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The carbodiphosphorane–CS_2 adduct as a complex ligand: Crystallographic characterization of $[I_2Pt\{S_2CC(PPh_3)_2\}]\cdot CH_2Cl_2$, $[Pt\{S_2CC(PPh_3)_2\}_2][SiF_5]_2\cdot 2CH_2Cl_2$ and $[(Me)_2PtFI\{S_2CC(PPh_3)_2\}]\cdot 2CH_2Cl_2$

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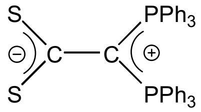
A B S T R A C T

The betain-like compound $S_2CC(PPh_3)_2$ (**1**), which is obtained from CS_2 and the double ylide $C(PPh_3)_2$, reacts with $[X_2Pt(COD)]$ (X = Cl, I) in THF to afford the complexes $[X_2Pt\{S_2CC(PPh_3)_2\}]$ (**2**, X = Cl; **3**, X = I) in quantitative yields. Both compounds are insoluble in all usual solvents, and **3** could be characterized by an X-ray analysis. For comparison, the structures of $[Pt(Me)_2FI\{S_2CC(PPh_3)_2\}]\cdot 2CH_2Cl_2$ ($\mathbf{4}\cdot 2CH_2Cl_2$) with Pt^{IV} and $[Pt\{S_2CC(PPh_3)_2\}_2][SiF_5]_2\cdot 2CH_2Cl_2$ ($\mathbf{5}\cdot 2CH_2Cl_2$) with Pt^{II} are also presented. The compounds are further characterized by ^{31}P NMR and IR spectroscopy.

1. Introduction

The Lewis acid CS_2 and the carbodiphosphorane $C(PPh_3)_2$ quantitatively form the yellow addition compound $S_2CC(PPh_3)_2$ (**1**), which has been known for many years [1]. In addition to **1**, further adducts with Lewis acids containing main group [2] or transition metal elements [3] were also described. Recently, we have studied the crystal structure of **1** and its ability as a possible complex ligand.



1

Thus, in $[M(CO)_6]$ (M = Cr, Mo, W) two carbonyl groups can be replaced to produce the corresponding $[(CO)_4M\{S_2CC(PPh_3)_2\}]$ complexes, in which **1** acts as a chelating ligand via the two sulfur atoms [4]. The same is true for cationic manganese and cobalt complexes [5]. An alternative coordination mode of **1** was found upon reaction with silver salts containing weakly coordinating anions; Ag_6^{6+} or Ag_4^{4+} clusters are held together by six or four molecules of **1**, respectively, and each S atom contacts up to two Ag atoms [6]. The $S_2C–CP_2$ bond length in **1** is shorter than a single bond and further shortening occurs upon complex formation, indicating an increase of bond strength. Calculations have shown that in **1** some π interaction exists between the occupied p orbital of the P_2C sp^2 carbon atom and the empty p orbital of the S_2C sp^2 carbon atom [4]. In this publication, we present the results of the reaction of **1** with some platinum complexes.

2. Results and discussion

Reactions of **1** turned out to be highly problematic because **1** is only slightly soluble in THF and insoluble in the usual non-polar solvents, and it decomposes at elevated temperatures or upon prolonged reaction time to give $SPPh_3$ and the heterocummulene $S{=}C{=}C{=}PPh_3$ [7]. Compound **1** is soluble in CH_2Cl_2 (^{31}P NMR in CH_2Cl_2: 17.11 ppm), but decomposition proceeds more rapidly in this solvent. However, in some cases the reaction products are soluble in THF, which allows sufficient characterization [4].

If a suspension of **1** in THF is treated with the platinum complexes $[X_2Pt(cod)]$ (X = Cl, I) reaction immediately occurs to produce red-brown precipitates of **2** and **3**, respectively, with release of COD. Both products are obtained in about quantitative yields according to the following equation:

$$[X_2Pt(COD)] + S_2CC(PPh_3)_2 \rightarrow [X_2Pt\{S_2CC(PPh_3)_2\}] + COD \qquad (1)$$

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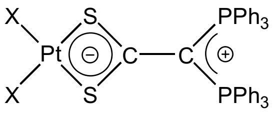

2 (X = Cl), **3** (X = I)

The new platinum complexes **2** and **3** are found to be insoluble in all common solvents including THF and CH_2Cl_2, but are slightly soluble in DMSO. If amorphous **3** from THF is kept in contact with CH_2Cl_2 a kind of mineralization proceeds and the precipitate takes up dichloromethane and is converted into small red crystals. However, the overstanding solution shows no signal in the ^{31}P NMR spectrum confirming the insolubility in this solvent. Unfortunately, no crystals of **2** could be obtained via this way. In the ^{31}P NMR spectra in DMSO singlets at 14.6 ppm (for **2**) and 14.0 ppm (for **3**) were recorded. The solid state IR spectra of **2** and **3** are very similar and contain the same number of bands, which indicate analogous structural properties. Strong absorptions at about 1049 and 1095 cm^{-1} were recorded, which can be assigned to the ν_{as} and ν_s CS_2 vibrations [8]. The related bands in **1** were found at 1067 and 1099 cm^{-1}. A strong band at 1250 cm^{-1} in both compounds can probably be attributed to the vibration of the $S_2C–CP_2$ bond of the ligand. According to the occupied p orbital at the P_2C carbon atom and the vacant p orbital at the S_2C carbon atom, additional to the σ donor bond a weak and polarized π-interaction is operative [4]. The related band in **1** is found at 1146 cm^{-1} and the shift to higher frequencies upon complex formation can be explained with an increase of the C–C double bond character, which is also expressed in a shorter C–C bond length in **3**.

Additionally, we present the crystal structures of two further compounds with the ligand **1** for comparison. Crystals of the complexes $[(Me)_2PtFI\{S_2CC(PPh_3)_2\}] \cdot 2CH_2Cl_2$ ($\mathbf{4} \cdot 2CH_2Cl_2$) and $[Pt\{S_2CC(PPh_3)_2\}_2][SiF_5]_2 \cdot 2CH_2Cl_2$ ($\mathbf{5} \cdot 2CH_2Cl_2$) were obtained by reacting **1** with a sample of an impure platinum compound which was formed as a result from attempts to fluorinate $[Me_2Pt(cod)]$ (still containing some $[Me(I)Pt(cod)]$) with XeF_2; the complex $[(CF_3)_2Pt(cod)]$ was expected [9]. The anion $[SiF_5]^-$ may originate from fluorination of some glass or grease by XeF_2.

3. Crystal structures

To get more insight into the nature of the complexes and the bonding situation an X-ray analysis of **3** was performed. Small dark red crystals of $\mathbf{3} \cdot CH_2Cl_2$ suitable for an X-ray analysis formed in a suspension of the powder in CH_2Cl_2 at room temperature. To our knowledge, no other platinum(II) compounds with an I_2PtS_2 arrangement are known in which the sulfur atoms come from a CS_2 adduct of the type S_2CR; only two Pt^{IV} complexes with a dithiocarbaminato ligand have been characterized by X-ray analyses [10]. Pt^{II} compounds with this core are described with thiourea derivatives [11], with dimethylsulfoxide [12] or with thioethers [13]. Pt^{II} complexes with other zwitterionic compounds are described with the ligand S_2CPR_3 [14]. For comparison we include the structures of $\mathbf{4} \cdot 2CH_2Cl_2$ and $\mathbf{5} \cdot 2CH_2Cl_2$, which we have obtained as described above. The molecular structures of $\mathbf{3} \cdot CH_2Cl_2$, $\mathbf{4} \cdot 2CH_2Cl_2$, and of the cation of $\mathbf{5} \cdot 2CH_2Cl_2$ are depicted in Figs. 1–3. Crystallographic data are listed in Table 1, and distances and angles are summarized in Tables 2–4.

3.1. Crystal structure of $\mathbf{3} \cdot CH_2Cl_2$

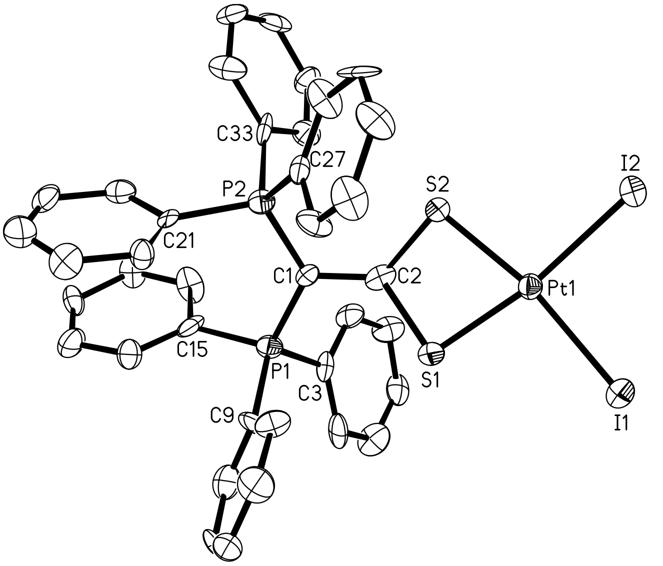

Fig. 1. Molecular structure of $\mathbf{3} \cdot CH_2Cl_2$ showing the atom numbering scheme. The ellipsoids are drawn at a 40% probability level; the H atoms at the phenyl rings and the CH_2Cl_2 molecule are omitted for clarity.

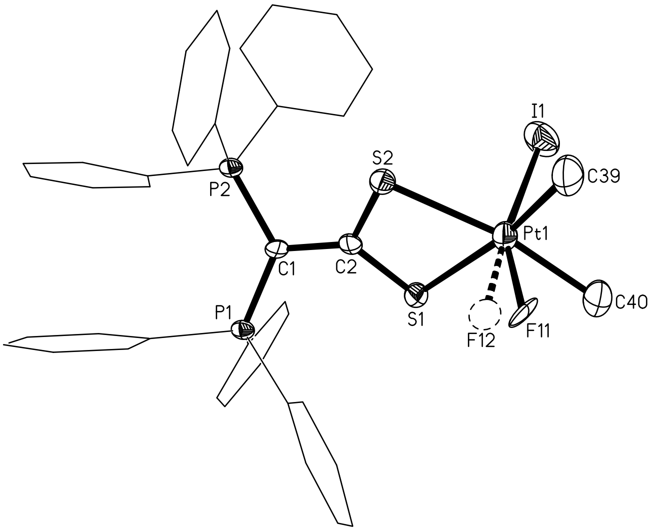

Fig. 2. Molecular structure of $\mathbf{4} \cdot 2CH_2Cl_2$ showing the atom numbering scheme. The ellipsoids are drawn at a 40% probability level; the H atoms at the phenyl rings and the CH_2Cl_2 molecules are omitted for clarity.

The environment of the platinum atom is planar as shown by the sum of the bond angles at the Pt atom of 360°; the crystal structure is shown in Fig. 1; the solvent molecule is omitted. On complex formation the ligand **1** undergoes some remarkable changes. The $S_2C–CP_2$ bond length decreases from 149.4(2) to 141(2) pm indicating an increased double bond character, and together with the $S_2C–CP_2$ bond lengths of **5** it is the shortest one found in complexes of **1**. The P–C distances to the ylidic carbon atom are slightly longer (mean 178 pm) than those in **1**; only the mean $P–C_{Ph}$ distances are the same as in the free ligand. A slight elongation of the C–S bond length is also observed. These changes in bond lengths upon complex formation can be interpreted in terms of a release of π electron density away from the ylidic carbon atom; the same trends were found in the $(CO)_4M$ adducts [4]. The S–Pt–S angle amounts to 74° and is larger than the corresponding S–M–S angle in the group 6 metal carbonyl derivatives, whereas the S–C–S bite angle is smaller (106°); in going from **1** to **3** a decrease of the bite angle of about 18° occurs, indicating the great

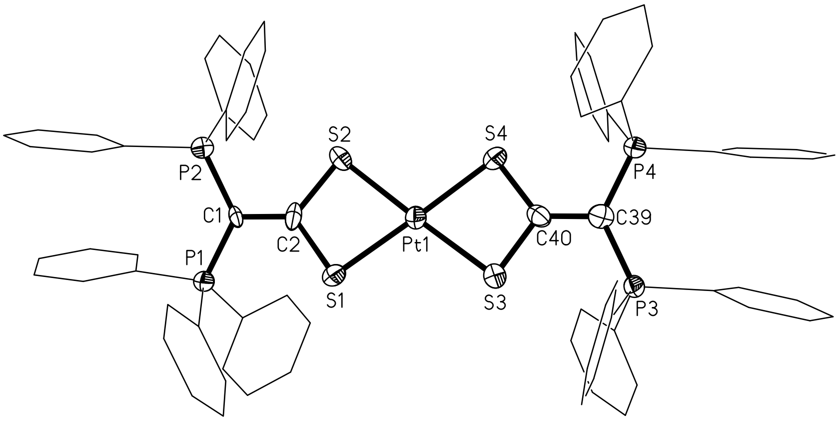

Fig. 3. Molecular structure of the cation of **5** · $2CH_2Cl_2$ omitting the solvent molecules and showing the atom numbering scheme. The ellipsoids are drawn at a 50% probability level; the phenyl groups are represented as thin lines omitting the H atoms for clarity.

Table 1
Crystal data and structure refinement details for the compounds **3** · CH_2Cl_2, **4** · $2CH_2Cl_2$ and **5** · $2CH_2Cl_2$

	3 · CH_2Cl_2	**4** · $2CH_2Cl_2$	**5** · $2CH_2Cl_2$
Formula	$C_{39}H_{32}Cl_2I_2P_2PtS_2$	$C_{42}H_{40}Cl_4FIP_2PtS_2$	$C_{78}H_{64}Cl_4F_{10}P_4PtS_4Si_2$
mw (g/mol)	1146.56	1153.66	1836.57
a (pm)	1104.6(1)	1105.0(1)	1442.1(2)
b (pm)	1832.1(2)	1252.0(2)	1567.7(2)
c (pm)	1965.9(3)	1766.4(2)	1829.8(2)
α (°)	90	71.30(1)	71.10(2)
β (°)	101.88(1)	76.38(1)	82.34(2)
γ (°)	90	74.84(1)	80.40(2)
Crystal size (mm)	0.08 × 0.04 × 0.02	0.29 × 0.2 × 0.05	0.18 × 0.13 × 0.04
Volume ($pm^3 \times 10^6$)	3893.2(8)	2203.2(5)	3845.0(8)
Z	4	2	2
d_{calc} (g/cm^3)	1.956	1.739	1.586
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$ (nr. 14)	$P\bar{1}$ (nr. 2)	$P\bar{1}$ (nr. 2)
Diffractometer	IPDS II (Stoe)	IPDS I (Stoe)	IPDS I (Stoe)
Radiation	Mo Kα	Mo Kα	Mo Kα
Temperature (K)	193	193	193
μ (cm^{-1})	55.4	43.3	22.5
$2\theta_{max}$ (°)	52.50	52.24	52.25
Index range	$-13 \leqslant h \leqslant 13$, $-22 \leqslant k \leqslant 22$, $-24 \leqslant l \leqslant 24$	$-12 \leqslant h \leqslant 12$, $-15 \leqslant k \leqslant 15$, $-21 \leqslant l \leqslant 21$	$-17 \leqslant h \leqslant 17$, $-19 \leqslant k \leqslant 19$, $-21 \leqslant l \leqslant 21$
Number of reflections collected	26549	21835	38256
Number of independent reflections (R_{int})	7699 (0.2251)	8068 (0.0674)	14085 (0.235)
Number of observed reflections with $F_0 > 4\sigma(F_0)$	3548	5542	4186
Parameters	434	490	706
Absorption correction	numerical	numerical	numerical
Structure solution	direct methods SIR-92 [19]	direct methods SIR-92 [19]	Patterson method SHELXTL-Plus [20]
Refinement against F^2	SHELXL-97 [21]	SHELXL-97 [21]	SHELXL-97 [21]
H atoms	[a]	[a]	[a]
R_1	0.0762	0.059	0.066
wR_2 (all data)	0.1625	0.1589	0.1441
Maximum electron density left (e/$pm^3 \times 10^{-6}$)	1.18	5.28	1.18

[a] Calculated positions with common displacement parameter.

flexibility of this angle according to the nature of the central metal atom. The dihedral angle between the S_2C and the P_2C planes amounts to 26° and is larger than that in the free ligand **1** (20°). The increased deviation from planarity may be due to interactions of the sulfur atoms with phenyl rings in such that one ring at P(1) is pushing up the sulfur atom S(1) and another one at P(2) is pushing down the S(2) atom, and the shorter S_2C–CP_2 bond in **3** relative to the free ligand brings the phenyl groups closer to the sulfur atoms which causes a further increase of the repulsion. The Pt–I distances (mean 262.5(1) pm) and the Pt–S distances (mean 229.2(4) pm) are typical for compounds of Pt^{II} with a PtS_2I_2 core and a *cis* arrangement of the I atoms; the same is true for the I–Pt–I angle [13a,13b,13c,13d,13e,13f,13g].

3.2. Crystal structure of **4** · $2CH_2Cl_2$

The neutral complex **4** contains Pt^{IV} in a distorted octahedral environment; the crystal structure is depicted in Fig. 2. Other Pt^{IV} compounds with the PtS_2 core are equipped either with dithiocarbaminato ligands [10] or pincer ligands with S donor atoms [15]. In **4** the dihedral angle between the S_2C and the P_2C planes amounts to 35° and is larger than that in **3**. The S_2C–CP_2 bond length is in

Table 2
Selected bond lengths (pm) and angles (°) in **3** · CH_2Cl_2

Bond lengths			
Pt(1)–I(1)	262.2(2)	Pt(1)–I(2)	262.8(1)
Pt(1)–S(1)	228.9(4)	Pt(1)–S(2)	229.5(5)
S(1)–C(2)	176(2)	S(2)–C(2)	170(2)
P(1)–C(1)	180(2)	P(1)–C(3)	186(2)
P(1)–C(9)	181(2)	P(1)–C(15)	181(2)
P(2)–C(1)	175(2)	P(2)–C(21)	180(2)
P(2)–C(27)	182(2)	P(2)–C(33)	183(2)
C(1)–C(2)	141(2)		
Bond angles			
I(1)–Pt(1)–I(2)	92.93(5)	I(1)–Pt(1)–S(1)	95.8(2)
I(1)–Pt(1)–S(2)	169.7(1)	I(2)–Pt(1)–S(1)	171.3(2)
I(2)–Pt(1)–S(2)	97.2(1)	S(1)–Pt(1)–S(2)	74.1(2)
Pt(1)–S(1)–C(2)	89.3(6)	Pt(1)–S(2)–C(2)	90.4(6)
C(1)–P(1)–C(3)	107.6(8)	C(1)–P(1)–C(9)	113.6(9)
C(1)–P(1)–C(15)	113.1(9)	C(3)–P(1)–C(9)	110.9(9)
C(3)–P(1)–C(15)	105.4(8)	C(9)–P(1)–C(15)	105.9(8)
C(1)–P(2)–C(21)	113.3(8)	C(1)–P(2)–C(27)	108.5(9)
C(1)–P(2)–C(33)	115.3(8)	C(21)–P(2)–C(27)	106.8(7)
C(21)–P(2)–C(33)	105.7(8)	C(27)–P(2)–C(33)	106.8(8)
P(1)–C(1)–P(2)	125.1(1)	P(1)–C(1)–C(2)	117.(1)
P(2)–C(1)–C(2)	118.(1)	S(1)–C(2)–S(2)	106.1(9)
S(1)–C(2)–C(1)	125.(1)	S(2)–C(2)–C(1)	129.(1)

Table 3
Selected bond lengths (pm) and angles (°) in **4** · $2CH_2Cl_2$

Bond lengths			
Pt(1)–I(1)	278.2(1)	Pt(1)–S(1)	248.0(2)
Pt(1)–S(2)	243.7(2)	Pt(1)–F(11)	198(1)
Pt(1)–F(12)	210(1)	Pt(1)–C(39)	205(1)
Pt(1)–C(40)	208(1)	S(1)–C(2)	171.4(8)
S(2)–C(2)	170.7(9)	P(1)–C(1)	174.1(8)
P(1)–C(3)	181.7(8)	P(1)–C(9)	180.6(8)
P(1)–C(15)	181.1(8)	P(2)–C(1)	175.8(8)
P(2)–C(21)	181.1(8)	P(2)–C(27)	183.8(8)
P(2)–C(33)	180.5(8)	C(1)–C(2)	145(1)
Bond angles			
I(1)–Pt(1)–S(1)	93.10(6)	I(1)–Pt(1)–S(2)	94.33(6)
I(1)–Pt(1)–F(11)	156.4(4)	I(1)–Pt(1)–F(12)	174.3(4)
I(1)–Pt(1)–C(39)	90.2(4)	I(1)–Pt(1)–C(40)	90.3(4)
S(1)–Pt(1)–S(2)	70.99(8)	S(1)–Pt(1)–F(11)	103.5(5)
S(1)–Pt(1)–F(12)	92.2(4)	S(1)–Pt(1)–C(39)	169.5(4)
S(1)–Pt(1)–C(40)	99.7(4)	S(2)–Pt(1)–F(11)	106.9(4)
S(2)–Pt(1)–F(12)	89.3(4)	S(2)–Pt(1)–C(39)	98.9(4)
S(2)–Pt(1)–C(40)	169.8(4)	F(11)–Pt(1)–C(40)	70.6(6)
F(11)–Pt(1)–C(39)	76.6(6)	F(12)–Pt(1)–C(40)	86.9(6)
F(12)–Pt(1)–C(39)	85.0(6)	Pt(1)–S(1)–C(2)	87.0(3)
C(39)–Pt(1)–C(40)	90.2(6)	C(1)–P(1)–C(3)	109.7(4)
Pt(1)–S(2)–C(2)	88.6(3)	C(1)–P(1)–C(15)	110.3(4)
C(1)–P(1)–C(9)	115.5(4)	C(1)–P(2)–C(21)	113.2(4)
C(1)–P(2)–C(27)	111.9(4)	C(1)–P(2)–C(33)	113.0(4)
P(1)–C(1)–C(2)	119.8(6)	P(1)–C(1)–P(2)	125.4(5)
S(1)–C(2)–S(2)	113.2(5)	P(2)–C(1)–C(2)	114.8(6)
S(2)–C(2)–C(1)	123.5(7)	S(1)–C(2)–C(1)	123.3(7)

Table 4
Selected bond lengths (pm) and angles (°) in the cation of **5** · $2CH_2Cl_2$

Bond lengths			
Pt(1)–S(1)	231.9(4)	Pt(1)–S(2)	228.9(4)
Pt(1)–S(3)	230.8(4)	Pt(1)–S(4)	229.8(5)
S(1)–C(2)	173(2)	S(2)–C(2)	175(2)
S(3)–C(40)	174(2)	S(4)–C(40)	174(2)
P(1)–C(1)	174(2)	P(1)–C(3)	181(2)
P(1)–C(9)	180(2)	P(1)–C(15)	181(2)
P(2)–C(1)	179(2)	P(2)–C(21)	180(2)
P(2)–C(27)	181(2)	P(2)–C(34)	182(2)
P(3)–C(39)	179(2)	P(3)–C(41)	182(2)
P(3)–C(47)	180(2)	P(3)–C(53)	180(2)
P(4)–C(65)	181(2)	P(4)–C(71)	180(2)
C(1)–C(2)	141(2)	C(3)–C(4)	139(2)
Bond angles			
S(1)–Pt(1)–S(2)	74.2(2)	S(1)–Pt(1)–S(3)	107.6(2)
S(1)–Pt(1)–S(4)	178.3(2)	S(2)–Pt(1)–S(3)	178.1(2)
S(2)–Pt(1)–S(4)	104.2(2)	S(3)–Pt(1)–S(4)	74.1(2)
Pt(1)–S(1)–C(2)	89.6(6)	Pt(1)–S(2)–C(2)	89.9(5)
Pt(1)–S(3)–C(40)	89.8(5)	Pt(1)–S(4)–C(40)	90.1(6)
C(1)–P(1)–C(3)	111.4(5)	C(1)–P(1)–C(9)	110.8(5)
C(1)–P(1)–C(15)	110.3(4)	C(3)–P(1)–C(9)	109.0(2)
C(3)–P(1)–C(15)	103.7(2)	C(9)–P(1)–C(15)	111.4(2)
C(1)–P(2)–C(21)	110.0(5)	C(1)–P(2)–C(27)	116.5(5)
C(1)–P(2)–C(34)	106.2(5)	C(21)–P(2)–C(27)	105.9(2)
C(21)–P(2)–C(34)	112.4(2)	C(27)–P(2)–C(34)	105.8(2)
C(39)–P(3)–C(41)	108.1(5)	C(39)–P(3)–C(47)	117.6(5)
C(39)–P(3)–C(53)	110.1(6)	C(41)–P(3)–C(47)	105.5(2)
C(41)–P(3)–C(53)	112.7(2)	C(47)–P(3)–C(53)	102.9(2)
C(39)–P(4)–C(59)	112.8(5)	C(39)–P(4)–C(65)	112.4(6)
C(39)–P(4)–C(71)	118.8(5)	C(59)–P(4)–C(65)	105.4(2)
C(59)–P(4)–C(71)	108.5(2)	C(65)–P(4)–C(71)	108.7(2)
P(1)–C(1)–P(2)	128.2(7)	P(1)–C(1)–C(2)	117.1(1)
P(2)–C(1)–C(2)	115(1)	S(1)–C(2)–S(2)	106.2(8)
S(1)–C(2)–C(1)	127(1)	S(2)–C(2)–C(1)	127(1)
P(3)–C(39)–P(4)	129.2(9)	P(3)–C(39)–C(40)	114(1)
P(4)–C(39)–C(40)	116(1)	S(3)–C(40)–S(4)	106.0(9)
S(3)–C(40)–C(39)	127(1)	S(4)–C(40)–C(39)	127(1)

between that of **1** and **3** amounting to 145(1) pm. The Pt–S bond lengths are up to 20 pm longer than in the Pt^{II} compounds **3** and **5**, while the C–S distances are only slightly shorter and close to that of the free ligand **1**. The higher charge at the central atom causes the S–C–S bite angle to increase and the S–Pt–S angle to decrease by about 7° and 3°, respectively, relative to the Pt(II) compounds. The F atom is disordered with a 0.5–0.5 distribution, and F(12) occupies more exactly the axial octahedron position while F(11) is slightly bent away from the S atoms. The distance between F(11) and F(12) is about 67 pm. According to our X-ray data there is no possibility to introduce a disorder between the positions of the methyl groups and the fluorine atoms because of the displacement parameters which fit only to the arrangement shown in Fig. 2. The Pt–I distance amounts to 278.2(1) pm and is longer than in other Pt^{IV} compounds with a related ligand arrangement [15]. It is about 16 pm longer than that in **3** to Pt^{II} but 5 pm shorter than the related distance in the tetrameric $[Me_3PtI]$ with a bridging I atom [16]. If we compare terminal and bridging F atoms as in **4** and $[Me_3PtF]_4$, respectively, the terminal one is about 20 pm shorter [17]. The methyl groups are in *trans* position to the sulfur atoms and the Pt–C distances are in the upper range of those in $[Me_3PtX]_4$ complexes [16,17].

3.3. Crystal structure of **5** · $2CH_2Cl_2$

The crystal structure of the dication **5** is shown in Fig. 3. One of the solvent molecules is disordered. The complex contains two molecules of **1** at Pt^{II} as chelating ligands. The dihedral angles between the S_2C and the P_2C planes amount to 19° and 9°, respectively; the environment at the central Pt atom is planar as shown by the sum of the angles of 360.1°, and the deviations of the five atoms from the best plane are very small (Pt(1), S(1), S(2), S(3), S(4) = −1, 0, 1, 0, 1 pm). The $S_2C–CP_2$ bond lengths are identical with those of **3**; similarly, the S–C–S bite angles and the S–Pt–S angles correspond to those of **3**. The mean Pt–S distance is only slightly longer than that in **3**, but the individual distances differ by about 3 pm, probably due to packing effects. Although compounds with a PtS_4 core are very common in platinum chemistry, cationic compounds with a spiro bicyclic CS_2PtS_2C arrangement have not yet been described. No nearer contacts exist between the cation and the anions. The Si–F distances in the $[SiF_5]^-$ anions range between 153(1) and 160(1) pm at Si(1) and 152(1) and 162(1) pm at Si(2).

4. Conclusion

In contrast to the carbodiphosphorane adducts of CO_2 and COS, which adopt η^1 or η^2 coordination, the CS_2 adduct **1** is found to act only as a chelating ligand towards transition metals as yet. If **1** is connected to Ag^+, aggregates of $Ag_4{}^{4+}$ or $Ag_6{}^{6+}$ cluster units are held together by the sulfur atom bonded each to one or two silver atoms [6]. For comparison, the most relevant bond lengths in the compounds **1** and **3**–**5** are summarized in Table 5. Whereas in the starting adduct **1** the $S_2C–CP_2$ distance is already shorter than a single bond, a further shortening is observed upon complex formation, indicating an increase in double bond character. In the Pt^{II} complexes the related $S_2C–CP_2$ distances are the shortest ones found as yet with 141(2) pm; they are close to those in aromatic ring systems. This electron release diminishes the P–C (p–σ^*) interaction leading to longer distances. This trend was also observed in the related carbonyl complexes $[(CO)_4MS_2CC(PPh_3)_2]$ where $S_2C–CP_2$ distances of about 145 pm were found [4]; similar values are also recorded in the silver clusters [6].

Thus, the occupied p orbital of the sp^2 CP_2 carbon atom in **1** and the vacant p orbital at the sp^2 CS_2 carbon atom form a partial double bond which, depending on the nature and charge of the metal, is increased upon coordination of the sulfur atoms at a metal atom. For the first time, we can compare compounds in which **1** is bonded to a metal in different oxidation states. There is a great difference in the coordination of **1** to a Pt^{II} or Pt^{IV} atom with a planar or and octahedral ligand arrangement, respectively. In spite of the higher charge of the central atom in **4** with Pt^{IV} a minor electron release is found, expressed by a longer $S_2C–CP_2$ bond accompanied by about 16 pm longer (mean) Pt–S distances. The differences in the bonding parameters indicate a weaker bond of the chelating ligand **1** in the complex **4**. Thus, the $S_2C–CP_2$ double bond character increases in the series **1** < **4** < **3**–**5** corresponding to a decrease of the P–C double bond character in this row. Because **5** is the result of Pt^{II} with weakly coordinating anions, further studies in this field are in progress. Furthermore, the coordination of **1** at Pt^{IV} compounds will also be of interest and the formation of cations with more than one neutral ligand **1**, such as compounds with $[PtS_4X_2]^{2+}$ or $[PtS_6]^{4+}$ cores, will be a challenge for the future.

5. Experimental

All operations were carried out under an argon atmosphere in dried and degassed solvents using Schlenk techniques. The solvents were thoroughly dried and freshly distilled prior to use. The IR spectra were run on a Nicolet 510 spectrometer. For the ^{31}P NMR spectra we used the instrument Bruker AC 200. Elemental analyses were performed by the analytical service of the Fachbereich Chemie der Universität Marburg (Germany). Compound **1** was prepared according to a modified literature procedure [1] by addition of CS_2 to a solution of $C(PPh_3)_2$ in toluene at room temperature. $[Cl_2Pt(cod)]$ and $[I_2Pt(cod)]$ were obtained according to literature procedures [18]. Information concerning the X-ray structure determination is given in Table 1. The residual electron density in $\mathbf{4} \cdot 2CH_2Cl_2$ is near the Pt atom.

Table 5
Comparison of important bond lengths in **1**, **3**, **4** and **5**

	1 [4]	**3**	**4**	**5**
Pt–S (mean)		229.2(4)	245.9(2)	230.4(4)
S–C	169.1(2)	173(2)	171.1(8)	174(2)
$S_2C–CP_2$	146.9(6)	141(2)	145(1)	141(2)
C–P	175.1(2)	178(2)	175.0(8)	177(2)

5.1. Preparation of $[Cl_2Pt\{S_2CC(PPh_3)_2\}]$ (**2**)

To a suspension of 520 mg (0.85 mmol) of $S_2CC(PPh_3)_2$ (**1**) in about 40 ml THF was added 320 mg (0.85 mmol) $[Cl_2Pt(cod)]$. The yellow suspension immediately turned red-brown. The mixture was stirred magnetically for about 1 h. Then the precipitate was filtered, washed with 1 ml THF and dried in vacuum. Yield 710 mg (95%). ^{31}P NMR (DMSO): 14.56 ppm. IR (Nujol): 1585 vw, 1497 m, 1438 s, 1253 vs, 1197 w, 1163 w, 1098 s, 1069 w, 1043 m, 1027 w, 998 m, 811 m, 749 m, 736 w, 721 m, 714 w, 690 s, 564 w, 556 w, 524 s, 506 s, 492 m (cm^{-1}). *Anal.* Calc. for $[Cl_2Pt\{S_2CC(PPh_3)_2\}]$ (**2**): C, 51.94; H, 3.44. Found: C, 50.38; H 3.65%.

5.2. Preparation of $[I_2Pt\{S_2CC(PPh_3)_2\}]$ (**3**)

In a similar procedure as outlined for the preparation of **2**, the red-brown complex **3** was obtained from 0.66 g (1.08 mmol) $[I_2Pt(cod)]$ and 0.60 g (1.08 mmol) of $S_2CC(PPh_3)_2$ (**1**). The dry red-brown powder was treated with CH_2Cl_2 which produced small dark red crystals of $\mathbf{3} \cdot CH_2Cl_2$ during several hours; yield 1.05 g (92%). ^{31}P NMR (DMSO): 13.96 ppm. IR (Nujol): 1586 vw, 1481 m, 1439 s, 1246 vs, 1192 w, 1163 w, 1096 s, 1073 w, 1049 s, 1024 w, 997 m, 806 m, 740 m, 723 m, 711 w, 693 s, 685 s, 570 w, 553 w, 522 s, 509 s, 494 m (cm^{-1}). *Anal.* Calc. for $[I_2Pt\{S_2CC(PPh_3)_2\}]$ (**3**): C, 42.99; H, 2.85. Found: C, 41.64; H, 2.91%.

5.3. Formation of $[Me_2FIPt(S_2CC(PPh_3)_2)]$ (**4**) and $[Pt(S_2CC(PPh_3)_2)_2][SiF_5]_2$ (**5**)

An impure sample obtained from fluorination of $[Me_2Pt(cod)/I_2Pt(cod)]$ with XeF_2 was used [9] for the reaction with **1** in CH_2Cl_2; the anion $[SiF_5]^-$ may originate from fluorination of glass or grease. Few crystals of **4** (small red blocks) and **5** (orange plates) were obtained from CH_2Cl_2 solutions upon layering with *n*-pentane; no further crystalline product was formed. Compound **4**, ^{31}P NMR (CH_2Cl_2): s, 14.8 ppm. Compound **5**, ^{31}P NMR (CH_2Cl_2): s, 13.3 ppm.

Supplementary material

CCDC 667634, 667635 and 667636 contain the supplementary crystallographic data for **3**, **4** and **5**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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