo (1977) abstr.

6 H. Schumann and L. Rösch, *Chem. Ber., 107,* 854 (1974).

7 E. L. Muetterties and C. W. Alegranti, *J. Am. Chem. Soc., 94,* 6386 (1972).

8 H. Schmidbaur, J. Adlkofer and K. Schwirten, *Chem. Ber., 105,* 3382 (1972).

9 Such structures were proposed by other authors for $t\text{-}Bu_3PAgX$, *cf.* ref. [5].

10 $(Me_3Ge)(Me_3C)_2PAgBr$, m.w. calc. 450.7; fd. 1650 ± 50; $(Me_3Si)(Me_3C)_2PAgBr$, m.w. calc. 406.2; fd. 1480 ± 50; $(Me_3C)_3PAgBr$, m.w. calc. 390.1; fd. 1490 ± 50; 10^{-2} *M* in benzene.