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Phosphine and Diphosphine Complexes of Silicon(IV) Halides

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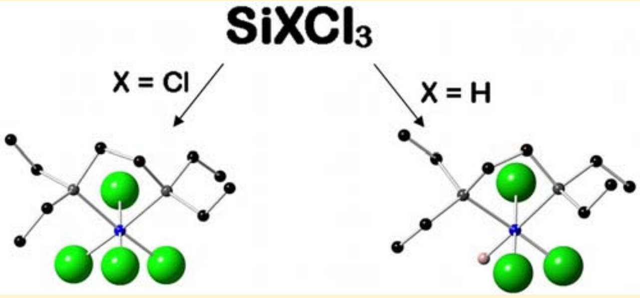
S *Supporting Information*



ABSTRACT: The reaction of SiX_4 (X = Cl or Br) with PMe_3 in anhydrous CH_2Cl_2 forms *trans*-$[SiX_4(PMe_3)_2]$, while the diphosphines, $Me_2P(CH_2)_2PMe_2$, $Et_2P(CH_2)_2PEt_2$, and *o*-$C_6H_4(PMe_2)_2$ form *cis*-[SiX_4(diphosphine)], all containing six-coordinate silicon centers. With $Me_2PCH_2PMe_2$ the product was *trans*-$[SiCl_4(\kappa^1\text{-}Me_2PCH_2PMe_2)_2]$. The complexes have been characterized by X-ray crystallography, microanalysis, IR, and multinuclear (^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$) NMR spectroscopies. The complexes are stable solids and not significantly dissociated in nondonor solvents, although they are very moisture and oxygen sensitive. This stability conflicts with the predictions of recent density functional theory (DFT) calculations (Wilson et al. *Inorg. Chem.* **2012**, *51*, 7657−7668) which suggested six-coordinate silicon phosphines would be unstable, and also contrasts with the failure to isolate complexes with SiF_4 (George et al. *Dalton Trans.* **2011**, *40,* 1584−1593). No reaction occurred between phosphines and SiI_4, or with SiX_4 and arsine ligands including $AsMe_3$ and *o*-$C_6H_4(AsMe_2)_2$. Attempts to make five-coordinate $[SiX_4(PR_3)]$ using the sterically bulky phosphines, P^tBu_3, P^iPr_3, or PCy_3 failed, with no apparent reaction occurring, consistent with predictions (Wilson et al. *Inorg. Chem.* **2012**, *51*, 7657−7668) that such compounds would be very endothermic, while the large cone angles of the phosphines presumably preclude formation of six-coordination at the small silicon center. The reaction of Si_2Cl_6 with PMe_3 or the diphosphines in CH_2Cl_2 results in instant disproportionation to the $SiCl_4$ adducts and polychlorosilanes, but from hexane solution very unstable white $[Si_2Cl_6(PMe_3)_2]$ and [Si_2Cl_6(diphosphine)] (diphosphine = $Me_2P(CH_2)_2PMe_2$ or *o*-$C_6H_4(PMe_2)_2$) precipitate. The reactions of $SiHCl_3$ with PMe_3 and $Me_2P(CH_2)_2PMe_2$ also produce the $SiCl_4$ adducts, but using $Et_2P(CH_2)_2PEt_2$, colorless $[SiHCl_3\{Et_2P(CH_2)_2PEt_2\}]$ was isolated, which was characterized by an X-ray structure which showed a pseudo-octahedral complex with the Si−H *trans* to P. Attempts to reduce the silicon(IV) phosphine complexes to silicon(II) were unsuccessful, contrasting with the isolation of stable N-heterocyclic carbene adducts of Si(II).

INTRODUCTION

Hypervalent silicon(IV) compounds, that is, compounds in which the silicon center formally exceeds eight electrons in its valence shell, have been a very active research area for many years, with the majority of compounds being organosilicon species or inorganic silicon complexes with bi- or poly dentate anionic N- or O-donor ligands.[1] Lewis base adducts of silicon(IV) halides are a further class of hypervalent derivatives and again the majority contain neutral N- (amine, N-heterocycles, etc.) or O- (ethers, pnictogen oxides, etc.) donor ligands.[2] N-heterocyclic carbene (NHC) adducts of SiX_4 (X = F, Cl, or Br) have attracted considerable recent effort, not least because they can be reduced under appropriate conditions to very rare examples of stable solid Si(II) compounds, and even to formal Si(I) or Si(0) in some cases.[3] A growing number of heterocyclic silylenes (Si(II) species) have also been described in recent work.[4] Computational studies have explored the factors involved in the formation and stability of NHC compounds of silicon,[5] and have also suggested that the NHC compounds have significantly higher stabilities than complexes with amines or phosphines. In fact, experimental studies on phosphine adducts of silicon(IV) halides are surprisingly few. Early work reported[6] monodentate phosphine adducts of SiX_4 (X = Cl or Br) characterized only by partial microanalysis, but subsequent studies[7] failed to reproduce these complexes which were suggested to be phosphine oxide adducts. The formation of $[SiX_4(PMe_3)_2]$ (X = Cl or Br) was demonstrated, and the products were identified by vibrational spectroscopy as *trans*-isomers,[8] also confirmed by a (low precision) X-ray crystal structure ($R_1 \sim 0.14$) of the chloride.[9] No complexation occurred between SiF_4 and PMe_3 at ambient temperatures, but tensimetric and Raman studies suggested both 1:1 and 2:1 adducts formed at low temperature (198 K), although neither was obtained pure.[8] No further studies of these complexes were reported after 1970, until our recent investigation[10] of the reaction of SiF_4 with a range of phosphine and diphosphine ligands, which found no evidence for adduct formation at ambient temperatures in the absence of a solvent, or in solution down to 180 K.

Comparisons with other Group 14 halides show the wide range of behavior found in this group. Germanium(IV) fluoride complexes, *trans*-$[GeF_4(PR_3)_2]$ (R = Me or Ph) and *cis*-

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[GeF$_4$(diphosphine)] (diphosphine = R$_2$P(CH$_2$)$_2$PR$_2$, R = Me, Et, Cy, Ph; *o*-C$_6$H$_4$(PMe$_2$)$_2$) are stable solids, although both water and oxygen sensitive.[11] In contrast, GeX$_4$ (X = Cl or Br) and phosphine ligands in noncoordinating solvents undergo redox chemistry to form [PR$_3$X][Ge^{II}X$_3$], although *trans*-[GeCl$_4$(PMe$_3$)$_2$] can be isolated by reaction of GeCl$_4$ and PMe$_3$ at low temperature in the absence of a solvent.[8,11,12] A wide range of GeX$_2$ (X = Cl, Br, or I) diphosphine and diarsine complexes have been made directly from the ligands and [GeCl$_2$(dioxane)] or GeX$_2$ (X = Br or I).[13] Phosphine complexes of tin(IV) halides SnX$_4$ (X = Cl, Br, or I) have long been known,[8,14] and more recently, we reported *trans*-[SnF$_4$(PR$_3$)$_2$] (R = Me, Cy, Ph) and *cis*-[SnF$_4$(diphosphine)] (diphosphine = R$_2$P(CH$_2$)$_2$PR$_2$, R = Me, Et, Ph; *o*-C$_6$H$_4$(PMe$_2$)$_2$).[15] Tertiary arsine and diarsine complexes are known for SnX$_4$ (X = Cl, Br, or I),[14] as are *trans*-[GeCl$_4$(AsR$_3$)$_2$],[11,12] but although some interaction is observed between AsMe$_3$ or *o*-C$_6$H$_4$(AsMe$_2$)$_2$ and GeF$_4$ or SnF$_4$, the complexes formed were too unstable to isolate or characterize.[11,15] Recent computational studies have suggested that formation of [SiCl$_4$(PR$_3$)] (R = Me or Ph) is energetically unfavorable, and that [SiCl$_4$(PMe$_3$)$_2$] would be of borderline stability, although it was calculated that [SiCl$_2$(PR$_3$)] should be stable entities.[5b]

We report here a systematic investigation of the synthesis, structures, and spectroscopic properties of phosphine and diphosphine adducts of SiCl$_4$ and SiBr$_4$, related chemistry with SiHCl$_3$ and Si$_2$Cl$_6$, and preliminary investigations into their reduction to Si(II). In addition to the fundamental interest in such compounds, we note that silicon plays a central role in the semiconductor industry, and new reagents for the production of silicon as nanowires or in nanoscale template structures by techniques such as supercritical fluid electrodeposition are currently under investigation.[16]

■ EXPERIMENTAL SECTION

All preparations were carried out under a dry dinitrogen atmosphere using standard Schlenk and glovebox techniques. SiCl$_4$, SiBr$_4$, SiHCl$_3$, and Si$_2$Cl$_6$ were obtained from Sigma Aldrich and distilled prior to use. Phosphines and arsines were obtained from Strem and used as received, apart from *o*-C$_6$H$_4$(PMe$_2$)$_2$ and *o*-C$_6$H$_4$(AsMe$_2$)$_2$, which were made by the literature methods.[17] CH$_2$Cl$_2$ was dried by distillation from CaH$_2$, tetrahydrofuran (thf), and hexane from sodium benzophenone ketyl.

Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer Spectrum 100 spectrometer over the range 4000−200 cm^{-1}. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded in CD$_2$Cl$_2$ solutions using Bruker AV-300 and DPX-400 spectrometers and are referenced to the residual CH$_2$Cl$_2$ resonance and external 85% H$_3$PO$_4$ respectively. Microanalyses were undertaken by Medac Ltd.

The same general method was used for all the phosphine complexes of SiX$_4$, described in detail here for complex (**1**).

***Trans*-[SiCl$_4$(PMe$_3$)$_2$] (1).** A solution of PMe$_3$ (0.456 g, 6.0 mmol) in CH$_2$Cl$_2$ (20 mL) was added to a solution of SiCl$_4$ (0.510 g, 3.0 mmol) in CH$_2$Cl$_2$ (20 mL). The solution was stirred for 16 h, concentrated to about 5 mL, and cooled to −18 °C, whereupon colorless crystals formed. Decanting the supernatant liquid and concentrating it to dryness afforded a second crop of the product. The overall yield was 0.816 g (84%). Anal. Calc. for C$_6$H$_{18}$Cl$_4$P$_2$Si: C, 22.4; H 5.6. Found: C, 22.3; H 6.0%. ^{1}H NMR (CD$_2$Cl$_2$, 295 K): δ = 1.62 (d, $^2J_{HP}$ = 12 Hz). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 295 K): δ = 13.45 (d, $^1J_{CP}$ = 35.3 Hz). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 295 K): δ = 2.3 (s, $^1J_{SiP}$ = 257 Hz). IR spectrum (Nujol): 417 (s) Si−Cl cm^{-1}.

***Trans*-[SiBr$_4$(PMe$_3$)$_2$] (2).** Compound **2** was made similarly from PMe$_3$ (0.152 g, 2.0 mmol) and SiBr$_4$ (0.348 g, 1.0 mmol) in CH$_2$Cl$_2$ (10 mL). Yield 0.367 g (73%). Anal. Calc. for C$_6$H$_{18}$Br$_4$P$_2$Si: C, 14.4; H 3.6. Found: C 14.3; H 3.8%. ^{1}H NMR (CD$_2$Cl$_2$, 295 K) δ = 1.72 (d, $^2J_{HP}$ = 12.5 Hz). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 295 K): δ = 14.53 (d, $^1J_{CP}$ = 35.4 Hz). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 295 K): δ = −1.2 (s, $^1J_{SiP}$ = 227 Hz); (223 K): δ = +0.05 (s). IR spectrum (Nujol): 321 (vs) Si−Br cm^{-1}.

[SiCl$_4${Me$_2$P(CH$_2$)$_2$PMe$_2$)] (3). Compound **3** was made from the diphosphine (dmpe) (0.150 g, 1.0 mmol) in CH$_2$Cl$_2$ (5 mL) and SiCl$_4$ (0.170 g, 1.0 mmol). Yield 0.301 g (94%). Anal. Calc. for C$_6$H$_{16}$Cl$_4$P$_2$Si: C 22.5; H 5.0. Found: C, 23.0; H, 5.5%. ^{1}H NMR (CD$_2$Cl$_2$, 295 K): δ = 1.63 (br s, [12H], CH$_3$), 2.13 (br s, [4H], CH$_2$); (223 K): δ = 1.64 (t, $^{2+5}J_{HP}$ = 5 Hz), 2.15 (br s). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 295 K): δ = 10.87 (t, $^1J_{CP}$ = 21.0 Hz), 18.36 (t, $^1J_{CP}$ = 13 Hz). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 295 K): δ = −11.4 (s); (233 K): δ = −10.8 (s, $^1J_{SiP}$= 119 Hz). IR spectrum (Nujol): 458 (s), 422 (m), 393 (s,br) Si−Cl cm^{-1}.

[SiBr$_4${Me$_2$P(CH$_2$)$_2$PMe$_2$}] (4). Compound **4** was made from dmpe (0.150 g, 1.0 mmol) and SiBr$_4$ (0.348 g, 1.0 mmol) in CH$_2$Cl$_2$ (10 mL). Yield 0.410 g (84%). Anal. Calc. for C$_6$H$_{16}$Br$_4$P$_2$Si: C, 14.8; H, 3.2. Found: C 15.1; H 3.6%. ^{1}H NMR (CD$_2$Cl$_2$, 295 K): δ = 1.75 (t, [12H], $^{2+5}J_{HP}$ = 5.1 Hz, CH$_3$), 2.21 (d,d, [4H], J = 1.8, 2.2 Hz, CH$_2$); (223 K): δ = 1.73 (t, CH$_3$), 2.21 (br s, CH$_2$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 295 K): δ = 12.65 (t, $^{1+4}J_{CP}$ = 18.8 Hz, CH$_3$), 17.62 (t, ^{1+3}J = 14.4 Hz, CH$_2$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 295 K): δ = −12.1 (s, $^1J_{SiP}$ = 112 Hz); (233 K): δ = −9.6 (s, 112 Hz). IR spectrum (Nujol): 394 (s), 310 (vs, br) Si−Br cm^{-1}.

[SiCl$_4${Et$_2$P(CH$_2$)$_2$PEt$_2$}] (5). Compound **5** was made using depe (0.515 g, 2.5 mmol) and SiCl$_4$ (0.425 g, 2.5 mmol). Yield 0.896 g (95%). Anal. Calc. for C$_{10}$H$_{24}$Cl$_4$P$_2$Si: C, 31.9; H, 6.4. Found: C, 31.6; H 6.6%. ^{1}H NMR (CD$_2$Cl$_2$, 295 K): δ = 1.21 (t, [12H], $^{2+5}J_{HP}$ = 6.0 Hz, CH$_3$), 1.96 (v br, [12H], CH$_2$); (233 K): δ = 1.25 (m, [12H], CH$_3$), 2.03 (m, [8H], CH$_2$), 2.25 (br s, [4H], CH$_2$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 295 K): δ = 7.60 (br s, CH$_3$), 14.81 (br s, CH$_2$), 15.26 (br s, CH$_2$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 295 K): δ = 0.7 (s); (233 K): 2.0 (s, $^1J_{SiP}$ = 134 Hz). IR spectrum (Nujol): 466 (s), 424 (m), 395 (s) Si−Cl cm^{-1}.

[SiBr$_4${Et$_2$P(CH$_2$)H$_2$PEt$_2$}] (6). Compound **6** was made using depe (0.206 g, 1.0 mmol) and SiBr$_4$ (0.348 g, 1.0 mmol). Yield 0.464 g (84%). Anal. Calc. for C$_{10}$H$_{24}$Br$_4$P$_2$Si: C, 21.7; H, 4.4. Found: C, 21.6; H, 4.5%. ^{1}H NMR (CD$_2$Cl$_2$, 295 K): δ = 1.32 (m, [12H], J ~ 8.0 Hz, CH$_3$), 2.06, (br, [4H], CH$_2$), 2.33 (m, [8H], CH$_2$); (223 K): 1.77 (t, J ~ 8 Hz), 2.05 (s), 2.34 (m). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 295 K): δ = 7.76 (s, CH$_3$), 14.20 (t, $^1J_{CP}$ = 14.4 Hz, CH$_2$), 16.90 (t, J = 15.5 Hz, CH$_2$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 295 K): δ = −2.1 (s, $^1J_{SiP}$ = 99 Hz); (233 K): δ = 0.1 (s, $^1J_{SiP}$ = 99 Hz). IR spectrum (Nujol): 392 (m), 383 (m), 345 (vs), 322 (s) Si−Br cm^{-1}.

[SiCl$_4${*o*-C$_6$H$_4$(PMe$_2$)$_2$}] (7). Compound **7** was made using diphos (0.198 g, 1.0 mmol) and SiCl$_4$ (0.170 g, 1.0 mmol). Yield 0.300 g (82%). Anal. Calc. for C$_{10}$H$_{16}$Cl$_4$P$_2$Si: C, 32.6; H, 4.4. Found: C, 32.5; H, 4.3%. ^{1}H NMR (CD$_2$Cl$_2$, 295 K): δ = 1.90 (t, ^{2+5}J = 5.5 Hz, [12H], CH$_3$), 7.77 (br m, [4H], C$_6$H$_4$); (223 K): δ = 1.86 (t, ^{2+5}J = 5.5 Hz, CH$_3$), 7.77 (m, [4H], C$_6$H$_4$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 295 K): δ = 13.91 (t, $^{1+4}J_{CP}$ = 17.7 Hz, CH$_3$), 132.19 (d, $^1J_{CP}$ = 15 Hz), 132.90 (s), 133.75 (s). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 295 K): δ = −14.2 (s, $^1J_{SiP}$ = 137 Hz); (233 K): δ = −11.9 (s, $^1J_{SiP}$ = 138 Hz), IR spectrum (Nujol): 481 (s), 433 (vs), 404 (s, br) Si−Cl cm^{-1}.

[SiBr$_4${*o*-C$_6$H$_4$(PMe$_2$)$_2$}] (8). Compound **8** was made using diphos (0.198 g, 1.0 mmol) and SiBr$_4$ (0.348 g, 1.0 mmol). Yield 0.525 g (96%). Anal. Calc. for C$_{10}$H$_{16}$Br$_4$P$_2$Si: C, 22.0; H, 3.0. Found: C, 22.0; H, 2.9%. ^{1}H NMR (CD$_2$Cl$_2$, 295 K): δ = 1.99 (t, $^{2+5}J_{HP}$ = 5.5 Hz, [12H], CH$_3$), 7.72−7.81 (m, [4H], C$_6$H$_4$); (223 K): δ = 1.96 (t, $^{2+5}J_{HP}$ = 5.5 Hz), 7.72−7.81 (m). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 295 K): δ = 15.64 (t, $^{1+4}J_{CP}$ = 19.0 Hz, CH$_3$), 132.90 (d, J = 13 Hz), 133.16 (s), 133.94 (s). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 295 K): δ = −14.9 (s, $^1J_{SiP}$ = 103 Hz); (233 K): δ = −12.9 (s). IR spectrum (Nujol): 400 (s), 391 (sh), 336 (s), 323 (s) Si−Br cm^{-1}.

***Trans*-[SiCl$_4$(Me$_2$PCH$_2$PMe$_2$)$_2$] (9).** A solution of the diphosphine (dmpm) (0.272 g, 2.0 mmol) in CH$_2$Cl$_2$ (10 mL) was added to SiCl$_4$ (0.170 g, 1.0 mmol) in CH$_2$Cl$_2$ (20 mL) and stirred for 16 h. The solvent was reduced to ~5 mL, hexane (30 mL) added, and the

Table 1. Crystallographic Data[a]

compound	1	2	3	4	5	6
formula	$C_6H_{18}Cl_4P_2Si$	$C_6H_{18}Br_4P_2Si$	$C_6H_{16}Cl_4P_2Si$	$C_6H_{16}Br_4P_2Si$	$C_{10}H_{24}Cl_4P_2Si$	$C_{10}H_{24}Br_4P_2Si$
M/g mol^{-1}	322.03	499.87	320.02	497.86	376.12	553.96
temp./K	120(2)	100(2)	100(2)	100(2)	100(2)	100(2)
crystal system	monoclinic	monoclinic	orthorhombic	tetragonal	monoclinic	monoclinic
space group (No.)	$P2_1/c$ (14)	$P2_1/c$ (14)	$Pna2_1$ (33)	$I4_1/a$ (88)	$C2/c$ (15)	$C2/c$ (15)
a/Å	6.5363(3)	14.408(5)	15.603(5)	11.285(3)	9.126(4)	9.353(3)
b/Å	8.2306(4)	8.465(3)	7.912(5)	11.285(3)	11.875(5)	11.954(4)
c/Å	13.1544(8)	13.448(5)	11.574(5)	23.54(1)	16.579(8)	17.285(6)
α/deg	90	90	90	90	90	90
β/deg	101.801(3)	113.561(4)	90	90	104.159(7)	104.902(4)
γ/deg	90	90	90	90	90	90
U/Å^3	692.76(6)	1503.4(9)	1429(1)	2998(2)	1742(1)	1868(1)
Z	2	4	4	8	4	4
μ(Mo−Kα)/mm^{-1}	1.132	10.964	1.098	10.996	0.912	8.837
F(000)	332	952	656	1888	784	1072
total reflections	4721	6426	6188	3037	3430	3781
unique reflections	1583	2627	2621	1316	1518	1635
R_{int}	0.017	0.032	0.058	0.025	0.209	0.015
goodness-of-fit on F^2	1.165	1.128	1.112	0.993	1.049	0.984
$R_1{}^b$ [$I_o > 2\sigma(I_o)$]	0.022	0.038	0.056	0.020	0.071	0.016
R_1 (all data)	0.023	0.052	0.063	0.024	0.084	0.018
$wR_2{}^b$ [$I_o > 2\sigma(I_o)$]	0.057	0.069	0.072	0.039	0.162	0.035
wR_2 (all data)	0.058	0.072	0.075	0.040	0.174	0.036

compound	7	8	9	13
formula	$C_{10}H_{16}Cl_4P_2Si$	$C_{10}H_{16}Br_4P_2Si\cdot0.5CH_2Cl_2$	$C_{10}H_{28}Cl_4P_4Si$	$C_{10}H_{25}Cl_3P_2Si$
M/g mol^{-1}	368.06	588.36	442.09	341.68
temp./K	120(2)	100(2)	100(2)	100(2)
crystal system	orthorhombic	monoclinic	triclinic	monoclinic
space group (No.)	$Pbca$ (61)	$P2_1/c$ (14)	$P\bar{1}$ (2)	$C2/c$ (15)
a/Å	12.9646(4)	6.871(2)	6.717(1)	9.209(6)
b/Å	15.2875(4)	16.284(6)	8.697(1)	11.870(7)
c/Å	16.321(1)	16.590(6)	8.915(1)	15.399(11)
α/deg	90	90	88.954(6)	90
β/deg	90	101.940(4)	89.753(6)	105.188(13)
γ/deg	90	90	86.672(7)	90
U/Å^3	3234.8(3)	1816(1)	519.9(1)	1624.5(19)
Z	8	4	1	4
μ(Mo−Kα)/mm^{-1}	0.981	9.237	0.922	0.811
F(000)	1504	1124	230	720
total reflections	27983	6976	5136	3814
unique reflections	3687	3251	2384	1845
R_{int}	0.032	0.027	0.036	0.037
goodness-of-fit on F^2	1.095	1.036	1.042	1.182
$R_1{}^b$ [$I_o > 2\sigma(I_o)$]	0.024	0.030	0.033	0.0741
R_1 (all data)	0.027	0.033	0.044	0.0941
$wR_2{}^b$ [$I_o > 2\sigma(I_o)$]	0.060	0.051	0.072	0.1149
wR_2 (all data)	0.061	0.052	0.076	0.1229

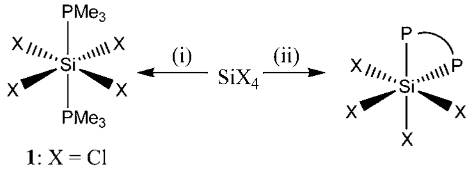
[a] Common items: wavelength (Mo−K$_\alpha$) = 0.71073 Å; θ(max) = 27.5°. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum wF_o{}^4]^{1/2}$.

mixture cooled to −18 °C. The white crystalline precipitate was isolated by decantation and dried in vacuo. Yield 0.380 g, (86%). Anal. Calc. for $C_{10}H_{28}Cl_4P_4Si$: C, 27.2; H, 6.4. Found: C, 27.0; H, 6.8%. ^{1}H NMR (CD_2Cl_2, 295 K): δ = 1.18 (d, J = 3.7 Hz, [12H], CH_3), 1.69 (d, J = 12 Hz, [12H], CH_3), 2.17 (dd, J = 10.8, 1.7 Hz, [4H], CH_2); (243 K): δ = 1.14 (d, J = 3.7 Hz, [12H], CH_3), 1.66 (d, J = 12 Hz, [12H], CH_3), 2.12 (d, J = 10 Hz, [4H], CH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2, 295 K): δ = 11.75 (dd, J_{CP} = 36.5, 9.9 Hz, CH_3), 16.90 (dd, J_{CP} = 14.4, 5.6 Hz), 28.28 (dd, J_{CP} = 33.2, 30.0 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2, 295 K): δ = −53.0 (d, $^2J_{PP}$ = 22 Hz), 10.3 (d, $^2J_{PP}$ = 21.6 Hz, $^1J_{SiP}$ = 254 Hz); (243 K): δ = −52.6 (d, $^2J_{PP}$ = 21.6 Hz), 8.27 (d, $^2J_{PP}$ = 22 Hz, $^1J_{SiP}$ = 254 Hz). IR spectrum (Nujol): 403 (vs) Si−Cl cm^{-1}.

[$Si_2Cl_6(PMe_3)_2$] (10). A solution of PMe_3 (0.076 g, 1.0 mmol) in hexane (5 mL) was added to a solution of Si_2Cl_6 (0.134 g, 0.5 mmol) in hexane (5 mL) resulting in a white precipitate which was immediately isolated by filtration and dried in vacuo. Yield 0.067 g, (22%). If the solid was left in hexane, it disproportionated in ~10 min. Disproportionation was instantaneous in CH_2Cl_2 solution (see text). Anal. Calc. for $C_6H_{18}Cl_6P_2Si_2$: C, 17.1; H, 4.3. Found: C, 17.0; H, 4.9%. IR spectrum (Nujol): 561 (m), 530 (sh), 415 (s) Si−Cl cm^{-1}.

[$Si_2Cl_6\{Me_2P(CH_2)_2PMe_2\}$] (11). Compound **11** was made similarly using a 1:1 molar ratio of diphosphine: Si_2Cl_6. IR spectrum (Nujol): 535 (s), 417 (m), 386 (s) Si−Cl cm^{-1}.

[$Si_2Cl_6\{o\text{-}C_6H_4(PMe_2)_2\}$] (12). Compound **12** was made similarly. Anal. Calc. for $C_{10}H_{16}Cl_6P_2Si_2$: C, 25.7; H, 3.5. Found: C, 26.8; H, Scheme 1. Synthesis of Complexes 1−8[a]



1: X = Cl
2: X = Br

3: X = Cl; P-P = $Me_2P(CH_2)_2PMe_2$
4: X = Br; P-P = $Me_2P(CH_2)_2PMe_2$
5: X = Cl, P-P = $Et_2P(CH_2)_2PEt_2$
6: X = Br, P-P = $Et_2P(CH_2)_2PEt_2$
7: X = Cl, P-P = o-$C_6H_4(PMe_2)_2$
8: X = Br, P-P = o-$C_6H_4(PMe_2)_2$

[a]Conditions: (i) 2 PMe_3, CH_2Cl_2; (ii) dmpe, depe or diphos, CH_2Cl_2.

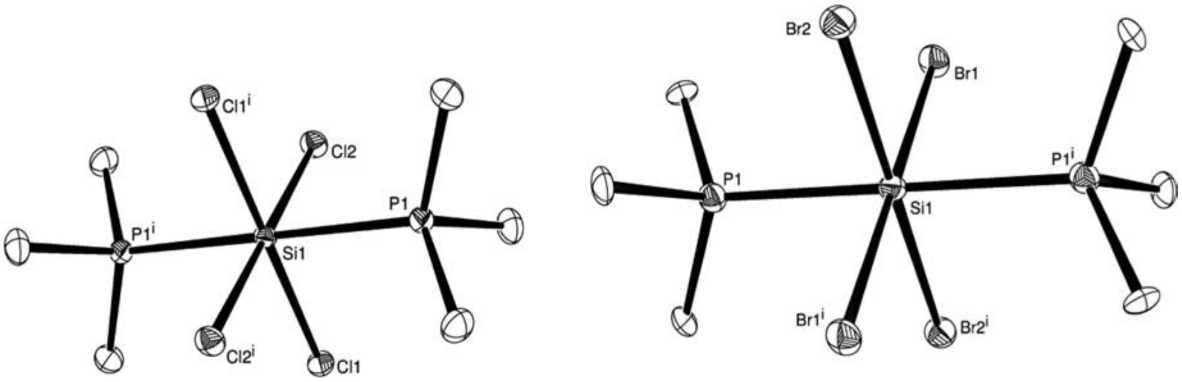


Figure 1. ORTEP representation of (a, left) $[SiCl_4(PMe_3)_2]$ (**1**) and (b, right) $[SiBr_4(PMe_3)_2]$ (**2**) showing one of two independent centrosymmetric molecules in the asymmetric unit. Thermal ellipsoids at 50% probability, hydrogens omitted for clarity. Symmetry codes: (a) $2 - x$, $-y$, $2 - z$; (b) $-x$, $1 - y$, $1 - z$. Selected bond lengths (Å) and angles (deg): (**1**) Si−P1 2.3484(3), Si−Cl1 2.2296(3), Si−Cl2 2.2069(3); Cl1−Si−Cl2 90.47(1), P1−Si−Cl1 87.52(1), P1−Si−Cl2 88.25(1); (**2**) Si−P1 2.359(2), Si−Br1 2.4145(7), Si−Br2 2.4033(9); Br1−Si−Br2 89.60(3), P−Si−Br1 92.77(4), P−Si−Br2 87.73(5).

3.5%. IR spectrum (Nujol): 539 (m), 529 (m), 395 (vs, br) Si−Cl cm^{-1}.

$[SiHCl_3\{Et_2P(CH_2)_2PEt_2\}]$ (13). A solution of depe (0.412 g, 2.0 mmol) in CH_2Cl_2 (10 mL) was added to a solution of $SiHCl_3$ (0.271 g, 2.0 mmol) in CH_2Cl_2 (10 mL). The solution was stirred for 4 h; then the solvent was concentrated to ~5 mL and cooled to −18 °C. Colorless crystals precipitated after 16 h which were isolated by decanting away the supernatant and drying in vacuo. A second crop could be isolated by further concentrating the supernatant and cooling to −18 °C for 16 h. Combined yield 0.341 g (50%). Further crops could not be obtained owing to decomposition of the compound. Anal. Calc. for $C_{10}H_{25}Cl_3P_2Si$: C, 35.2; H, 7.4. Found: C 35.2; H, 7.9%. ^1H NMR (CD_2Cl_2, 295 K): δ = 1.06 (br t, $^2J_{HH}$ = 6.9 Hz, [12H], CH_3), 1.46 (s, [12H], CH_2), 6.18 (s, [1H] $^1J_{SiH}$ = 375 Hz, SiH); (190 K): 1.88 (br m, [12H], CH_3), 2.02 (m, [8H], CH_2), 2.20 (m, [4H], CH_2), 6.30 (dd $^2J_{HP}$ = 92, 15 Hz, [1H], SiH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 295 K): δ = 9.58 (s, CH_3), 18.68 (br s, CH_2Me), 20.93 (br s, CH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 295 K): δ = −17.7 (br); (190 K): −8.8 (d, $^2J_{PP}$ = 162 Hz, P_{transH}), −5.3 (d, $^2J_{PP}$ = 162 Hz, $P_{transCl}$). IR spectrum (Nujol): 2087 Si−H, 437 (m), 405 (m) Si−Cl cm^{-1}.

X-ray Crystallography. Crystals were obtained as described above. Details of the crystallographic data collection and refinement are in Table 1. Diffractometers: (1) Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum rotating anode generator (λ_1 = 0.71073 Å) with VHF Varimax optics (70 μm focus) (**2**−**6**, **8**−**9**, **13**); (2) Rigaku R-Axis Spider including curved Fujifilm image plate and a graphite monochromated sealed tube Mo generator (λ_1 = 0.71073 Å) (**1**, **7**). Cell determination, data collection, data reduction, cell refinement, and absorption correction: CrystalClear-SM Expert 2.0 r7.[18a] Structure solution and refinement were routine using WinGX,[18b] PLATON,[18c] and software packages within[18] except for compounds **8** and **13**. Compound **8** crystallized as a nonmerohedral twin (BASF 0.45) and also exhibited positional disorder of the CH_2Cl_2 solvent. This was satisfactorily modeled using DFIX and DANG restraints. Compound **13** had partial occupation of hydride and chloride trans to phosphorus. The chloride occupancy refined to ~0.5 and was fixed at this value. A Q-peak was observed ~1.5 Å from silicon in the direction of the Si−Cl bond, which was assigned as hydrogen (fixed occupancy 0.5) and allowed to refine freely. ORTEP-3[18d] and enCIFer[18e] were used to generate graphics and edit CIFs respectively. CCDC reference numbers CCDC 919065−919075 crystallographic data in cif format.

■ RESULTS AND DISCUSSION

SiX_4 Complexes of Phosphines. The literature routes to *trans*-$[SiX_4(PMe_3)_2]$ (X = Cl, Br) required the condensation of an excess of PMe_3 onto an Et_2O solution of SiX_4 at −78 °C, or direct combination in the absence of a solvent at low temperatures, under reduced pressure.[8] A simpler, and higher-yielding route involves the addition of a CH_2Cl_2 solution of PMe_3 to a CH_2Cl_2 solution of SiX_4 under ambient conditions (Scheme 1). The complexes form colorless crystals or white powders, which are hydrolytically very sensitive both in the solid state and in solutions in chlorocarbons.

Upon cooling the CH_2Cl_2 solution (−18 °C), large colorless crystals formed which were suitable for single crystal X-ray diffraction (Figure 1a). For the bromide analogue, neat PMe_3 was added to a CH_2Cl_2 solution of $SiBr_4$; crystallization again occurred upon cooling of the solution (Figure 1b).

The X-ray structure analyses in both cases confirm the *trans* arrangement of PMe_3 ligands around silicon. The unit cell parameters of complex **1** are in good agreement with those previously reported.[9] For complex **2** there is a doubling of the volume, resulting from the presence of two symmetry-independent molecules in the asymmetric unit. Looking down the P−Si−P axis of each molecule (Figure 2) shows the methyl groups attached to the PMe_3 ligands are either completely staggered (left) or partially eclipsed (right) with respect to the bromides, giving rise to two slightly different solid-state geometries.

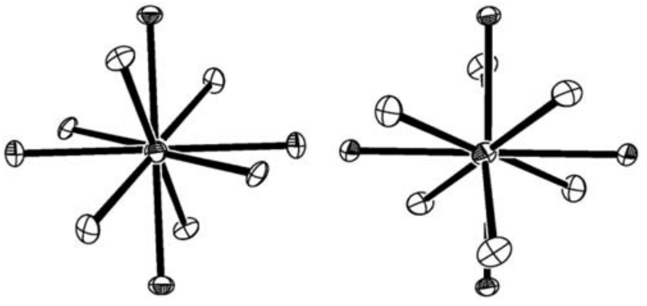


Figure 2. ORTEP representation of the two symmetry-independent molecules of $[SiBr_4(PMe_3)_2]$ (**2**) looking down the P−Si−P bond. Heteroatoms (P, Br) are represented by shaded ellipsoids, methyl carbons by unshaded ellipsoids. Thermal ellipsoids at 50% probability, hydrogen atoms omitted for clarity.

The Si−X distances in (**1** and **2**) are longer than in (T_d) $SiCl_4$ (2.007−2.010 Å) or $SiBr_4$ (2.165(2)−2.193(2) Å),[19] attributable to the increased coordination number, but in both (**1**) and (**2**) the Si−P are similar, suggesting little difference in bond strength or Lewis acidity. Attempts to prepare the five-coordinate $[SiCl_4(PMe_3)]$ by the reaction of $SiCl_4$ and PMe_3 in a 1:1 ratio merely led to the formation of (**1**) in reduced yield, consistent with the density functional theory (DFT) calculations which suggest five-coordinate complexes are energetically disfavored.[5b] Attempts to prepare 1:1 $SiCl_4$ complexes with other phosphines including PPh_3, PCy_3, P^iPr_3 or P^tBu_3 were unsuccessful, and the in situ $^{31}P\{^1H\}$ NMR spectra (CH_2Cl_2) showed no evidence for complexation, again consistent with the predictions.[5b] The PPh_3 is a markedly weaker donor than PMe_3, but the others are strong σ-donors, and their inability to form isolable SiX_4 adducts is probably mainly steric in origin, the increasingly bulky phosphines being unable to approach sufficiently close to the small silicon center to produce a viable bonding interaction in a 2:1 complex.[20] There was no evident adduct formation between SiI_4 and PMe_3. No reaction occurred between $SiCl_4$ and $AsMe_3$, and since the cone angle of the latter is very similar (121°) to that of PMe_3 (118°), the failure here must be due to the poorer match of the large arsenic σ-donor orbital to the small silicon center, and contrasts with the ready isolation of *trans*-$[GeCl_4(AsR_3)_2]$ (R = Me or Et).[11,12]

The IR spectra of $[SiX_4(PMe_3)_2]$ are in excellent agreement with literature reports.[8] The ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra (Experimental Section) are consistent with the structures, and apart from small temperature drifts in the ^{31}P resonances, show very little change over the temperature range 295−190 K, suggesting ligand dissociation is minimal. The phosphorus chemical shifts (295 K), δ +2.3 (X = Cl) or −1.2 (X = Br), are very substantially to high frequency of free PMe_3 (−62.0), and weak $^1J_{SiP}$ satellites (X = Cl: 257 Hz; X = Br: 227 Hz) were resolved.

SiX_4 Complexes of Diphosphines. Complexes with three chelating alkyldiphosphines (Scheme 1, compounds **3**−**8**) were readily obtained by combination of the ligands and SiX_4 in anhydrous CH_2Cl_2, but attempts to form adducts of the bulkier and weaker donors *o*-$C_6H_4(PPh_2)_2$ or $Ph_2P(CH_2)_2PPh_2$ failed. Crystals of all six compounds were grown by cooling CH_2Cl_2 solutions to −18 °C, and show six-coordinate silicon centers with chelating diphosphine ligands (Figures 3−5).

All six complexes have *cis*-pseudo-octahedral geometries with chelating diphosphines and chelate P−Si−P angles of ~85−86°. The *d*(Si−P) show only very small differences between the complexes of the three diphosphines and are not significantly different between corresponding chloride and bromide complexes. Comparison with the *trans*-$[SiX_4(PMe_3)_2]$ (above) also show very slightly longer $Si{-}P_{transX}$ distances compared with $Si{-}P_{transP}$, while $Si{-}X_{transX}$ are slightly longer than $Si{-}X_{transP}$. Considering these results in the light of the 3c-4e bonding model often used for hypervalent main group elements,[2] suggests that Si−X bonding is slightly more dominant than Si−P, but there is nothing in the structural data to indicate that SiX_4−phosphine bonding is unfavorable or leads to particularly unstable compounds, as suggested by the recent theoretical studies.[5] However, there was no complex formation between $SiCl_4$ and *o*-$C_6H_4(AsMe_2)_2$. The strongly chelating bidentate also failed to form a complex with $GeCl_4$,[11] in contrast to the formation of *trans*-$[GeCl_4(AsR_3)_2]$, which suggests that there is a stereochemical factor present in the germanium case at least, whereas for silicon it is likely that the

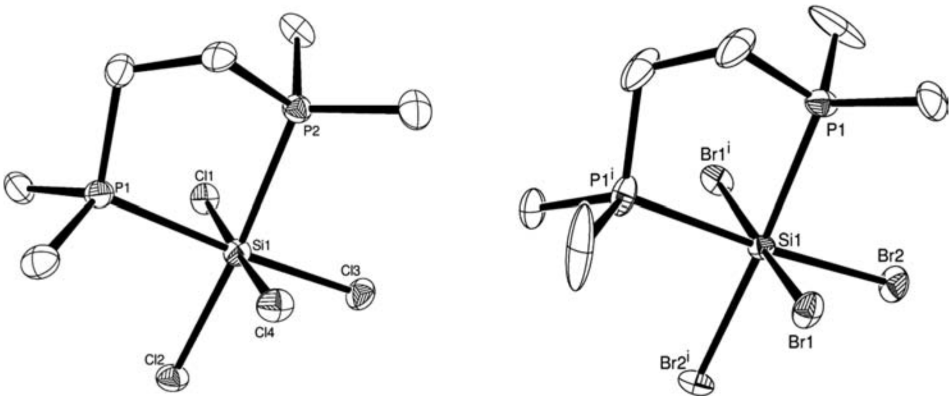


Figure 3. ORTEP representation of $[SiCl_4(dmpe)]$ (**3**) (left) and $[SiBr_4(dmpe)]$ (**4**) (right). Thermal ellipsoids at 50% probability, hydrogen atoms omitted for clarity. Symmetry code: (**4**) −*x*, 1.5 − *y*, *z*. Selected bond lengths (Å) and angles (deg): (**3**) Si−P1 2.373(2), Si−P2 2.351(2), Si1−Cl3 2.187(2), Si1−Cl2 2.189(2), Si1−Cl1 2.203(2), Si1−Cl4 2.245(2), P1−Si−P2 85.10(8), Cl3−Si1−Cl2 95.50(9), Cl3−Si1−Cl1 91.70(7), Cl2−Si1−Cl1 92.32(8), Cl3−Si1−Cl4 90.91(8), Cl2−Si1−Cl4 91.67(8), Cl3−Si1−P2 90.84(7), Cl1−Si1−P2 90.73(8), Cl4−Si1−P2 84.97(7), Cl2−Si1−P1 88.55(7), Cl1−Si1−P1 88.49(7), Cl4−Si1−P1 88.60(7). (**4**) Si−P1 2.360(1), Si−Br1 2.4261(8), Si−Br2 2.348(1); P1−Si−P1^i 86.58(6), Br1−Si−Br2 91.76(2), Br2−Si1−Br2^i 94.72(5), Br2−Si1−P1 89.37(4), Br2−Si1−Br1 92.14(2), P1−Si1−Br1 89.57(3), P1−Si1−Br1 86.24(3).

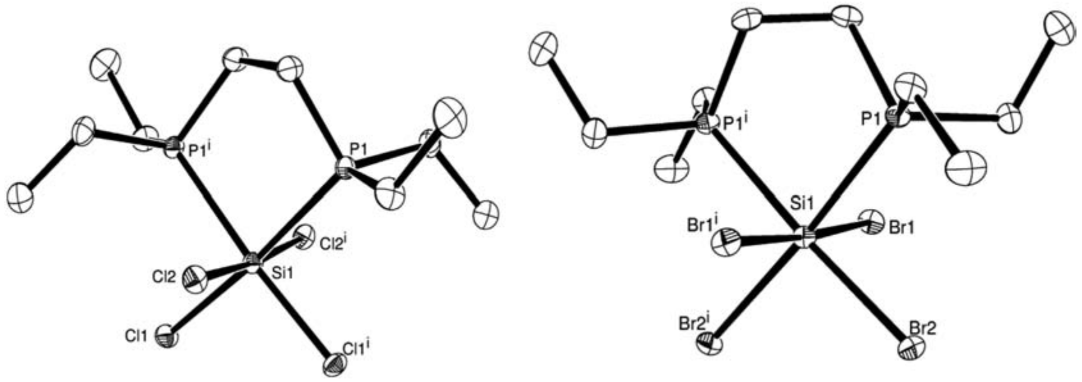


Figure 4. ORTEP representation of [SiCl$_4$(depe)] (**5**, left) and [SiBr$_4$(depe)] (**6**, right). Thermal ellipsoids at 50% probability, hydrogen atoms omitted for clarity. Symmetry code: (**5**) 2 − *x*, *y*, 0.5 − *z*; (**6**) 1 − *x*, *y*, 1.5 − *z*. Selected bond lengths (Å) and angles (deg): (**5**) Si−P1 2.379(2), Si−Cl1 2.181(2), Si−Cl2 2.224(1); P−Si−P^i 85.87(8), Cl1−Si−Cl2 92.57(5), Cl1−Si1−Cl1^i 95.12(9) Cl1−Si1−Cl2^i 91.01(5), Cl1−Si1−P1 89.50(5), Cl2−Si1−P1 87.00(5), Cl2−Si1−P1 89.11(6). (**6**) Si−P1 2.3802(9), Si−Br1 2.4128(8), Si−Br2 2.3701(8); P1−Si−P1^i 86.59(4), Br1−Si−Br(2) 90.56(2), Br2−Si1−Br2^i 94.39(4), Br2−Si1−P1 89.51(3), Br2−Si1−Br1^i 92.20(2), P1−Si1−Br1 87.43(2), P1−Si1−Br1^i 89.62(2).

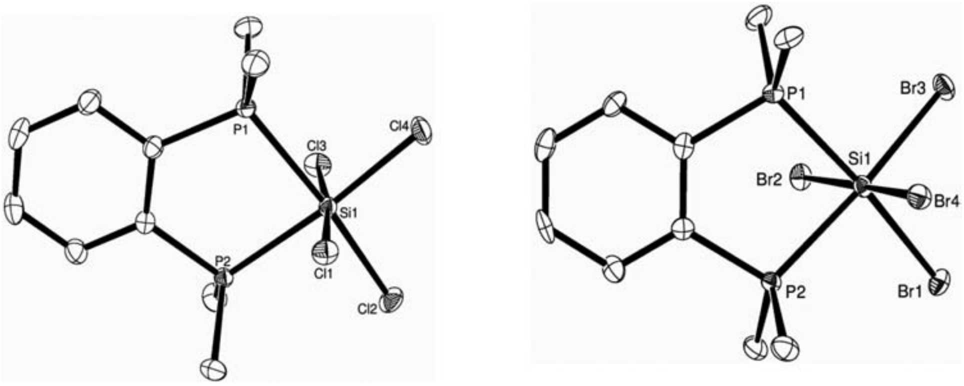


Figure 5. ORTEP representation of [SiCl$_4$(diphos)] (**7**, left) and [SiBr$_4$(diphos)] (**8**, right). Thermal ellipsoids at 50% probability, hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): (**7**) Si−P1 2.3642(5), Si−P2 2.3565(5), Si1−Cl2 2.1582(5), Si1−Cl4 2.1760(5), Si1−Cl1 2.2070(5), Si1−Cl3 2.2248(5), P1−Si−P2 85.64(2), Cl2−Si1−Cl4 96.24(2), Cl2−Si1−Cl1 92.83(2), Cl4−Si1−Cl1 92.08(2), Cl2−Si1−Cl3 92.29(2), Cl4−Si1−Cl3 91.68(2), Cl2−Si1−P2 89.21(2), Cl1−Si1−P2 87.26(2), Cl3−Si1−P2 88.47(2), Cl4−Si1−P1 88.91(2), Cl1−Si1− P1 86.87(2), Cl3−Si1−P1 87.64(2). (**8**) Si−P1 2.360(2), Si−P2 2.366(2), Si1−Br3 2.366(2), Si1−Br1 2.366(2), Si1−Br4 2.372(2), Si1−Br2 2.430(2), P1−Si−P2 85.86(7), P1−Si1−Br3 90.33(6), Br3−Si1−Br1 93.86(6), P2−Si1−Br1 89.80(6), P1−Si1−Br4 90.83(7), Br3−Si1−Br4 91.92(6), P2−Si1−Br4 90.76(6), Br1−Si1−Br4 92.42(6), P1−Si1−Br2 84.75(6), Br3−Si1−Br2 92.02(5), P2−Si1−Br2 85.03(6), Br1−Si1−Br2 91.70(6).

weak Si−As bonds do not compensate for the reorganization/distortion energy.

The two main energy terms affecting the stability of Group 14 tetrahalide complexes are the energy needed to distort the tetrahedron in the parent halide to the four-coordinate fragment present in the octahedron ("molecular floppyness"), and the bond energy of the element-donor bonds formed.[2,21] The first term is strongly endothermic, the second exothermic, and often they are of similar magnitude, which means that other more minor contributions such as lattice energies, or solvation energies in solution can be of key importance to whether the complex is stable or not. The modeling studies refer to the gas phase and do not take these other terms into account. Most DFT studies of silicon halide complexes have focused on N-donor ligands,[21] but if we assume that Si−P is a weaker bond than Si−N, this rationalizes the absence[10] of SiF$_4$-phosphine adducts, since the deformation energies fall SiF$_4$ > SiCl$_4$ > SiBr$_4$, and hence weaker Si−P bond formation produces an inadequate energy gain to offset the endothermic deformation energy for SiF$_4$. However, the present series of compounds show that stable phosphine adducts of SiCl$_4$ and SiBr$_4$ are obtainable with small, strong σ-donor phosphines, and suggest as indicated above that failure of other phosphine ligands to afford similar complexes may be largely steric in origin.

The solution behavior of the [SiX$_4$(diphosphine)] complexes also shows the complexes are stable in nondonor solvents in the absence of moisture and dioxygen. The multinuclear NMR (^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H}) spectra are fully consistent with the complexes showing no marked dissociation in solution in chlorocarbons, and show only small changes with temperature over the range 295−190 K. The CH$_3$ resonances in both the ^{1}H and ^{13}C{^{1}H} NMR spectra typically show second order coupling patterns due to strong P−P coupling. All the complexes exhibit substantial high frequency coordination shifts in the ^{31}P{^{1}H} NMR spectra, consistent with strong P−Si bonding. Comparison of the $^1J_{\mathrm{SiP}}$ couplings show that they are smaller in the cases of the *cis* isomers than the *trans* forms discussed above ($^1J_{\mathrm{SiP\ transP}}$ > $^1J_{\mathrm{SiP\ transX}}$) and for both geometries are smaller for the bromo-complexes. Attempts to obtain useful ^{29}Si NMR spectra were unsuccessful. The difficulties of observing ^{29}Si resonances arise from the long T_1's and the negative magnetogyric ratio (the latter results in signal diminution or even "nulling" in ^{1}H decoupled spectra).[22a]

Both issues are usually addressed by using a relaxation agent such as [Cr(acac)$_3$] or TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl), but we found that both agents appeared to chemically react with the silicon halide phosphine complexes, the ^{31}P NMR spectra of such solutions being different to spectra obtained in the absence of a relaxation agent. We note that a silicon complex with TEMPO, [Si(TEMPO)Cl$_3$], is known.[22b]

The reaction of $Me_2PCH_2PMe_2$ with $SiCl_4$ affords the complex *trans*-[SiCl$_4$(κ^1-Me$_2$PCH$_2$PMe$_2$)$_2$] (**9**) (Figure 6) irrespective of the ratio of reactants used. The structural parameters are very similar to those of *trans*-[SiCl$_4$(PMe$_3$)$_2$], and the NMR spectroscopic data shows no evidence of exchange between the free and the coordinated -PMe$_2$ groups in solution on the NMR time scale, which again suggests a strong Si−P bond. The failure to form *cis*-[SiCl$_4$(Me$_2$PCH$_2$PMe$_2$)] with a chelating diphosphine, even with a deficit of ligand, is attributable to the strain which would be present in the four-membered chelate ring formed. As expected the complex is very sensitive to dioxygen and water.

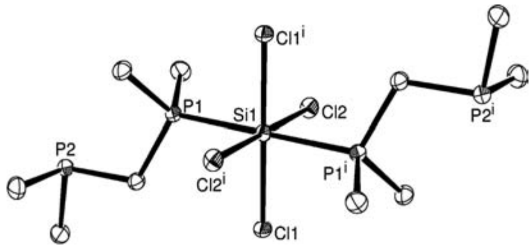
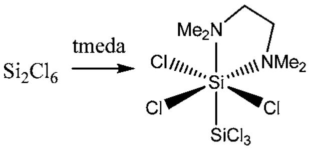


Figure 6. ORTEP representation of the centrosymmetric *trans*-[SiCl$_4$(κ^1-Me$_2$PCH$_2$PMe$_2$)$_2$] (**9**). Thermal ellipsoids at 50% probability, hydrogen atoms omitted for clarity. Symmetry code $-x$, $1 - y$, $1 - z$. Selected bond lengths (Å) and angles (deg): Si1−Cl1 2.2116(6), Si1−Cl2 2.2170(5), Si1−P1 2.3513(6), P1−C1−P2 114.48(11), Cl1−Si1−Cl2 89.62(2), Cl−Si1−Cl2 90.38(2), Cl1−Si1−P1 92.32(2), Cl1−Si1−P1 87.68(2), Cl2−Si1−P1 92.21(2), Cl2−Si1−P1 87.79(2).

Reactions of Si$_2$Cl$_6$ with Phosphine Ligands. The reaction of Si$_2$Cl$_6$ with tertiary amines NR$_3$ has long been known to produce disproportionation to SiCl$_4$ and Si(SiCl$_3$)$_4$.[23] Very recently it has been shown that the corresponding reaction using Me$_2$N(CH$_2$)$_2$NMe$_2$ (tmeda) in benzene solution precipitated white [Cl$_3$SiSiCl$_3$(tmeda)] (I), and crystals of the complex could be obtained by gas phase diffusion of the reagents.[24]



(I)

The structure (I) reveals four- and six-coordinate silicon centers linked by an unbridged Si−Si bond, with a chelating tmeda. In CH$_2$Cl$_2$ solution this complex disproportionates into oligochlorosilanes, Si$_n$Cl$_{2n}$ (n = 4, 6, 8, 10), which precipitate and dianions, [Si$_n$Cl$_{2n+2}$]$^{2-}$, which remain in solution.[24] The reaction of PMe$_3$ or any of the diphosphines with Si$_2$Cl$_6$ in CH$_2$Cl$_2$ results in immediate formation of the SiCl$_4$ complexes, identified spectroscopically by comparison with the complexes made directly (above), and a yellow solution assumed to contain oligomeric chlorosilanes. However, if the reactions were conducted in dry hexane, white precipitates were immediately obtained, identified as [Si$_2$Cl$_6$(PMe$_3$)$_2$] (**10**), [Si$_2$Cl$_6${Me$_2$P(CH$_2$)$_2$PMe$_2$}] (**11**), and [Si$_2$Cl$_6${*o*-C$_6$H$_4$(PMe$_2$)$_2$}] (**12**), which slowly (>10 min) decomposed to the SiCl$_4$ complexes and yellow oligomeric products. If the white solids were immediately filtered off and dried, they were stable for some days at room temperature, although immediately decomposed on dissolution in weakly polar solvents such as chlorocarbons. The IR spectrum of Si$_2$Cl$_6$ contains strong Si−Cl stretches at 528 and 457 cm^{-1}. The IR spectra of the complexes were complicated in the region 600−350 cm^{-1} but by comparison of the spectra with those of the corresponding SiX$_4$ adducts, strong bands >500 cm^{-1} were tentatively assigned to Si−Cl stretches of the SiCl$_3$ group and bands ~390−450 cm^{-1} to the SiCl$_3$P$_2$ unit (Experimental Section). The phosphine complexes of Si$_2$Cl$_6$ are decomposed immediately in solution preventing growth of crystals for an X-ray study and any solution spectroscopic measurements. Attempts to produce crystals of (**10**) by vapor diffusion of the reagents (cf. the tmeda complex) were unsuccessful, crystals of *trans*-[SiCl$_4$(PMe$_3$)$_2$] being isolated, and the diphosphines are insufficiently volatile for this approach. Although clearly unstable, their formation was completely unexpected and suggests that complexes of Si$_2$Cl$_6$ with other ligands may form under appropriate synthetic conditions.

SiHCl$_3$ Complexes. Although silane, SiH$_4$, is not known to form adducts, complexes of the chlorosilanes, SiHCl$_3$ and SiH$_2$Cl$_2$ with nitrogen bases have been known for many years, and have recently been reinvestigated as reagents for CVD of silicon in electronic applications.[2,25,26] Depending upon the particular system the products range from 1:1, 1:2 and 1:4 Si:base adducts, although in some systems disproportionation to other halosilane complexes occurs. In the present study the reaction of SiHCl$_3$ with phosphine ligands was explored. The reaction of SiHCl$_3$ with PMe$_3$ in thf afforded crystals of *trans*-[SiCl$_4$(PMe$_3$)$_2$] identified by a unit cell check, while crystals obtained from CH$_2$Cl$_2$ solution proved to be the phosphonium salt [PMe$_3$(CH$_2$Cl)]Cl (see the Supporting Information for details of the spectroscopic and structural data).

Similarly, the reactions of diphos or dmpe with SiHCl$_3$ in thf gave the SiCl$_4$ complexes described above indicative of disproportionation of the trichlorosilane. However, using SiHCl$_3$ and depe in CH$_2$Cl$_2$ solution, produced an unstable white solid, and colorless crystals were grown from a refrigerated CH$_2$Cl$_2$ solution. The structure determination showed the crystals to be the trichlorosilane adduct [SiHCl$_3${Et$_2$P(CH$_2$)$_2$PEt$_2$}] (**13**, Figure 7). The crystals showed H/Cl disorder *trans* to the diphosphine, but this was modeled satisfactorily with a site occupancy of 0.5, although the disorder limits the detailed comparisons of structural parameters with those of the SiCl$_4$ adducts.

The complex is much less stable than the SiCl$_4$ analogue, and it is significantly decomposed over a few days, even in a freezer (−18 °C), to [SiCl$_4${Et$_2$P(CH$_2$)$_2$PEt$_2$}] and other unidentified products. Consistent with the reduced Lewis acidity of SiHCl$_3$ compared to SiCl$_4$, a CD$_2$Cl$_2$ solution of (**13**) at ambient temperatures shows the depe is substantially dissociated from the silicon, with ^{1}H NMR resonances due to the depe and a sharp singlet at δ = 6.18 ($^1J_{SiH}$ = 375 Hz) due to Si−H. On cooling the solution below ~260 K the proton NMR resonances of the depe show significant high frequency shifts and the Si−H resonance shifts to high frequency and shows resolved splitting. At 190 K, the depe proton resonances are overlapping multiplets, consistent with inequivalent Et$_2$P− groups, and the Si−H resonance is a doublet of doublets, δ =

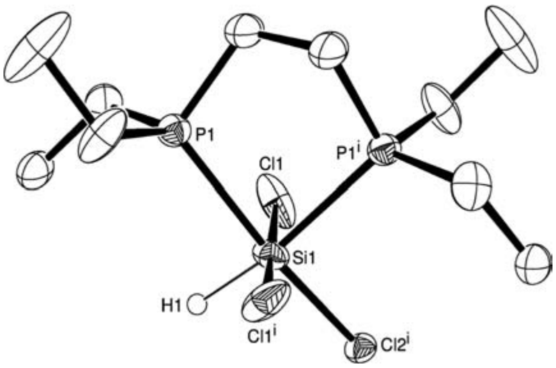


Figure 7. ORTEP representation of [$SiHCl_3$(depe)] (**13**). Thermal ellipsoids at 50% probability, hydrogen atoms omitted for clarity. The molecule has 2-fold symmetry with disorder involving Cl2 and H1. Symmetry operation: a = −*x*, *y*, 1/2 − *z*. Selected bond lengths (Å) and angles (deg): Si1−Cl1 = 2.240(2), Si1−Cl2 = 2.141(2), Si1−P1 = 2.395(2), Si1−H = 1.51(7), Cl1−Si1−Cl1 = 174.11(11), Cl2−Si1−Cl1 = 99.33(8), Cl2−Si1−Cl1 = 84.76(8), P1−Si1−P1^i = 84.44(9).

6.30 ($^2J_{HP}$ = 92, 15 Hz), due to couplings to the *trans* and *cis* phosphine groups. The $^{31}P\{^1H\}$ NMR spectrum at ambient temperature is a broad singlet at δ = −17.7, very close to the value of the ligand itself, although the broadness indicates an extensively dissociated exchanging system. The effect of cooling the solution replicates those observed in the ^1H NMR data, and at 190 K, two doublets of equal intensity are present at δ = −8.8 ($^2J_{PP}$ = 162 Hz), −5.3 ($^2J_{PP}$ = 162 Hz), assigned as P_{transH} and $P_{transCl}$ by comparison with the $SiCl_4$ complex data. The effects of temperature on the NMR spectra are reversible on warming the solution, although over time (>30 min) features due to [$SiCl_4\{Et_2P(CH_2)_2PEt_2\}$] and uncoordinated depe grow, along with other unidentified resonances, due to decomposition. The [$SiHCl_3\{Et_2P(CH_2)_2PEt_2\}$] complex, which is the first phosphine adduct of a chlorosilane, is much less stable than (**5**), and as noted, significantly decomposed in the solid state after a few days even at low temperatures, and quite rapidly in solution. On this basis, our failure to isolate analogues with dmpe, diphos, or PMe_3 is not too surprising—small differences in stability or rate of disproportionation would be sufficient to account for the failures.

Attempted Reductions to Si(II). A major advance in the chemistry of silicon was the isolation of very rare examples of stable solid Si(II) compounds supported by NHC ligands.[3] This raised the possibility that Si(II) phosphine complexes might be obtainable, and computational studies have suggested that Si(II) phosphines may even be more stable than their Si(IV) analogues, the Δ*G* of formation of [$SiCl_2(PMe_3)$] being calculated at −56.1 kJ mol^{-1}.[5b] However, our preliminary attempts to reduce the [$SiCl_4$(diphosphine)] described above to Si(II) complexes were unsuccessful. No reduction occurred with C_8K, and the silicon(IV) starting complexes were recovered, while using a potassium mirror gave the free diphosphine and a black pyrophoric solid. *Trans*-[$SiCl_4(PMe_3)_2$] did not react with sodium naphthalenide, and free PMe_3 formed on reaction with the Mg(I) reagent [$(DiPPNacNac)Mg]_2$,[27] where DiPPNacNac is [$\{$(2,6-di-isopropylphenyl)NCMe$\}_2$CH$\}]^-$.

CONCLUSIONS

Surprisingly robust complexes of SiX_4 (X = Cl or Br) with PMe_3, $Me_2P(CH_2)_2PMe_2$, $Et_2P(CH_2)_2PEt_2$, *o*-$C_6H_4(PMe_2)_2$, and $Me_2PCH_2PMe_2$ have been isolated and fully characterized. All contain six-coordinate silicon centers, are not appreciably dissociated in chlorocarbon solvents, and are indefinitely stable at room temperature in the absence of water or dioxygen. This stability contrasts with theoretical predictions[5b] which suggested that such silicon(IV) phosphines would be of borderline stability, although our failure to obtain five-coordinate (1:1) complexes is consistent with predictions.[5b] The structural and spectroscopic data show only small differences in Lewis acidity between $SiCl_4$ and $SiBr_4$. The failure to obtain complexes of SiI_4 is consistent both with steric hindrance at the small silicon center and weaker Lewis acidity, while the failure to isolate adducts with SiF_4 reported previously[10] most probably indicates that the large deformation energy of SiF_4 is not repaid by the formation of two Si−P bonds. The results with SiX_4 also contrast with those reported for germanium(IV) halides,[11,12] namely, stable adducts with GeF_4 but reduction to Ge(II) with GeX_4 (X = Cl or Br). The ready formation of *trans*-[$GeCl_4(AsR_3)_2$][11,12] also contrast with the lack of any reaction between SiX_4 and AsR_3. The formation of the first phosphine adducts of Si_2Cl_6, and of [$SiHCl_3\{Et_2P(CH_2)_2PEt_2\}$], the first phosphine complex of a halosilane, were also unexpected, and reveal that silicon(IV) coordination chemistry is far from fully explored. The failure thus far to obtain any evidence for the formation of silicon(II) phosphine adducts, contrasts both with the ready formation of GeX_2 adducts[13] and with the formation of stable silicon(II) complexes with N-heterocyclic carbenes.[3] While we cannot rule out that Si(II) phosphine complexes may be obtainable by other routes or with phosphines which have specific steric or electronic properties, it seems that isolation of such complexes will be extremely challenging. Overall this study taken in comparison with recent work on other silicon and germanium systems, reveals the rich and unpredictable chemistry of these two elements.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Preparative details for [$PMe_3(CH_2Cl)$]Cl. CIF files for all the crystal structures described. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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