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Tellurium complexes with new, large-bite dithio ligands. The crystal structures of *cis*- and *trans*- $[Te\{Ph_2P(S)–N–P(S)(OPh)_2\}_2]$ and $[(4\text{-}MeOC_6H_4TeCl_3)_2\{\mu\text{-}{}^iPr_2P(S)–Fc–P(S){}^iPr_2\}]$

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Abstract

Reaction of the protonated large-bite bidentate ligand $Ph_2P(S)–NH–P(S)(OPh)_2$ with $[Te\{NH_2)_2CS\}_4]Cl_2$ resulted in the complex $[Te(L–L)_2]$, (**1a**), where $(L–L)^- = Ph_2P(S)–N–P(S)(OPh)_2$. When $(L–L)^-$ reacted with $4\text{-}MeOC_6H_4TeCl_3$, an isomeric complex, **1b**, resulted. Reaction between the less basic ligand ${}^iPr_2P(S)–Fc–P(S){}^iPr_2$ (Fc = ferrocene) and $4\text{-}MeOC_6H_4TeCl_3$ yielded the complex $[(4\text{-}MeOC_6H_4TeCl_3)_2\ \{\mu\text{-}{}^iPr_2P(S)–Fc–P(S){}^iPr_2\}]$, (**2**). X-ray crystallographic studies show that **1a** and **1b** both are square planar complexes of Te(II), **1a** being asymmetric and '*cis*' with two short Te–S bonds *trans* to two long Te–S bonds (average bond lengths being 2.5415 and 2.9050 Å). Isomer **1b** is centrosymmetric, '*trans*', with nearly equal Te–S bond lengths averaging 2.6805 Å. Complex **2** is an addition compound where the large dithio ligand bridges two $4\text{-}MeOC_6H_4TeCl_3$ units through weak Te–S bonds. The resulting coordination around each Te(IV) atom is ψ-octahedral with the lone pair of electrons and aryl in axial positions relative to the $TeCl_3S$ equatorial plane. Here the Te–S bond lengths are 2.7560(16) and 2.6910(12) Å. The *trans* influence of the dithio ligand in **2** is smaller than that of Cl^-, resulting in an average Te–Cl bond length *trans* to sulfur of only 2.4196 Å, while the other Te–Cl bond lengths average 2.4959 Å. The reason for the lower basic nature of the ligand with a P–Fc–P backbone compared to those with P–N–P backbones, is that it lacks a central charge donating group like $\ddot{N}^{-}$. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Tellurium(II) and (IV) complexes; New dithio ligands; Crystal structures

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1. Introduction

The coordination of the flexible, large-bite ligand $[Ph_2P(E)–N–P(E)Ph_2]^-$ (E = S, Se) with Te(II) mostly results in square planar complexes with a TeE_4 coordination sphere. The two Te(II) complexes with E = S and Se [1,2] respectively, are isomorphous with the square planar complexes of divalent Se (E = Se) and Sn (E = Se) [3,4]. So far, the only Te(IV) complex known with this ligand is $[Ph_3Te\{Ph_2P(S)–N–P(S)Ph_2\}]$[5]. Addition of the ligand to $ArTeCl_3$ results in disproportionation and formation of a twelve-membered cyclic dimer, $[TeAr\{Ph_2P(S)–N–P(S)Ph_2\}]_2$ with a T-shaped $TeCS_2$ coordination for each Te(II) atom [2,6]. More recently, analogous ligands with P–N–P backbones of the type $[R_2P(E)–N–P(E')R'_2]^-$ have been prepared with a variety of R groups (aryl, alkyl, aryloxy and alkoxy) and E's (O,S,Se). These ligands may be symmetric (R = R′ and E = E′), or asymmetric (R ≠ R′, E ≠ E′; R ≠ R′, E = E′; R = R′, E ≠ E′) [7–12]. Quite recently, a series of Te complexes with such ligands have been prepared and their structures solved [13,14]. Other, related types of large-bite ligands where the nitrogen atoms of the P–N–P backbone of $[Ph_2P(S)–N–P(S)Ph_2]^-$ have been replaced by $–CH_2–$ or $–CH_2CH_2–$ have been found to react with $TeCl_4$ and $ArTeCl_3$. The reactions are typical addition reactions and result in Te(IV) complexes $[TeCl_4(L–L)]$ and $[(ArTeCl_3]_2\cdot\mu\text{-}(L–L)]$ [13,15]. These ligands have a smaller basicity than those with a P–N–P backbone and form weaker Te–S bonds. To extend our studies on Te

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complexes with large-bite ligands we have prepared ligands of both types above and studied their reactions with selected tellurium compounds.

2. Experimental

2.1. General and instrumental

The ^{31}P-NMR spectra were recorded in CH_2Cl_2 on a Bruker AVANCE DRX 500 instrument using H_3PO_4 (85%) as external standard. IR spectra were recorded on Nujol mulls using a Bruker IFS 28 spectrometer. All reactions were performed under argon in anhydrous conditions. $[Te(tu)_4]Cl_2 \cdot 2H_2O$ (tu = thiourea) and $[4\text{-}MeOC_6H_4TeCl_3]$ were prepared according to literature [16,17].

2.2. $Ph_2P(S)\text{–}NH\text{–}P(S)(OPh)_2$

Synthesized according to literature [18].

2.3. $^iPr_2P(S)\text{–}Fc\text{–}P(S)^iPr_2$

Synthesized according to literature [19].

2.4. Acentric $[Te\{Ph_2P(S)\text{–}N\text{–}P(S)(OPh)_2\}_2]$, (**1a**)

A solution of $[Te(tu)_4]Cl_2 \cdot 2H_2O$ (0.170 g, 0.315 mmol) in MeOH (15 ml) was added to a solution of $Ph_2P(S)\text{–}NH\text{–}P(S)(OPh)_2$ (0.300 g, 0.623 mmol) in MeOH (10 ml) at room temperature. The mixture was stirred for 1 h. The yellow precipitate was collected by filtration and dried in vacuum. Yield: 0.100 g (29%); m.p.: 241–242°C. IR (cm^{-1}): ν_{as}(PNP) 1205sh, 1184s; ν_s(PS) 593m; ν_{as}(PS) 542s. ^{31}P-{^{1}H}-NMR: multiplets 43.39 ppm and 35.43 ppm. *Anal.* Calc. for $C_{48}H_{40}N_2O_4P_4S_4Te$: C, 52.95; H, 3.70; N, 2.57; S, 11.76. Found: C, 53.09; H, 3.81; N, 2.66; S, 12.09%.

2.5. Centric $[Te\{Ph_2P(S)\text{–}N\text{–}P(S)(OPh)_2\}_2]$, (**1b**)

A solution of $4\text{-}MeOC_6H_4TeCl_3$ (0.177 g, 0.519 mmol) in MeOH (8 ml) was added to a solution of $Ph_2P(S)\text{–}NH\text{–}P(S)(OPh)_2$ (0.250 g, 0.519 mmol) and KO^{t}Bu (0.058 g, 0.519 mmol) in MeOH (10 ml). A yellow precipitate appeared after 30 min and the mixture was stirred overnight. The precipitate was collected by filtration and dried in vacuo.

Yield: 0.060 g (21%); m.p.: 214–215°C. IR (cm^{-1}): ν_{as}(PNP) 1200s, 1184s; ν_s(PS) 576m; ν_{as}(PS) 542s. ^{31}P{^{1}H}-NMR: doublets 27.18 ppm and 51.14 ppm, ^2J(P–P) 28.96 Hz. Microanalysis calculated as for **1a**. Found: C, 52.81; H, 3.73; N, 2.71; S, 11.93%.

2.6. $[(4\text{-}MeOC_6H_4TeCl_3)_2\ \{\mu\text{-}^iPr_2P(S)\text{–}Fc\text{–}P(S)^iPr_2\}]$

A saturated solution of $^iPr_2P(S)\text{–}Fc\text{–}P(S)^iPr_2$ (0.200 g, 0.415 mmol) in dichloromethane was added to a solution of $4\text{-}MeOC_6H_4TeCl_3$ (0.290 g, 0.850 mmol) in acetonitrile (15 ml). The resulting mixture was then refluxed for 10 min, and an orange solid formed. After cooling, the precipitate was collected by filtration and dried in vacuo.

Yield: 0.300 g (62%); m.p.: 157–160°C (dec.). IR (cm^{-1}): ν_s (PS) 629m; ν_{as}(PS) 586s, 581s. ^{31}P{^{1}H}-NMR: singlet at 66.56 ppm. Microanalysis calculated for $C_{36}H_{50}Cl_6FeO_2P_2S_2Te_2$: C, 37.12; H, 4.33; S, 5.50. Found: C, 37.28; H, 4.41; S, 5.83%.

2.7. X-ray structure determination

Diffraction data were collected on a KUMA KM-4 κ-axis diffractometer fitted with an area detector. Structures were solved by direct methods and refined by full-matrix least-squares methods using anisotropic thermal parameters for the non-hydrogen atoms. The programs used were: DATPROC9 and KM4RED of the KM-4 software [21] for the data reduction, SHELXS-86 for the structure solutions [22], SHELXL-93 for the structure refinement [23]. Crystallographic data and refinement parameters are given in Table 1.

3. Results and discussion

3.1. Synthesis

The two isomers of $[Te\{Ph_2P(S)\text{–}N\text{–}P(S)(OPh)_2\}_2]$, (**1a**) (acentric) and (**1b**) (centrosymmetric) were made by different procedures. **1a** was made by a displacement of the thiourea ligands in the complex $[Te(tu)_4]Cl_2 \cdot 2H_2O$ by the protonated form of the ligand $Ph_2P(S)\text{–}NH\text{–}P(S)(OPh)_2$, which was deprotonated in the process. The centrosymmetric complex, **1b,** was a quite unexpected product resulting from addition of the anionic form of the ligand to $4\text{-}MeOC_6H_4TeCl_3$. Normally, aryl ligands are hard to remove because of the strong Te–C bond. Nevertheless, the only explanation for the resulting product is that all four monodentate groups also here are displaced by the large dithiolate ligands in a process involving disproportionation resulting in reduction of Te(IV) to Te(II). Displacement of an aryl group bonded to tellurium has been observed before in our labs [20]. The complex $[(4\text{-}MeOC_6H_4TeCl_3)_2\{\mu\text{-}^iPrP(S)\text{–}F_c\text{–}P(S)^iPr_2\}]$, (**2**), was the result of a simple addition reaction between two $4\text{-}MeOC_6H_4TeCl_3$ molecules and the large-bite dithio ligand.

3.2. Crystal structures

The structures of **1a** and **1b** are shown in Fig. 1. Both complexes are square planar complexes [$Te^{II}L_2$], where $L = Ph_2P(S)–N–P(S)(OPh)_2^-$. L is bidentate, forming six-membered chelate rings, TeS_2P_2N, in both complexes. The two lone pairs of electrons on tellurium are located above and below the coordination planes. The acentric or *cis* isomer **1a** is more distorted compared to its centrosymmetric, *trans* isomer, **1b**. In **1a** the greatest deviation from planarity in the coordination plane, is 0.148 Å, the maximum difference in Te–S bond lengths is 0.406 Å, compared to absolute planarity and a maximum Te–S bond length difference of only 0.009 Å in **1b**. Furthermore the chelate rings of **1a** have different conformations, the Te(1) to N(1) ring having the chair form while the Te(1) to N(2) ring has the boat form. In **1b**, the rings are required by symmetry to have the same form, which is the chair form, the most common form in chelate complexes with such ligands.

The structure of **2**, shown in Fig. 2, is similar to the structure of [$(4\text{-}MeOC_6H_4TeCl_3)_2\{\mu\text{-}Ph_2P(S)–CH_2CH_2–P(S)Ph_2\}$] [13]. Thus the neutral, potentially bidentate ligand, $^iPr_2P(S)–Fc–P(S)^iPr_2$, acts as a bridge between two $4\text{-}MeOC_6H_4TeCl_3$ groups, its two sulfur atoms attaching to two different Te(IV) atoms. Both tellurium atoms have ψ-octahedral coordination with the aryl group and the lone pair of electrons in axial positions relative to the $TeCl_3S$ equatorial plane. The eclipsed ferrocene moiety in the center of the molecule is connected to the two $^iPr_2P(S)$ groups of the ligand in a 'trans' fashion, where each group is connected to a different cyclopentadienyl ring (Fig. 2).

3.3. Tellurium-ligand bonding

The Te–S bonds are quite asymmetric in **1a**, there are two long bonds [Te(1)–S(1) = 2.8728(8) and Te(1)–S(3) = 2.9372(12) Å] *trans* to two short bonds [Te(1)–S(4) = 2.5311(8) and Te(1)–S(2) = 2.5520(10) Å]. Also the coordination angles differ, $<S(1)–Te(1)–S(3) \approx <S(2)–Te(1)–S(4) \approx 95°$ while $<S(1)–Te(1)–S(2) \approx <S(3)–Te(1)–S(4) \approx 85°$.

Table 1
Crystal data and refinement parameters for complexes **1a**, **1b** and **2**

Complex	**1a**	**1b**	**2**
Empirical formula	$C_{48}H_{40}N_2O_4P_4S_4Te$	$C_{48}H_{40}N_2O_4P_4S_4Te$	$C_{36}H_{50}C_{16}FeO_2P_2S_2Te_2$
Formula weight	1088.54	1088.54	1164.57
Temperature (K)	130(2)	120(2)	130(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	Triclinic, $P1$	Triclinic, $P1$	Triclinic, $P1$
Unit cell dimensions			
a (Å)	10.575(2)	10.878(2)	10.511(2)
b (Å)	12.787(3)	10.955(2)	14.855(3)
c (Å)	19.796(4)	11.336(2)	16.135(3)
α (°)	71.48(3)	107.55(3)	63.25(3)
β (°)	76.87(3)	106.96(3)	79.63(3)
γ (°)	69.55(3)	96.71(3)	81.66(3)
V (Å^3)	2357.9(9)	1200.5(4)	2207.1(7)
Z	2	1	2
D_{calc} (g cm^{-3})	1.533	1.506	1.752
Absorption coefficient (mm^{-1})	0.990	0.972	2.199
F (000)	1100	550	1152
Crystal size (mm)	0.50 × 0.50 × 0.20	0.40 × 0.40 × 0.05	0.20 × 0.20 × 0.10
Theta range for data collection (°)	3.41–29.31	3.30–28.43	3.25–28.59
Index ranges	$-13 \leqslant h \leqslant 13$, $-16 \leqslant k \leqslant 17$, $-26 \leqslant l \leqslant 10$	$-14 \leqslant h \leqslant 14$, $-14 \leqslant k \leqslant 14$, $-14 \leqslant l \leqslant 15$	$-14 \leqslant h \leqslant 6$, $-19 \leqslant k \leqslant 19$, $-21 \leqslant l \leqslant 21$
Reflections collected/unique	11773/8948 [R(int) = 0.0197]	8394/5248 [R(int) = 0.0438]	14403/9622 [R(int) = 0.0436]
Completeness to 2 theta = 25.00 (%)	82.4	97.0	96.3
Max/min transmission	0.8265, 0.6373	0.9530, 0.6971	0.8100, 0.6674
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	8948/0/728	5248/0/286	9622/0/470
Goodness-of-fit on F^2	1.069	1.188	1.041
Final R indices [$I > \sigma(I)$]	$R_1 = 0.0312$, $wR_2 = 0.0816$	$R_1 = 0.0532$, $wR_2 = 0.1468$	$R_1 = 0.0383$, $wR_2 = 0.1018$
R indices (all data)	$R_1 = 0.0337$, $wR_2 = 0.0830$	$R_1 = 0.0694$, $wR_2 = 0.1542$	$R_1 = 0.0547$, $wR_2 = 0.1052$
Largest diff. peak and hole (e Å^{-3})	1.027 and −1.846	1.264 and −1.224	0.963 and −0.798

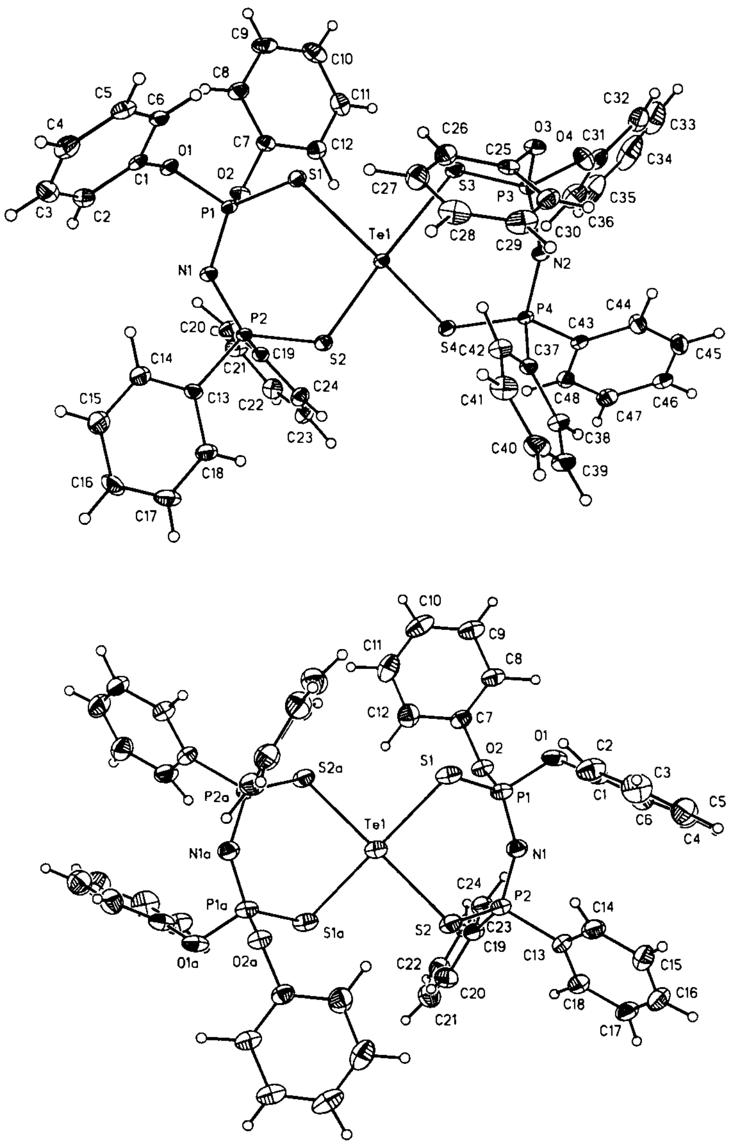

Fig. 1. The molecular structures of **1a** (top) and **1b** (bottom). Anisotropic displacement parameters are drawn at the 50% probability level.

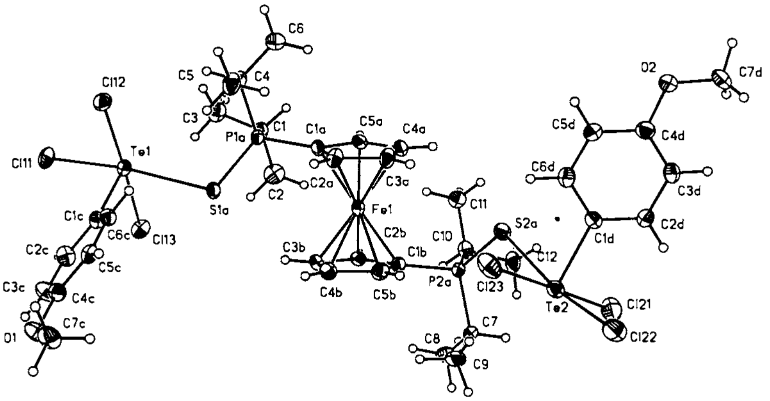

Fig. 2. The molecular structure of **2**. Anisotropic displacement parameters are drawn at the 50% probability level.

A similar asymmetry in Te–S bonding is found in [Te{Et$_2$P(S)–N–P(S)(OPh)$_2$}$_2$] where the long bonds are close to 2.91 Å and the short ones are close to 2.52 Å [14]. This difference in bonding was therein explained as being a result of the difference in electronic properties of the substituents on the phosphorus atoms connected to sulfur. In both complexes, the (PhO)$_2$P(S) part of the ligand forms the longer (weaker) Te–S bonds. The average Te–S bond length is 2.723 Å in **1a**, nearly the same as in the similar complex above. Subtracting the covalent radius of 1.04 Å for sulfur gives a radius for Te(II) of 1.68 Å. This may be compared to 1.64 Å found for most square-planar Te(II) complexes with monodentate ligands and for asymmetric complexes with bidentate small bite ligands like dialkyldithiocarbamates and alkylxanthates [24]. A radius of 1.64 Å usually corresponds to symmetric, linear 3-center, four-electron bonding based on overlap between a 5p orbital on tellurium and suitable orbitals on two ligands. In a square planar complex, there are two such systems at right angles to each other. It is also found that the apparent Te(II) radius increases with increasing asymmetry in such systems [24].

Table 2
Selected bond lengths (Å) and angles (°) for **1a** and **1b**

	1a	**1b**
Bond lengths		
Te(1)–S(1)	2.8728(8)	2.6759(16)
Te(1)–S(2)	2.5520(10)	2.6851(12)
Te(1)–S(3)	2.9372(12)	
Te(1)–S(4)	2.5311(8)	
P(1)–S(1)	1.9719(10)	2.0061(16)
P(2)–S(2)	2.0554(10)	2.0134(16)
P(3)–S(3)	1.9736(10)	
P(4)–S(4)	2.0604(10)	
P(1)–N(1)	1.5744(19)	1.554(3)
P(2)–N(1)	1.5793(19)	1.585(4)
P(3)–N(2)	1.5665(19)	
P(4)–N(2)	1.5795(19)	
P(1)–O(1)	1.6000(19)	1.596(3)
P(1)–O(2)	1.5992(16)	1.590(3)
P(3)–O(3)	1.6092(17)	
P(3)–O(4)	1.590(2)	
P(2)–C(13)	1.806(2)	1.809(4)
P(2)–C(19)	1.804(2)	1.809(4)
P(4)–C(37)	1.804(2)	
P(4)–C(43)	1.798(2)	
Bond angles		
S(1)–Te(1)–S(2)	85.30(3)	87.11(4)
S(1)–Te(1)–S(2a)		92.89(4)
S(1)–Te(1)–S(3)	95.08(3)	
S(2)–Te(1)–S(4)	95.53(3)	
S(3)–Te(1)–S(4)	84.61(3)	
S(1)–Te(1)–S(4)	175.65(2)	
S(2)–Te(1)–S(3)	173.08(2)	
Te(1)–S(1)–P(1)	94.19(4)	97.85(6)
Te(1)–S(2)–P(2)	98.52(4)	97.03(6)
Te(1)–S(3)–P(3)	94.95(4)	
Te(1)–S(4)–P(4)	98.40(4)	
S(1)–P(1)–N(1)	119.11(8)	120.48(15)
S(2)–P(2)–N(1)	118.17(8)	118.23(14)
S(3)–P(3)–N(2)	118.83(8)	
S(4)–P(4)–N(2)	117.52(8)	
P(1)–N(1)–P(2)	133.75(14)	141.4(2)
P(3)–N(2)–P(4)	140.77(12)	
P(1)–O(1)–C(1)	121.52(13)	120.4(3)
P(1)–O(2)–C(7)	124.02(13)	123.0(3)
P(3)–O(3)–C(25)	120.25(13)	
P(3)–O(4)–C(31)	129.27(16)	
O(1)–P(1)–O(2)	99.06(9)	100.57(16)
O(3)–P(3)–O(4)	93.47(9)	

Complex **1b** is centrosymmetric with nearly identical Te–S bond lengths [Te(1)–S(1) = 2.6759(16) and Te(1)–S(2) = 2.6851(12) Å] averaging 2.681 Å, corresponding to a normal Te(II) radius of 1.64 Å. Here, the bidentate ligands are identical to those of **1a**, with identical thiol groups *trans* to each other in each of the two 3-center 4-electron S–Te–S systems in **1b**, the Te–S bond lengths are all expected to be close to 2.68 Å [24].

For **2**, a complex of Te(IV), the tellurium-ligand bonding is more complex. The Te–C bonds are nearly identical, averaging 2.111 Å which is normal for such a bond [25]. The Te–S bond lengths differ by 0.065 Å being Te(1)–S(1) = 2.7560(16) and Te(2)–S(2) = 2.6910(13) Å. These sulfur atoms are *trans* to Cl$^-$ ligands, the corresponding Te–Cl bond lengths are Te(1)–Cl(11) = 2.4215(15) and Te(2)–Cl(22) = 2.4176(13) Å. The remaining Te–Cl bonds are pairwise *trans* to each other with an average length of 2.496 Å, close to the lower quartile of Te–Cl bonds [25]. That the Te–Cl bonds *trans* to sulfur are significantly shorter than the other Te–Cl bonds is due to the *trans* influence. Since the large dithio ligand is neutral and lacks a central electron donating group like the ligand in **1a** and **1b**, it is a weak donor with a smaller trans influence than Cl$^-$. This is comparable to what is found in the analogous complex, [(4-MeOC$_6$H$_4$TeCl$_3$)$_2${μ-Ph$_2$P(S)–CH$_2$CH$_2$–P(S)Ph$_2$}] [13]. There the central part of the ligand is –CH$_2$CH$_2$– instead of Fc in **2**. The average Te–Cl bond length *trans* to S is 2.432 Å while the average Te–S bond length is 2.797 Å. A similar relation is found in the octahedral complex, [TeCl$_4${Ph$_2$P(S)–CH$_2$–P(S)Ph$_2$}] [15]. Comparison with the Te(IV) complexes [4-MeOC$_6$H$_4$TeCl$_2${^{i}Pr$_2$P(S)–N–P(S)^{i}Pr$_2$}] and [4-MeOC$_6$H$_4$TeCl$_2${^{i}Pr$_2$P(S)–N–P(S)Ph$_2$}] shows that in these two complexes, the large bidentate dithio ligand is a stronger base than the corresponding ligand in **2** [14]. The two complexes both have a ψ-octahedral coordination sphere like in **2** with the aryl ligand and the lone pair of electrons in axial positions relative to an equatorial TeCl$_2$S$_2$ plane where each S atom is *trans* to a Cl atom. The average Te–S bond length in these complexes is ca. 0.1 Å shorter and the average Te–Cl bond length ca. 0.1 Å longer than the corresponding bond lengths found in **2**. Selected bond lengths and angles are given in Tables 2 and 3.

Table 3
Selected bond lengths (Å) and angles (°) for **2**

Bond lengths	
Te(1)–S(1a)	2.7560(16)
Te(1)–Cl(11)	2.4215(15)
Te(1)–Cl(12)	2.4995(13)
Te(1)–Cl(13)	2.4863(13)
Te(1)–C(1c)	2.109(4)
Te(2)–S(2a)	2.6910(12)
Te(2)–Cl(21)	2.4521(15)
Te(2)–Cl(22)	2.4176(13)
Te(2)–Cl(23)	2.5457(15)
Te(2)–C(1d)	2.112(4)
P(1a)–S(1a)	2.0062(17)
P(2a)–S(2a)	1.9994(16)
P(1a)–C(1a)	1.768(4)
P(2a)–C(5b)	1.771(4)
P–C(^{i}Pr, ave)	1.818(13)
C–C(Fc, ave)	1.415(19)
C–Fe(Fc, ave)	2.037(17)
Bond angles	
S(1a)–Te(1)–Cl(11)	173.57(4)
S(1a)–Te(1)–Cl(12)	94.90(4)
S(1a)–Te(1)–Cl(13)	87.25(4)
S(1a)–Te(1)–C(1c)	82.91(11)
Cl(11)–Te(1)–Cl(12)	89.41(5)
Cl(11)–Te(1)–Cl(13)	88.39(4)
Cl(12)–Te(1)–Cl(13)	177.72(4)
Cl(12)–Te(1)–C(1c)	89.76(12)
S(2a)–Te(2)–Cl(21)	91.09(6)
S(2a)–Te(2)–Cl(22)	169.14(4)
S(2a)–Te(2)–Cl(23)	86.25(5)
S(2a)–Te(2)–C(1d)	80.04(12)
Cl(21)–Te(2)–Cl(22)	91.21(6)
Cl(21)–Te(2)–Cl(23)	177.00(5)
Cl(21)–Te(2)–C(1d)	90.97(13)
Cl(22)–Te(2)–Cl(23)	91.66(6)
Te(1)–S(1a)–P(1a)	105.69(6)
S(1a)–P(1a)–C(1a)	110.30(15)
Te(2)–S(2)–P(2)	111.69(6)
S(2)–P(2a)–C(10a)	110.54(16)
C(1a)–Fe–C(5b)	165.46(18)

3.4. Bonding in the ligands

In **1a**, the asymmetry in the Te–S bonds is reflected in the P–S bonds. To the weak Te–S bonds, there correspond strong P–S bonds and vice versa. The strong P–S bonds [P(1)–S(1), P(3)–S(3)] have an average bond length of 1.973 Å, somewhat longer than a double bond [1.913(14) Å] [26]. It may also be compared to 1.965 Å, the average in the similar asymmetric complex with a $Et_2P(S)–N–P(S)(OPh)_2^-$ dithio ligand [14]. The weak P–S bonds have an average bond length of 2.058 Å, close to the value of 2.050 Å found in the other asymmetric complex [14]. The P–N bonds are, however, quite similar ranging from 1.5665(19) to 1.5795(19) Å. This is a normal range for such ligands and indicates some double bond character related to the delocalization of the negative charge on nitrogen towards the sulfur atoms, especially those more strongly bonding to tellurium [13]. The P–N–P angles are different, 133.75(14)° for P(1)–N(1)–P(2) and 140.77(12)° for P(3)–N(2)–P(4), but both are within the normal range for such flexible ligands [13].

In **1b**, the dithio ligands are approximately symmetrically bonded to the central tellurium atom, consequently the P–S and P–N bonds are similar. The average bond lengths are 2.010 and 1.570 Å, respectively. These values are close to the average values found in **1a**. The P–N–P angle is large. The observed value, 141.4(2)° is at the upper end of the range for such ligands in complexes [13].

The dithio ligand in **2** has two $^i\mathrm{Pr}_2\mathrm{P(S)}$ groups connected through P–C bonds via a disubstituted ferrocene (Fig. 2). There is no through-conjugation involving electron donating groups connecting the sulfur atoms like in **1a** and **1b**. Also this ligand is neutral. It is so weakly basic that it adds to the $4\text{-MeOC}_6H_4TeCl_3$ molecules instead of displacing any Cl^- ligands. This is reflected in the weak Te–S bonding and the medium strong P–S bonds [P(1a)–S(1a) = 2.0062(17) and P(2a)–S(2a) = 1.9994(16) Å]. This is a bit shorter than the corresponding average bond lengths in **1a** and **b**, but very close to the P–S bond length in the similar complex with the ligand $Ph_2P(S)–CH_2CH_2–P(S)Ph_2$, where the average value is 2.000 Å [13]. The higher frequency for the P–S stretch in **2** as compared to **1a** and **b** supports this. The bond lengths and angles of the eclipsed Fc group are normal. The average Fe–C bond length of 2.037(17) Å is close to the lower quartile of the average for such bonds (2.052 Å), the average C–C bond length of 1.415(19) Å is equal to the upper quartile (1.415 Å) for these bonds [26].

For all thio ligands in the three complexes, the P–C, P–O and C–C bonds are quite normal. The same holds for the C–C and C–O bonds in the aryl ligands of **2**.

3.5. Packing

There are no especially short intermolecular contacts in the complexes **1a** and **1b**, but the asymmetry in the Te–S bonds (being of the 3-center 4-electron type with average bond order only $\approx 1/2$) is probably partly due to packing effects. In **2** there are intermolecular contacts C–H···Cl [Cl(23)–H(6b) $(x+1, y, z) = 2.77(5)$ Å, and H(3d1)–Cl(12) $(x-1, y-1, z+1) = 2.88(6)$ Å. H(6b) is bonded to C(6)/(^{i}Pr) and H(3d1) is bonded to C(3d)/(Ph)]. This indicates weak Cl···H–C hydrogen bonding connecting the molecules of **2** into a three-dimensional network in the solid state.

4. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre (CCDC) CCDC no. 147427-147429. Copies of data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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