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P-functionally substituted aminoiminophosphoranate chelates of Ti, Zr, and Sn — synthesis and structural investigations

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Dedicated to Professor Alfred Schmidpeter on the occasion of his 70th birthday.

Abstract

Reactions of various $XYP(NSiMe_3)N(SiMe_3)_2$ compounds with the tetrachlorides of Ti, Zr, and Sn afford aminoimino phosphate and phosphonate chelates $XYP(NSiMe_3)_2[M]$ of the respective metals. The X-ray structures of **1** (X = Y = MeO, $[M] = TiCl_3{\cdot}MeCN$), **2** (X = Y = MeO, $[M] = ZrCl_3{\cdot}MeCN$), **9** ($X_2 = (CF_3CS)_2$, $[M] = TiCl_3$) and **11** (X = Cl, Y = CCl_3, $[M] = TiCl_3$) have been determined. In addition to the monochelates, bischelates $[X_2P(NSiMe_3)_2]MCl_2$, **5** (X = EtO, M = Sn), and **10** ($X_2 = (CF_3CS)_2$, M = Ti) have been synthesized by varying the stoichiometry. The X-ray structure of **5** is described.

Keywords: Diazaphosphametalletidines; Metallaspirobicycloheptanes; Titanium; Zirconium; Tin; X-ray

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1. Introduction

N,*N*′-bis(trimethylsilyl) substituted aminoiminophosphinate chelates have been considered to be steric equivalents to the pentamethylcyclopentadienyl ligand [1]. While the latter complexes of almost all d-block metals in medium to high oxidation states are known with various ligands on the metal [2], information on the former is scarce [3]. The limitation is based on the availability of suitable phosphorus precursors and metal compounds prone to form four-membered rings. Four major types of reactions have found application in the synthesis of diazaphosphametalletidines: (i) abstraction of alkali or trimethylsilyl halides from metal halides and the corresponding aminoiminophosphoranes; (ii) elimination of stable hydrocarbons from organosubstituted metal compounds; (iii) oxidation of stable or intermediate P(III)-precursors either in situ or with migration of metal or nitrogen bound groups, and (iv) increase in the coordination number of aminodiiminophosphoranes [3]. While the second method is restricted to main group metals, the first reaction has been found suitable, thus far, only for tetrahalides of the titanium triad [4,5] and f-block elements [1]. With $VOCl_3$ an eight-membered ring is formed [6], and WCl_6 only leads to an open-chain compound [7].

In this article we wish to report on aminoiminophosphorane chelates of Ti, Zr, and Sn with functional groups attached to the phosphorus atom. Compounds of this type might be useful candidates for catalysts in olefin polymerization as has been shown in corresponding benzamidinate chelates of Ti and Zr [8].

$$XYP(NSiMe_3)N(SiMe_3)_2 + MCl_4 \xrightarrow[-Me_3SiCl]{} XYP(NSiMe_3)_2MCl_3$$

X = Y = MeO		M = Ti	**1**
X = Y = MeO		Zr	**2**
X = X = MeO		Sn	**6**
X = Y = MeO	3	Sn	**4**
X = Y = Cl		Ti	**7**
XY = $(CF_3CS)_2$	8	Ti	**9**
X = Cl, Y = CCl_3		Ti	**11**

Scheme 1.

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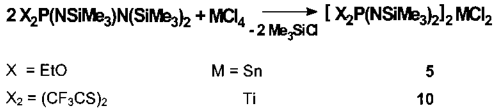


$$2\,X_2P(NSiMe_3)N(SiMe_3)_2 + MCl_4 \xrightarrow[-2\,Me_3SiCl]{} [X_2P(NSiMe_3)_2]_2MCl_2$$

Scheme 2.

2. Results and discussion

2.1. Synthesis of compounds **1–11**

The reactions of P-functionalized bis(trimethylsilyl)amino-trimethylsilyliminophosphoranes with the tetrachlorides of titanium, zirconium, and tin in CH_2Cl_2 or MeCN in a 1:1 ratio lead in high yields to the four-membered metallaphosphazenes **1**, **2**, **4**, **6**, and **9**. In the case of **1** and **2** the reaction must be carried out in MeCN to generate the Lewis-base adducts $MCl_4 \cdot 2MeCN$ prior to reaction, otherwise as yet unidentified compounds are formed with Michaelis–Arbuzov type [9] elimination of MeCl. The Lewis-acid strength of $SnCl_4$ seems to be low enough to avoid this side reaction. During the synthesis of **7** and **11** the pentavalent phosphorus precursors are generated in situ [10] by reacting $Me_3SiNPN(SiMe_3)_2$ [11] with chlorine in $CFCl_3$, or CCl_4, respectively (Scheme 1).

In the case of **1** and **2** the MeCN adducts are formed. The alkoxy-substituted compounds **1**, **2**, **4**, and **6** are excellently soluble in polar solvents such as MeCN or CH_2Cl_2 and insoluble in Et_2O and hydrocarbons. In contrast, **7** and **9** are also soluble in Et_2O and *n*-hexane, the bright yellow chlorine compound **7** decomposes in MeCN to leave a brown oil, and after removal of the solvent an uncharacterizable brownish powder remains. The newly synthesized metal chelates are crystalline solids (yellow with Ti, colorless with Zr and Sn) of limited air stability, decomposition in solution proceeds even faster.

While compounds **1** and **2** can only be crystallized in the presence of coordinating solvents, the monochelates **7** and **9** are obtained solvate-free even from aprotic solvents like diethyl ether or *n*-hexane. No MeCN has been detected by ^{1}H-NMR spectroscopy when tin compounds **4** and **6** were recrystallized from this solvent.

By varying the stoichiometry to 2:1 the bischelates **5** and **10** can be obtained (Scheme 2). No such products have been detected in the reactions of the transition metal halides with the other precursors.

The bischelates are less moisture sensitive than their monosubstituted analogues and show similar solubilities. P,P′,Ti-trispirocyclic (**10**) can be recrystallized from MeCN to yield orange plates. While compound **5** is formed under mild conditions, for the synthesis of **10** a reaction temperature of 60°C is required, otherwise mixtures of **8**, **9**, and **10** are obtained which are difficult to separate.

Polar solvents are required in all these reactions; the use of *n*-hexane in the attempted synthesis of **7** and **9** led to recovery of the starting materials. $CFCl_3$ seems to be polar enough to enable reaction; other solvents will react with the aminoiminophosphane precursor as seen, e.g. in the synthesis of **11**. Attempts to isolate transition metal chelates of tervalent phosphorus are as yet unsuccessful, although extreme low-field signals in the ^{31}P-NMR indicate their formation. Such compounds are known for Al [12], Sn [13], Cd, and Zn [14].

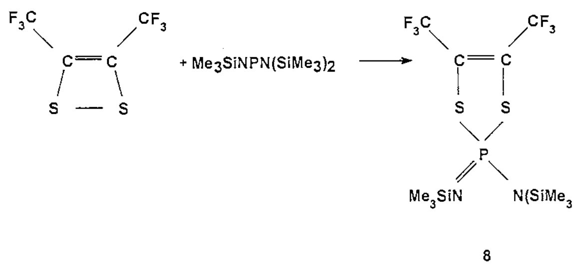
The hitherto unknown ethoxy-substituted aminoiminophosphorane (**3**) was synthesized via Staudinger oxidation of $(EtO)_2PN(SiMe_3)_2$ [15] with Me_3SiN_3 following the procedure of Scherer and Thalacker [16] and fully characterized spectroscopically.

Denney and co-workers [17] have described the oxidation of tervalent three-coordinated phosphorus compounds with bis(trifluoromethyl)dithiete [18]. This reaction type is also applicable to the aminoiminophosphane. In $CFCl_3$ at −80°C compound **8** is formed which can be isolated after evaporation and sublimation as a yellow solid in high yield (Scheme 3).

Compound **8** was included in our systematic investigation of diaminophosphoranate chelates because a rearrangement at the phosphorus atom is prohibited in contrast to the alkoxy species. Compounds **9** and **10** are composed of nine different atoms.

2.2. Spectroscopic investigations

In the mass spectra of the tin compounds **4–6** the molecular ions have been detected with low intensities. All compounds exhibit a similar fragmentation pattern with (M–Me) and (M–Cl) (and additionally MeCN for the solvate adducts) as the predominant species, in most cases the former is the base peak. Only in the halogen-rich compounds **7–10** (Me_2SiCl), (Me_2SiF), and (Me_3Si) have been found as base peaks. Compound **9** exhibits a somewhat different behavior: the ion (M–Cl) was not detected, instead a fragment (M–Cl–Me + F) occurred. The peaks of lower mass result from loss of the metal center and fragmentation of the aminoiminophosphorane ligands.



Scheme 3.

The ^{1}H-NMR spectra of the monochelates show singlets or doublets due to $^4J(^1H–^{31}P)$ coupling ≤ 0.4 Hz in the $(CH_3)_3Si$ region. The bischelates **5** and **10** have two singlets due to the different chemical environments of the $(CH_3)_3Si$ groups. The signals downfield are tentatively assigned to the groups facing both chlorine atoms. An interesting feature has been found in the ^{1}H-NMR spectra of the ethyl compounds **3** and **5**: the non-equivalence of the ethyl groups as seen from the X-ray structure of **5** (vide infra) is also persistent in solution, as well as in the precursor $(EtO)_2PN(SiMe_3)_2$ [19]. This is in sharp contrast to the ^{1}H-NMR of **4** where only two sets of signals can be observed, a doublet of quartets at δ 4.25 ppm for the CH_2 protons with almost equal $^3J(^1H–^1H)$ and $^3J(^1H–^{31}P)$ coupling constants of 7 Hz and a doublet of triplets for the CH_3 protons at δ 1.34 ppm with $^3J(^1H–^1H) = 7$ Hz further split by $^4J(^1H–^{31}P) = 1.2$ Hz. The ^{19}F-NMR spectra of **8** and **9** show doublets due to coupling to the ^{31}P nucleus. The ^{19}F-NMR spectrum of **10** exhibits the A_3B_3 part of an A_3B_3X system, the $^5J(^{19}F–^{31}P)$ coupling can be estimated to ca. 12 Hz, further splitting of ca. 2 Hz occurs due to $^4J(^{19}F–^{31}P)$ coupling (Fig. 1).

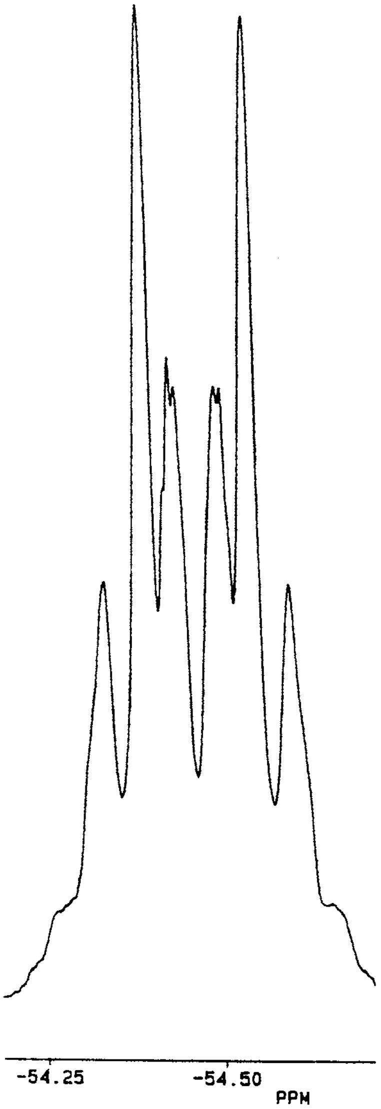


Fig. 1. ^{19}F-NMR spectrum of compound **10** at 188 MHz.

Table 1
Comparison of the ^{31}P-NMR chemical shifts (in ppm)

X = Y	Precursor	M	Monochelate	Bischelate
MeO	5.2	Ti	(**1**) 17.3	
MeO		Zr	(**2**) 16.0	
MeO		Sn	(**6**) 34.0	32.4 [a]
EtO (**3**)	2.3	Sn	(**4**) 29.7	(**5**) 26.3
Cl	−24.0 [b]	Ti	(**7**) 16.2	
1/2$(CF_3CS)_2$ (**8**)	−1.7	Ti	(**9**) 50.2	(**10**) 47.7
Cl, Y = CCl_3	3.8 [b]	Ti	(**11**) 29.8	

[a] Ref. [19].

[b] Taken from Ref. [10].

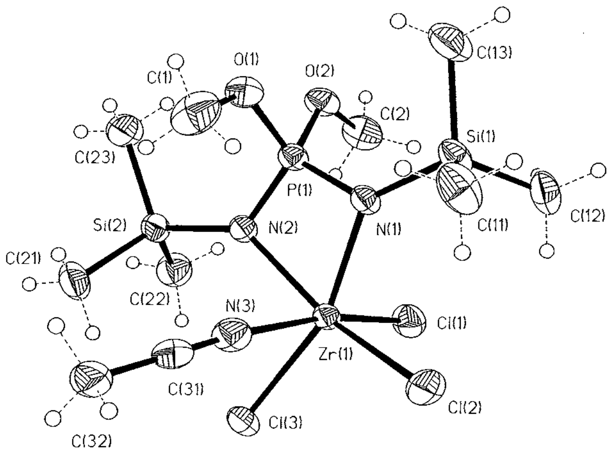


Fig. 2. Molecular structure of compound **2**.

The incorporation of the phosphorus atom into a four-membered ring together with a different bonding situation exerts a downfield shift on the ^{31}P-NMR signal of the chelates compared with the starting materials; the signals of the bischelates are slightly upfield from those of the monochelates (Table 1).

Unresolved $^2J(^{31}P–^{117/119}Sn)$ coupling 37.3, 40.1, and 34.0 Hz is observed in the ^{31}P-NMR spectra of **4**, **5**, and **6**, respectively.

*2.3. Molecular structures of **1**, **2**, **5**, **9**, and **11***

The molecular structures of **1**, **2**, **5**, **9**, and **11** have been determined by single-crystal X-ray crystallography. Compounds **1** and **2** are isostructural. The structures of **2**, **5**, **9**, and **11** are depicted in Figs. 2–5 together with their atom labeling scheme (thermal ellipsoids with 50% probability). Only molecule **1** of the six independent molecules in the asymmetric unit of **9** is represented in Fig. 4.

All molecules have in common a kite-shaped four-membered MN_2P ring with the angles at the metal atoms being more acute than at the phosphorus atom, and the bond lengths from the nitrogen atoms to their neighbors are pairwise almost equal. Selected averaged bond distances and angles are listed in Table 2.

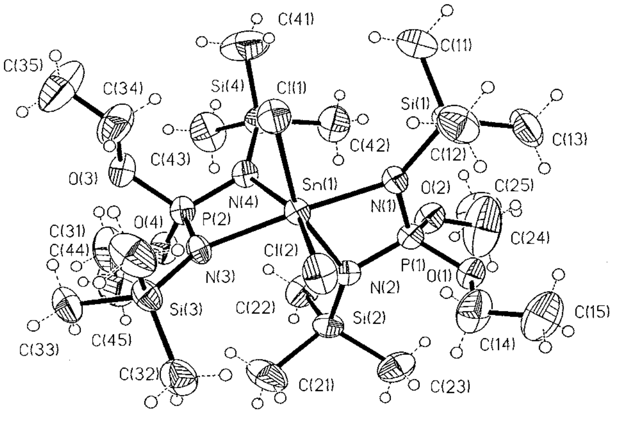


Fig. 3. Molecular structure of compound **5**.

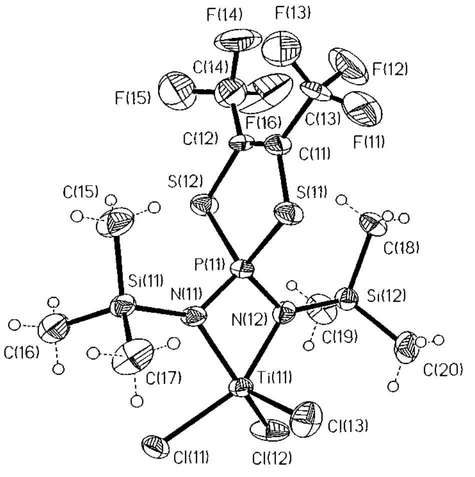


Fig. 4. Molecular structure of compound **9**.

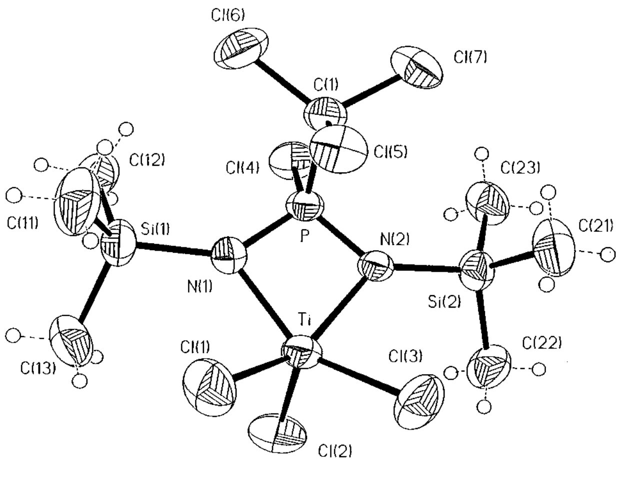


Fig. 5. Molecular structure of compound **11**.

The bond parameters of the titanium and zirconium compounds do not differ significantly from those of the previously described compounds reported by us [3,4], Niecke et al. [20], and Chernega and co-workers [21]. The Ti–N bonds are ca. 0.1 Å shorter than in the bis-chelate $[Ph_2P(NSiMe_3)_2]_2Ti{=}N\textit{t}Bu$ synthesized by Edelmann and co-workers [22]. The average M–N bonds of the Ti- and Zr-heterocycles are longer than in the previously reported P-phenyl-substituted chelates (Ti: 2.030(3) Å, Zr: 2.178(4) Å), while the corresponding P–N bonds are shorter (Ti: 1.619(3) Å, Zr: 1.608(5) Å, all average) [3,4]. The spirocyclic tin compound **5** possesses a centre of chirality, both enantiomers are present in the unit cell. The environment at the tin atom is distorted octahedral with the chlorine atoms in the *cis* position, the Sn–N bonds facing both of them are slightly shorter than the other two. The structure is consistent with the ^{1}H-NMR spectrum of **5**, which shows two sets of signals for the $(CH_3)_3Si$ and C_2H_5 protons. One ethoxy group is tilted away from the ring plane, while the other is directed towards the plane as depicted in Fig. 6.

This is in contrast to compounds **1** and **2** where the methyl groups are both tilted away. On the basis of these results, compound **6** can be assigned an analogous geometry around the phosphorus atom.

Bischelate **10** represents a trispirocyclic system with two central four-membered PN_2Ti rings and two outer five-membered PS_2C_2 rings with almost perpendicular orientations to each other as derived from the X-ray structures of **5** and **9** and spectroscopic data. In contrast to one other titanium compound having two aminoiminophosphoranate ligands where only one chelate is formed, the other ligand forms a chain under migration of a silyl group [3]. This might be due to the greater steric requirement of the phenyl groups in the latter. Reduction of steric congestion by replacing the two chlorine atoms by an imido group in the aforementioned complex of Edelmann and co-workers [22] also results in the formation of a bischelate, as does the increase of the atomic radius of the central metal (Ti: 1.40 Å versus Na: 1.80 Å, Sm: 1.85 Å [23]) where anionic bis(diphenylaminoiminophosphoranate) chelates of Na [24] and Sm [25] have been found and structurally characterized. Interestingly, the Sm-bischelate anion, which is structurally related to **5**, shows only one signal for the $(CH_3)_3Si$ protons [25], indicating a different behaviour in solution.

The central four-membered rings are almost planar as are the environments at the nitrogen atoms. The phosphorus atoms are almost ideally tetrahedral coordinated, a slight elongation is found along the ring axis. The hexa-coordinated metal atoms in **1**, **2**, and **5** have distorted octahedral geometries with the chlorine atoms in **1** and **2** in a *cis*-arrangement, while the penta-coordi-

Table 2
Selected bond distances (Å) and angles (°) for **1**, **9**, **11** (M = Ti), **2** (M = Zr), and **5** (M = Sn) (averaged with ranges in square brackets and maximum estimated S.D.s of unique parameters in parentheses)

	1	**2**	**5**	**9** [a]	**11**
M–N	2.053 [0.045] (3)	2.188 [0.075] (3)	2.187 [0.019] (2)	2.074 [0.063] (10)	2.066 [0.014] (4)
M–$NCCH_3$	2.237 (4)	2.354 (3)	–	–	–
M–Cl	2.297 [0.059] (2)	2.4247 [0.0491] (9)	2.4104 [0.0182] (8)	2.232 [0.078] (5)	2.220 [0.216] (2)
N–Si	1.764 [0.007] (3)	1.765 [0.001] (3)	1.749 [0.005] (2)	1.784 [0.043] (11)	1.787 [0.002] (5)
N–P	1.592 [0.009] (3)	1.596 [0.002] (3)	1.595 [0.011] (3)	1.599 [0.039] (11)	1.578 [–] (4)
P–O	1.570 [0.006] (3)	1.576 [0.014] (3)	1.576 [0.021] (2)	–	–
O–C	1.444 [0.007] (5)	1.438 [0.012] (5)	1.442 [0.049] (4)	–	–
P–S	–	–	–	2.101 [0.038] (5)	–
S–C	–	–	–	1.753 [0.082] (14)	–
C=C	–	–	–	1.345 [0.105] (18)	–
P–C	–	–	–	–	1.881 (5)
P–Cl	–	–	–	–	1.996 (2)
N–M–N (*endo*)	72.79 (13)	68.59 (10)	69.16 [0.01] (9)	72.8 [1.3] (4)	73.0 (2)
M–N–P	93.6 [1.4] (2)	95.00 [1.06] (12)	94.34 [0.48] (11)	93.3 [1.8] (5)	92.0 [0.5] (2)
N–P–N	99.8 (2)	101.12 (14)	102.14 [0.34] (13)	100.3 [3.2] (5)	102.3 (2)
P (*exo*)	96.0 (2)	95.96 (13)	99.83 [0.16] (12)	89.92 [0.81] (19)	102.3 (2)
N–P–O	115.5 [2.7] (2)	115.17 [1.81] (14)	113.85 [2.88] (12)	–	–
N–P–S	–	–	–	114.6 [4.3] (4)	–
P–S–C	–	–	–	98.0 [2.4] (5)	–
S–C–C (double)	–	–	–	121.8 [6.1] (10)	–
S–C–C (single)	–	–	–	112.8 [6.1] (11)	–
C–C–C	–	–	–	125.8 [7.6] (13)	–
N–P–C	–	–	–	–	111.2 [0.7] (2)
N–P–Cl	–	–	–	–	115.2 [0.4] (2)
Σ ring	359.79	359.71	359.97	359.8	359.2
Σ N	359.65	359.80	358.69	359.0	360.0

[a] Averaged over the six independent molecules in the asymmetric unit.

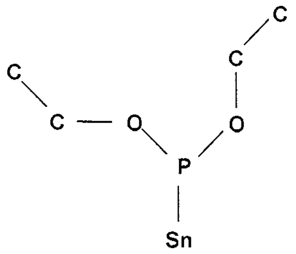


Fig. 6. Schematic arrangement of the phosphorus substituents in **5** (P–Sn denotes the ring plane).

nated titanium atoms in **9** and **11** show arrays between square-pyramidal and trigonal-bipyramidal. According to O'Keeffe and Brese [26] the bond order for the P–N bonds is somewhat higher than a single bond, while the bond order for the M–N bonds can be estimated to be ca. 0.7.

Chelates **9** and **11** comprise rare examples of compounds of five-coordinated titanium not supported by cyclopentadienyl ligands or a Ti=N double bond that have been structurally characterized; no additional short intermolecular contacts to the metal atoms have been detected in the crystal packing of these compounds. The six independent molecules in the unit cell of **9** differ by up to 8% in their bonding parameters, the main effect is imposed by the non-planarity of the PS_2C_2 ring and its relative orientation with respect to the three chlorine atoms arising from crystal packing effects, since NMR spectra show the same pattern down to temperatures where crystallization starts, where only line broadening has been observed [19]. Interestingly, the occupancy of the tilting of the PS_2C_2 five-membered rings in the asymmetric unit is 4:2 with respect to the mirror plane through the apical chlorine and phosphorus atoms. The mean C=C double bond length of **9** is about 0.05 Å shorter than in the starting dithiete which has been studied by vapour phase electron diffraction [27], while two bonds of the six independent molecules are in the same range and the C–S bonds are almost identical.

3. Experimental

3.1. General remarks

All reactions were performed in vacuo or under an atmosphere of either dry nitrogen or argon using Schlenk line techniques or in an inert gas glove box. Solvents were dried by known methods, distilled and transferred in vacuo into the reaction vessels. The starting materials $(CF_3CS)_2$ [18], $Me_3SiNPN(SiMe_3)_2$ [11], and $(MeO)_2P(NSiMe_3)N(SiMe_3)_2$ [16] were prepared according to literature methods. The hitherto unknown $(EtO)_2P(NSiMe_3)N(SiMe_3)_2$ (**3**), b.p. 80°C/10^{-5} bar, ^{31}P-NMR δ 2.3 ppm, was prepared in analogy to its methyl analogue. NMR spectra were recorded on Bruker AM 200, AM 250, and MSL 400 spectrometers. ^{1}H, ^{19}F, and ^{31}P data are listed in ppm, positive signs being downfield from external $SiMe_4$, $CFCl_3$ and 85% H_3PO_4, respectively. Heteronuclear NMR spectra were recorded ^{1}H-decoupled. EI mass spectra were obtained on Finnigan MAT System 8230 or Varian MAT CH 5 mass spectrometers. IR spectra were recorded as Nujol mulls between KBr disks on a Bio-Rad FTS 7 spectrophotometer. Melting points were determined on HWS-SG 3000 and Büchi B-540 apparatus. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie.

3.2. Synthesis

*3.2.1. Preparation of $(MeO)_2P(NSiMe_3)_2MCl_3 \cdot MeCN$, M = Ti (**1**), Zr (**2**)*

In total 50 ml of MeCN was condensed at −196°C onto 10 mmol of the metal tetrahalide, 1.9 g (M = Ti), 2.3 g (M = Zr), warmed to ambient temperature, and after formation of the complexes $MCl_4 \cdot 2MeCN$ (ca. 15 min stirring) and recooling to −196°C, 3.4 g (10 mmol) $(MeO)_2P(NSiMe_3)N(SiMe_3)_2$ were added via syringe. After reaching room temperature (r.t.) the mixtures were stirred for additional 4 h and then volatiles pumped off in vacuo leaving the chelates in yields and purities > 80% as seen from NMR spectra. Recrystallization of the crude products from small amounts of MeCN or $CHCl_3$ afforded pure yellow **1**, m.p. 124°C, and colourless **2**, m.p. 198°C, under substantial loss.

1: Anal. $C_{10}H_{27}Cl_3N_3O_2PSi_2Ti$ (462.75 g mol^{-1}). Found: C, 25.4; H, 5.9; Cl, 22.6; N, 8.8; P, 6.6. Calc.: C, 26.0; H, 5.9; Cl, 23.0; N, 9.1; P, 6.7%. IR: 2314 (m), 2286 (m), 1251 (s), 1175 (m), 1136 (m), 1082 (vs), 1027 (vs), 898 (vs), 845 (vs), 758 (s), 650 (m), 617 (s), 534 (m), 516 (m), 437 (s) cm^{-1}. MS: *m*/*z* 407 (M–MeCN–Me, 100), 385 (M–MeCN–Cl, 15), 297 (M–MeCN–Me–Me_3SiCl, 17%). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 0.37 (s, 18H, $(CH_3)_3Si$), 1.99 (s, 3H, CH_3CN), 3.76 (d, $^3J(^1H–^{31}P) = 12.6$ Hz, 6H, CH_3O) ppm. ^{31}P-NMR (101 MHz, $CDCl_3$): δ 17.3 ppm.

2: Anal. $C_{10}H_{27}Cl_3N_3O_2PSi_2Zr$ (506.07 g mol^{-1}). Found: C, 23.6; H, 5.4; Cl, 20.4; N, 8.1. Calc.: C, 23.7; H, 5.4; Cl, 21.0; N, 8.3%. IR: 2314 (s), 2284 (s), 1267 (m, sh), 1253 (s), 1181 (m), 1130 (m), 1083 (vs), 1018 (vs), 903 (vs), 763 (s), 661 (m), 537 (m), 521 (m), 358 (s) cm^{-1}. MS: *m*/*z* 449 (M–MeCN–Me, 100), 431 (M–MeCN–Cl, 5), 73 (Me_3Si, 55%). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.29 (s, 18H, $(CH_3)_3Si$), 2.27 (s, 3H, CH_3CN), 3.77 (d, $^3J(^1H–^{31}P) = 12.2$ Hz, 6H, CH_3O) ppm. ^{31}P-NMR (101 MHz, $CDCl_3$): δ 16.6 ppm.

*3.2.2. Preparation of $(EtO)_2P(NSiMe_3)_2SnCl_3$ (**4**) $[(EtO)_2P(NSiMe_3)_2]_2SnCl_2$ (**5**), and $(MeO)_2P(NSiMe_3)_2SnCl_3$ (**6**)*

To 2.6 g (10 mmol) $SnCl_4$ were condensed 50 ml CH_2Cl_2 in vacuo at −196°C and then $(EtO)_2P(NSiMe_3)N(SiMe_3)_2$ (**3**) was added, 3.7 g (10 mmol) for **4**, 7.4 g (20 mmol) for **5**, and $(MeO)_2P(NSiMe_3)N(SiMe_3)_2$, 3.4 g for **6**, respectively. After warming to ambient temperature and stirring for 4 h, the volatiles were removed in vacuo leaving white powders of **4**, **5**, and **6** in yields and purities of greater than 85%, as seen from NMR spectra. Purification was achieved by several recrystallizations from MeCN with substantial loss. **4** melts at 116°C, **5** at 157°C, and **6** at 102°C.

4: Anal. $C_{10}H_{28}Cl_3N_2O_2PSi_2Sn$ (520.56 g mol^{-1}). Found: C, 23.9; H, 5.4; Cl, 20.7; N, 5.3; P, 6.2. Calc.: C, 23.1; H, 5.4; Cl, 20.4; N, 5.4; P, 6.0%. IR: 1256 (vs), 1160 (s), 1142 (s), 1099 (vs), 1070 (vs), 1018 (vs), 979 (s), 890 (m), 843 (vs), 759 (s), 721 (m), 688 (s), 661 (s), 620 (m), 543 (m), 525 (m), 496 (m), 451 (m), 349 (s) cm^{-1}. MS: *m*/*z* 520 (M, 5), 505 (M–Me, 100), 485 (M–Cl, 30), 435 (M–Me–2Cl, 42), 193 ($EtO_2PN_2SiMe_3$, 48%). ^{1}H-NMR (250 MHz, CD_3CN): δ 0.22 (s, 18H, $(CH_3)_3Si$), 1.34 (dt, $^3J(^1H–^1H) = 7$ Hz, $^4J(^1H–^{31}P) = 1.2$ Hz, 6H, CH_3C), 4.25 (dq, $^3J(^1H–^1H) \approx {}^3J(^1H–^{31}P) \approx 7$ Hz, 4H, CH_2 ppm. ^{31}P-NMR (162 MHz, CD_3CN): δ 29.7 (s, $^2J(^{31}P–^{117/119}Sn) = 37.3$ Hz) ppm.

5: Anal. $C_{20}H_{56}Cl_2N_4O_4P_2Si_4Sn$ (716.58 g mol^{-1}). Found: C, 30.7; H, 7.1; N, 7.0; P, 8.2; Si, 15.0. Calc.: C, 30.8; H, 7.2; N, 7.2; P, 7.9; Si 14.4%. IR: 1445 (m), 1252 (vs), 1143 (s), 1096 (vs), 1071 (sh), 1028 (vs), 994 (s), 987 (sh), 891 (m), 862 (sh), 846 (s), 789 (m), 762 (m), 689 (sh), 668 (m), 610 (m), 538 (m), 518 (m), 417 (m), 365 (m) cm^{-1}. MS: *m*/*z* 780 (M, 11), 765 (M–Me, 100), 745 (M–Cl, 11), 485 ($(EtO)_2P(NSiMe_3)_2SnCl_2$, 75%). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 0.18 (s, 18H, $(CH_3)_3Si$), 0.27 (s, 18H, $(CH_3)_3Si$), 1.31 (m, 12H, CH_3), 4.03 (m, 2H, CH_2), 4.26 (m, 4H, CH_2), 4.47 (m, 2H, CH_2) ppm. ^{31}P-NMR (162 MHz, $CDCl_3$): δ 26.3 (s, $^2J(^{31}P–^{117/119}Sn) = 40.1$ Hz) ppm.

6: Anal. $C_8H_{24}Cl_3N_2O_2PSi_2Sn$ (492.50 g mol^{-1}). Found: C, 19.6; H, 4.9; Cl, 21.8; N, 5.7; P, 6.1; Si 11.3. Calc.: C, 19.5; H, 4.9; Cl, 21.6; N, 5.7; P, 6.3; Si, 11.4%. IR: 1254 (s), 1182 (s), 1125 (m), 1060 (vs), 1030 (vs, br), 880 (m, br), 846 (s, br), 797 (m), 768 (m), 689 (m), 667 (s), 630 (m), 571 (m), 515 (m), 415 (m), 380 (m), 311 (m) cm^{-1}. MS: *m*/*z* 492 (M, 2.5), 477 (M–Me, 100), 457 (M–Cl, 20), 407 (M–2Cl–Me, 30), 253 ($(MeO)_2PN(SiMe_3)_2$, 30), 237 ($MeOP(NSiMe_3)NHSiMe_3$, 40), 207 ($OPN(SiMe_3)_2$, 25%). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 0.23 (s, 18H, $(CH_3)_3Si$), 3.84 (d, 6H, $^3J(^1H–^{31}P) =$

12.7 Hz, CH_3O) ppm. ^{31}P-NMR (162 MHz, $CDCl_3$): δ 34.0 (s, $^2J(^{31}P–^{117/119}Sn) = 34.0$ Hz) ppm.

3.2.3. Preparation of $Cl_2P(NSiMe_3)_2TiCl_3$ (7)

At −196°C 50 ml $CFCl_3$ were condensed to 2.8 g (10 mmol) $Me_3SiNPN(SiMe_3)_2$ and 0.7 g (10 mmol) Cl_2, preweighed in a separate trap, added. After warming to ca. −80°C the mixture was stirred for 30 min, recooled to −196°C and 1.9 g (10 mmol) $TiCl_4$ condensed. After slow warming to ambient temperature the yellow suspension was stirred for an additional 6 h, volatiles removed in vacuo, and the remaining yellow solid extracted with 50 ml of *n*-hexane. Cooling this solution to −30°C overnight afforded 2.4 g (56%) of bright lemon colored crystals of **7**, m.p. 78°C. An additional but impure crop has been obtained by partial removal of the solvent and recooling.

Anal. $C_6H_{18}Cl_5N_2PSi_2Ti$ (430.51). Found: C, 16.7; H, 4.3; Cl, 41.0; N, 6.4; P, 7.2; Si, 13.1. Calc.: C, 16.7; H, 4.2; Cl, 41.2; N, 6.2; P, 7.2; Si, 13.6%. IR: 1256 (s), 1166 (m), 1131 (vs), 849 (vs), 787 (s), 736 (m), 650 (m), 564 (s), 461 (m), 406 (m), 392 (s) cm^{-1}. MS: *m*/*z* 415 (M–Me, 36), 395 (M–Cl, 8), 380 (M–Cl–Me, 6) 365 (M–Cl–2Me, 12), 93 (Me_2SiCl, 100), 73 (Me_3Si, 60%). ^1H-NMR (250 MHz, $CDCl_3$): 0.42 (d, $^4J(^1H–^{31}P) = 0.3$ Hz) ppm. ^{31}P-NMR (162 MHz, $CDCl_3$): δ 16.2 ppm.

3.2.4. Preparation of $(CF_3CS)_2P(NSiMe_3)N(SiMe_3)_2$ (8)

To 14.3 g (51.5 mmol) $Me_3SiNPN(SiMe_3)_2$ were condensed 150 ml $CFCl_3$ and 11.6 g (51.5 mmol) $(CF_3CS)_2$ in vacuo at 196°C. After stirring at ca. −80°C for 15 min the reaction mixture was warmed to ambient temperature, the solvent removed and the residue sublimed in vacuo at 90°C to leave 23.1 g (89%) of **8** as light-yellow crystals, m.p. 106°C (dec.). Anal. $C_{13}H_{27}F_6N_2PS_2Si_3$ (504.73 g mol^{-1}). Found: C, 30.6; H, 5.4; F, 21.9; N, 5.7; P, 6.8; S, 13.4; Calc.: C, 30.9; H, 5.4; F, 22.6; N, 5.6; P, 7.1; S, 12.7%. IR: 1549 (m), 1457 (s), 1401 (m), 1377 (m), 1333 (vs), 1260 (vs), 1180 (s), 1163 (s), 998 (m), 849 (vs), 774 (m), 678 (m), 585 (m), 507 (m), 494 (m) cm^{-1}. MS: *m*/*z* 504 (M, 15), 489 (M–Me, 100), 485 (M–F, 7), 342 ($(Me_3Si)_3N_2PS_2$, 65), 327 ($Me_8Si_3N_2PS_2$, 85), 73 (Me_3Si, 65%).^1H-NMR (200 MHz, $CDCl_3$): δ 0.01 (d, $^4J(^1H–^{31}P) = 0.1$ Hz, 9H, $(CH_3)_3SiN$), 0.37 (s, 18H, $[(CH_3)_3Si]_2N$) ppm. ^{19}F-NMR (188 MHz, $CDCl_3$): δ −54.89 (d, $^4J(^{19}F–^{31}P) = 1.7$ Hz) ppm. ^{31}P-NMR: (101 MHz, $CDCl_3$) δ −1.7 (sept, $^4J(^{31}P–^{19}F) = 1.7$ Hz) ppm.

3.2.5. Preparation of $(CF_3CS)_2P(NSiMe_3)_2TiCl_3$ (9)

Onto 4.0 g (8 mmol) **8** were condensed, at −196°C in vacuo, 1.5 g (8 mmol) $TiCl_4$. After reaching ambient temperature the greenish–yellow solution was stirred for an additional 8 h, and then volatiles were stripped off. Recrystallization from *n*-hexane afforded yellow crystals of **9** with great substantial loss. Higher yields of **9** have been obtained by slow sublimation at 5×10^{-6} bar and a bath temperature just below 100°C, temperatures greater 100°C resulted in partial decomposition to a tarry black mass. The yield of **9** gained by sublimation was 3.8 g (81%), m.p. 111°C (dec.). Anal. $C_{10}H_{18}Cl_3F_6N_2PS_2Si_2Ti$ (585.78). Found: C, 20.4; H, 3.2; Cl, 18.6; F, 19.0; N, 4.8; P, 5.1. Calc.: C, 20.5; H, 3.1; Cl, 18.2; F, 19.5; N, 4.8; P, 5.3%. IR: 1572 (s), 1333 (m), 1260 (vs), 1180 (vs), 1132 (sh), 1093 (vs), 849 (vs), 788 (s), 735 (m), 718 (m), 697 (m), 649 (m), 593 (m), 524 (m), 455 (m), 415 (s), 381 (s), 347 (m) cm^{-1}. MS: *m*/*z* 571 (M–Me, 95), 553 (M–Cl–Me + F, 55), 77 (Me_2SiF, 100), 73 (Me_3Si, 50%). ^1H-NMR (200 MHz, $CDCl_3$): δ 0.41 (d, $^4J(^1H–^{31}P) = 0.37$ Hz) ppm. ^{19}F-NMR (188 MHz, $CDCl_3$): δ −54.43 (d, $^4J(^{19}F–^{31}P) = 2.1$ Hz) ppm. ^{31}P-NMR (101 MHz, $CDCl_3$): δ 50.2 (s, br) ppm.

3.2.6. Preparation of $[(CF_3CS)_2P(NSiMe_3)_2]_2TiCl_2$ (10)

A total of 1.1 g (5.8 mmol) $TiCl_4$ were condensed in vacuo at −196°C to a mixture of 5.8 g (11.5 mmol) **8** and 60 ml MeCN. The mixture was rapidly warmed to ambient temperature, stirred for 30 min, and then heated to 60°C for 5 h. After removal of volatiles the violet solid was redissolved in MeCN, decanted from some tarry residue, and stored at −15°C for crystallization leaving **10** as orange plates, m.p. 158°C (dec.). An additional crop has been obtained by reducing the solvent, the total yield was 2.5 g (44%). The remainder contained impurities of **8** and **9**. Anal. $C_{20}H_{36}Cl_2F_{12}N_4P_2S_4Si_4Ti$ (981.85). Found C, 24.5; H, 3.6; Cl, 7.8; F, 22.9; N, 5.7; P, 7.0. Calc.: C, 24.4; H, 3.7; Cl, 7.2; F, 23.2; N, 5.7; P, 6.3%. IR: 1570 (s), 1260 (vs), 1180 (vs), 1134 (m), 1099 (s), 913 (m), 848 (vs), 780 (s), 718 (m), 649 (m), 590 (m), 512 (m), 379 (m), 349 (m) cm^{-1}. MS: *m*/*z* 982 (M, 4), 967 (M–Me, 100), 945 (M–Cl, 30) 930 (M–Cl–Me, 10) 549 ($(CF_3CS)_2P(NSiMe_3)_2TiCl_2$, 60), 77 ($Me_2SiF$, 16), 73 ($Me_3Si$, 100%). ^1H-NMR (200 MHz, $CDCl_3$): δ 0.27 (s, 18H, $(CH_3)_3Si$)), 0.42 (s, 18H, $(CH_3)_3Si$) ppm. ^{19}F-NMR (188 MHz, $CDCl_3$): δ −54.47 (m, A_3B_3X-system, $^5J(^{19}F_A–^{19}F_B) \approx 12$ Hz, $^4J(^{19}F–^{31}P) \approx 2$ Hz) ppm. ^{31}P-NMR (162 MHz, $CDCl_3$): δ 47.7 (s, br) ppm.

3.2.7. Preparation of $Cl_3C(Cl)P(NSiMe_3)_2TiCl_3$ (11)

A total of 2.8 g (10 mmol) $Me_3SiNPN(SiMe_3)_2$ were added, at −20°C via syringe, to 50 ml CCl_4 and stirred for 1 h. Subsequently, 1.9 g (10 mmol) $TiCl_4$ were added dropwise with stirring. After complete addition the solution was warmed to r.t., stirred for 6 h, and then stored at +4°C for 48 h. Yellow crystals of **11** (2.6 g, 51%) had formed, which were filtered off and dried in vacuo, m.p. 165°C. An additional crop was obtained by partial evaporation of the solvent. Anal. $C_7H_{18}Cl_7N_2PSi_2Ti$ (513.42). Found: C, 16.3; H, 3.6; Cl, 47.6; N, 5.4; Ti, 8.8. Calc.: C, 16.4; H, 3.5; Cl, 48.3; N,

Table 3
Crystal data for **1**, **2**, **5**, **9**, and **11**

Compound	**1**	**2**	**5**	**9**	**11**
Formula	$C_{10}H_{27}Cl_3N_3O_2PSi_2Ti$	$C_{10}H_{27}Cl_3N_3O_2PSi_2Zr$	$C_{20}H_{56}Cl_2N_4O_4P_2Si_4Sn$	$C_{10}H_{18}Cl_3F_6N_2PS_2Si_2Ti$	$C_7H_{18}C_{17}N_2PSi_2Ti$
Molecular weight	462.75	506.07	780.58	585.78	513.42
Temperature (K)	153(2)	150(2)	213(2)	133(2)	293(2)
Crystal size (mm^3)	0.90 × 0.30 × 0.20	1.00 × 0.90 × 0.80	0.90 × 0.50 × 0.40	0.50 × 0.50 × 0.10	0.40 × 0.50 × 0.60
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Triclinic	Monoclinic
Space group	*Pbca*	*Pbca*	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a (Å)	16.751(9)	17.026(2)	10.0010(10)	16.608(3)	13.990(2)
b (Å)	14.790(11)	14.885(3)	24.139(5)	20.114(4)	11.520(2)
c (Å)	18.098(12)	18.293(3)	16.2450(10)	23.536(5)	14.821(3)
α (°)	90	90	90	90.16(3)	90
β (°)	90	90	100.320(10)	90.56(3)	115.470(10)
γ (°)	90	90	90	110.94(3)	90
V (Å^3)	4484(5)	4636.0(13)	3858.3(9)	7342(3)	2156.5(7)
Z	8	8	4	12	4
$D_{calc.}$ (g cm^{-3})	1.371	1.450	1.344	1.590	1.581
μ (mm^{-1})	0.924	0.999	1.037	1.056	1.441
F (000)	1920	2064	1624	3528	1032
θ range (°)	3.56–24.98	3.53–25.05	3.59–22.55	2.04–25.87	4.01-22.49
Reflections collected	9971	5505	9304	47186	8264
Independent reflections	3900	4080	5065	24332	2798
Data/restraints/parameters	3893/0/208	4078/0/208	5058/0/351	24332/0/1495	2798/0/205
Goodness-of-fit on F^2	1.061	1.081	1.056	1.065	1.031
R_1 [$I>2\sigma(I)$]	0.0440	0.0361	0.0281	0.1052	0.0482
R_1 (all data)	0.0698	0.0476	0.0302	0.1604	0.0706
wR_2 (all data)	0.1184	0.0935	0.0773	0.2981	0.1325
Largest difference peak and hole (e A^{-3})	0.390 and −0.381	0.744 and −0.433	0.709 and −0.553	1.264 and −0.753	0.530 and −0.355

5.4; Ti, 9.3%. IR: 1257 (s), 1143 (s), 1123 (s), 848 (vs), 777 (s), 643 (m), 629 (m), 559 (s), 496 (m), 458 (m) cm^{-1}. MS: *m*/*z* 497 (M–Me, 11), 93 (Me_2SiCl, 53), 73 (Me_3Si, 100%). ^{1}H-NMR (250 MHz, C_6D_6): δ 0.42 (s) ppm. ^{31}P-NMR (101 MHz, C_6D_6): δ 27.9 ppm.

3.3. X-ray crystallography

Crystals suitable for X-ray determinations of **1**, **2**, and **5** were grown from MeCN solutions at −30°C, of **11** from CCl_4 at +4°C, and of **9** from *n*-hexane at −5°C. Relevant crystallographic data for the compounds are listed in Table 3. The data for **1**, **2**, **5**, and **11** were collected on a Stoe–Siemens four-circle diffractometer, those of **9** on a Stoe–Siemens–Huber four-circle diffractometer with a Bruker CCD area detector with graphite monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å) at the temperature given in Table 3. The data collection of **9** was achieved by φ-scans with an increment width of 0.5°, integration of the data was performed with SAINT V 5.00 [28], for correction of the reflection intensities the program SADABS [29] was used, and for determination of the space group and the preparation of the data the program XPREP [30] was employed. The structures were solved by direct methods with SHELXS-90 [31] and refined by full-matrix least-squares on F^2 using SHELXL-93 [32] or SHELXL-97 [33] in the case of **9**. Apparently, a phase transition occurred during the data collection for **9**, thus accounting for the rather high *R* values. Hydrogen atoms were located geometrically and refined using a riding model. Absorption corrections by azimuthal scans were applied using a semiempirical method [34].

4. Supplementary material

Tables of fractional coordinates and equivalent isotropic displacement parameters and a complete list of bond lengths have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 120184 (**1**), 120185 (**2**), 120186 (**5**), 120187 (**9**), 120188 (**11**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Selected bond parameters of the compounds are listed in Table 2.

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