Synthesis and Carbonylation of Platinum(II) Organometallic Complexes with Bis(phosphanyl) Monosulfides − Crystal Structures of [κ^2*P*,*S*-{$Ph_2CH_2P(S)Ph_2$}Pt(CH_3)(Cl)] and [κ*P*,μ-κ*S*-{$Ph_2CH_2CH_2P(S)Ph_2$}Pt-(CH_3)]$_2$[BF_4]$_2$

Piero Mastrorilli,[a] Cosimo F. Nobile,*[a] Gian P. Suranna,[a] Francesco P. Fanizzi,[b,f] Giuseppe Ciccarella,[c] Ulli Englert,[d] and Qi Li[e]

Dedicated to Professor Adriano Sacco on the occasion of his 80th birthday

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The neutral complexes of formula [κ^2*P*,*S*-(dppmS)Pt(CH_3)(Cl)] (**1**) and [κ^2*P*,*S*-(dppeS)Pt(CH_3)(Cl)] (**2**) [dppmS = $Ph_2PCH_2P(S)Ph_2$, dppeS = $Ph_2P(CH_2)_2P(S)Ph_2$] have been synthesised and characterised. Reaction of **1** and **2** with $AgBF_4$ carried out in CH_3CN or CH_3CN/CH_2Cl_2 affords the corresponding monomeric cationic complexes [κ^2*P*,*S*-(dppmS)Pt(CH_3CN)(CH_3)][BF_4] (**3**) and [κ^2*P*,*S*-(dppeS)Pt(CH_3CN)(CH_3)][BF_4] (**4**). Complexes **3** and **4** partially dissociate in CD_2Cl_2, giving, in the case of **3**, the asymmetric dimer {[κ^2*P*,*S*-(dppmS)](CH_3)Pt{κ*P*,μ-κ*S*-(dppmS)}Pt(CH_3)(CH_3CN)][BF_4]$_2$ (**5**), and, in the case of **4**, the symmetrical sulfur-bridged dimer [κ*P*,μ-κ*S*-(dppeS)Pt(CH_3)]$_2$[BF_4]$_2$ (**6**). Pure **6** can be obtained by heating **4** under vacuum. Exposing CD_2Cl_2 solutions of the cationic complexes **3** and **4** to CO at ambient conditions brings about the formation of the monomeric methyl carbonyl complexes [κ^2*P*,*S*-(dppmS)Pt(CO)(CH_3)][BF_4] (CO *trans* to P, **7a**) and [κ^2*P*,*S*-(dppeS)Pt(CO)(CH_3)][BF_4] (CO *trans* to P, **8a**), which slowly transform into their CO *cis* to P isomers **7b** and **8b**, respectively. The single-crystal X-ray diffraction studies of **1**·CD_2Cl_2 and **6**·2CD_2Cl_2 are reported. Mass spectrometric analyses with APCI and ESI interfaces were also performed for all new complexes.

Introduction

Heteroditopic ligands, those ligands that possess at least two types of chemical functionality capable of binding to a metal centre, have been receiving ever-growing attention in the field of coordination and organometallic chemistry. Such ligands, characterised by the stability advantages typical for chelates, may also confer interesting catalytic properties to their metal complexes owing to the generation of very different *trans* effects and, therefore, reactive sites within the same molecule.[1−3]

In this framework P,S bidentate ligands are appealing since the peculiar features of sulfur favour a strong coordination to soft metal centres.[4,5] In particular P,(P)S ligands exhibit a heteroditopic behaviour[6−12]that has been recently exploited in catalysis.[13,14]

Following our studies in the coordination chemistry of heteroditopic ligands,[15−17] we became interested in the synthesis and reactivity of neutral and cationic methyl complexes of platinum(II) with the heteroditopic ligands dppmS and dppeS.

Results and Discussion

The synthesis of the complexes [κ^2*P*,*S*-(dppmS)Pt(CH_3)Cl] (**1**) and [κ^2*P*,*S*-(dppeS)Pt(CH_3)Cl] (**2**) was carried out starting from [(cod)Pt(CH_3)(Cl)] (cod = 1,5-cyclooctadiene) and an equivalent of the appropriate bis(phosphanyl) monosulfide ligand.

[a] Dipartimento di Ingegneria delle Acque e di Chimica, Polytechnic of Bari and CNR Centre I.C.C.O.M., Via Orabona, 4, 70125 Bari, Italy
Fax: (internat.) + 39-080-5963611
E-mail: nobile@poliba.it
[b] Dipartimento di Scienze e Tecnologie Biologiche e Ambientali, University of Lecce, Via Monteroni, 73100, Lecce, Italy
[c] Dipartimento di Ingegneria dell'Innovazione, University of Lecce, Via Monteroni, 73100, Lecce, Italy
[d] Institut für Anorganische Chemie der RWTH, Prof. Pirlet Str. 1, 52074 Aachen, Germany
[e] Department of Chemistry, Beijing Normal University, Beijing 100875, P. R. China
[f] Consortium C.A.R.S.O., Cancer Research Center 70010, Valenzano-Bari, Italy

Subsequently, the coordinated chlorides of **1** and **2** were removed by reaction with silver tetrafluoroborate in acetonitrile or acetonitrile/dichloromethane. The absence of the IR bands of Pt−Cl stretching at 276 cm^{-1} for **1** and 273 cm^{-1} for **2** is evidence for the effective chloride abstraction.

The vacant coordination site was occupied by the acetonitrile, thus obtaining the cationic complexes [κ^2P,S-(dppmS)Pt(CH_3)(CH_3CN)][BF_4] (**3**) and [κ^2P,S-(dppeS)Pt(CH_3)(CH_3CN)][BF_4] (**4**) (Scheme 1). End-on coordination of the acetonitrile leads to two $\tilde{\nu}_{C\equiv N}$ bands in the IR spectra (at 2325 and 2297 cm^{-1} for **3**, and 2323 and 2295 cm^{-1} for **4**), both blue-shifted with respect to free CH_3CN.

The spectroscopic data both in solution (NMR) and in the solid state (IR) confirm a κ^2P,S coordination for complexes **1**−**4**. A first evidence in this respect is given by the 20−25 cm^{-1} red-shift of the phosphanyl sulfide stretching frequencies in the IR spectrum. The $\tilde{\nu}_{(P=S)}$ bands at 605 cm^{-1} (dppmS) and at 610 cm^{-1} (dppeS) of the free ligands are shifted in the neutral complexes **1** and **2** to 585 cm^{-1} and 591 cm^{-1}, respectively. In the case of cationic complexes **3** and **4** the $\tilde{\nu}_{(P=S)}$ bands are found at 580 cm^{-1} and 586 cm^{-1}, respectively.

Consistently, the $^{31}P\{^1H\}$ NMR signals ascribed to the sulfur-bound phosphorus in **1**−**4** are all flanked by ^{195}Pt satellites due to ^2J[P(S),Pt] (23 Hz for **1**, 58 Hz for **2**, 39 Hz for **3**, and 55 Hz for **4**).

The direct ^1J(P,Pt) values found for **1**−**4**, ranging from 4606 to 4695 Hz (Table 1), are in agreement with a relatively weak *trans* influence of the ligand positioned *trans* to coordinated P,[18] chloride for **1** and **2**, CH_3CN for **3** and **4**.

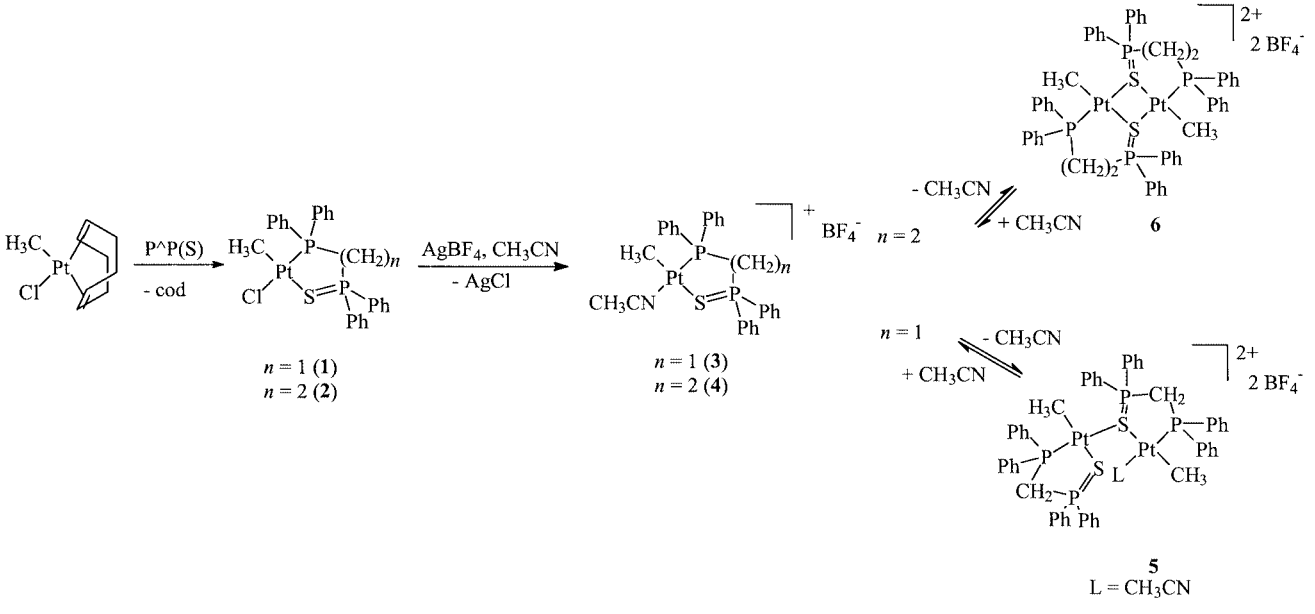
Moreover the values of the coupling constants for the ^1H and $^{13}C\{^1H\}$ NMR methyl signals of complexes **1**−**4** are entirely in agreement with a configuration in which the methyl group is *cis* with respect to the phosphorus atom directly coordinated to the platinum centre.[18−20] The observed ranges are: ^3J(H,P) = 3.4−4.6, ^2J(H,Pt) = 68−74, ^2J(C,P) = 5.8−8.3 Hz, and ^1J(C,Pt) = 605−650 Hz.

Table 1. $^{31}P\{1H\}$ and $^{195}Pt\{1H\}$ NMR spectroscopic data (δ, ppm, CD_2Cl_2, 298 K) (see Figure 3 for numbering of **5**)

	δ(P)	δ[P(S)]	δ(Pt)	J(P,P) Hz	^1J(P,Pt) Hz	^2J(P,Pt) Hz
1	15.4	50.8	−4354	29	4609	23
2	10.1	36.6	−4390	8	4606	58
3	14.1	52.7	−4532	24	4694	39
4	7.6	39.7	−4517	7	4695	55
5	12.8 (P^3)	52.0 (P^4)	−4512 (Pt^2)	20 (P^3,P^4)	4724(Pt^2,P^3)	[a]
	22.3 (P^1)	52.1 (P^2)	−4502 (Pt^1)	28 (P^1,P^2)	4469(Pt^1,P^1)	[a]
6	16.1	38.0	−3982	[a]	4331	[a]

[a] Signal not resolved.

Crystals of **1** suitable for XRD analysis were obtained by solvent evaporation from a CD_2Cl_2 solution. An ORTEP view of its molecular structure in the crystal is given in Figure 1. The crystals contain one molecule of clathrated CD_2Cl_2 per complex molecule.



Scheme 1. Synthesis of neutral and cationic Pt^{II} complexes

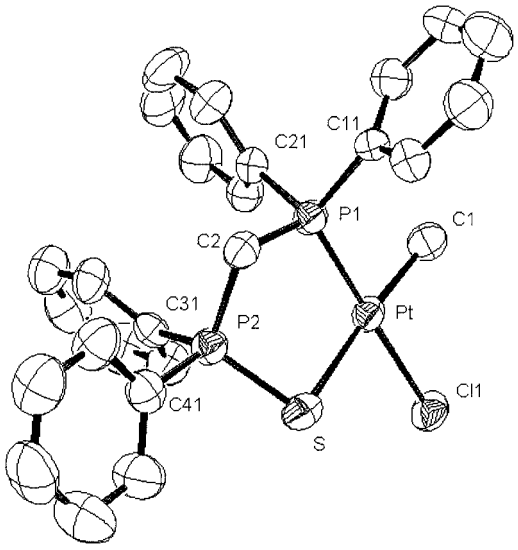


Figure 1. ORTEP drawing of **1**. The solvent molecule was omitted for clarity; displacement ellipsoids are scaled to 50% probability

Table 2. Selected bond lengths (Å) and angles (°) for **1**·CD_2Cl_2 and **6**·$2CD_2Cl_2$

1		**6**	
Pt−Cl(1)	2.3775(14)	Pt(1)−C(27)	2.069(10)
Pt−P(1)	2.1806(15)	Pt(1)−P(1)	2.220(3)
Pt−S	2.4243(18)	Pt(1)−S(1_2)	2.403(3)
Pt−C(1)	2.056(6)	Pt(1)−S(1)	2.427(3)
P(2)−S	1.993(2)	S(1)−P(2)	2.043(4)
Cl(1)−Pt−P(1)	177.71(7)	C(27)−Pt(1)−P(1)	89.3(4)
Cl(1)−Pt−S	87.74(6)	C(27)−Pt(1)−S(1_2)	95.1(4)
Cl(1)−Pt−C(1)	88.71(17)	P(1)−Pt(1)−S(1_2)	167.80(9)
P(1)−Pt−S	94.46(6)	C(27)−Pt(1)−S(1)	172.6(4)
P(1)−Pt−C(1)	89.12(17)	P(1)−Pt(1)−S(1)	96.33(9)
S−Pt−C(1)	175.87(18)	S(1_2)−Pt(1)−S(1)	80.41(9)
		P(2)−S(1)−Pt(1_2)	117.57(14)
		P(2)−S(1)−Pt(1)	103.27(13)
		Pt(1_2)−S(1)−Pt(1)	99.59(9)

Pt and its coordinating atoms P(1), S, C(1), and Cl(1) occur with an essentially square-planar geometry. The maximum deviation of a least-squares study occurs for C(1) and amounts to 0.032(6) Å. The platinum coordination is characterised by metal-centred angles between 89.12(17)° and 87.74(6)°. The sum of the four angles on platinum is 360.03(18)°. Interestingly, the different *trans* influence of phosphorus and sulfur can be evidenced by comparison of Pt−Cl and Pt−C bond lengths with similar compounds: for instance, the Pt−C(1) bond length [2.056 (6) Å] is considerably shortened due to the presence of the *trans* sulfur donor atom with respect to a complex in which the methyl group is *trans* to a P^{III} atom as in the bridging complex [$Pt_2Me_4(\mu$-dmpm$)_2$] [dmpm: bis(dimethylphosphanyl)methane] (Table 2).[22] As for the Pt−Cl(1) and Pt−P(1) bond lengths, they are similar to other platinum complexes embodying the *trans* P−Pt−Cl substructure such as complexes of formula {bis[bis(*o*-isopropylphenyl)phosphanyl]-methane}$PtCl_2$ [20] and (P^N)Pt(Me)Cl (P^N: chiral phosphanyl oxazoline).[23]

When the cationic species **3** and **4** are dissolved in CH_2Cl_2, a dissociation equilibrium of CH_3CN takes place as evidenced by the appearance in the IR, ^1H and ^{13}C NMR spectra (CD_2Cl_2 solutions) of free acetonitrile signals.

In the case of **4**, the $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 shows the appearance of ca. 25% of a new species **6**, which gives two broad singlets centred at δ = 16.1 and δ = 38.0 ppm. The signal at δ = 16.1 ppm, ascribable to a P atom directly bound to the platinum centre, is flanked by ^{195}Pt satellites from which a ^1J(P,Pt) of 4331 Hz could be extracted. The signal at δ = 38.0 ppm, ascribable to a P atom bound to a coordinated sulfur atom, only shows broadening at the base which could be due to unresolved ^{195}Pt satellites with a small ^2J(P,Pt) value.

In principle, acetonitrile dissociation which takes place by dissolving **4** in dichloromethane (or CD_2Cl_2) could result in *i*) BF_4^- coordination in the place of CH_3CN; *ii*) CH_2Cl_2 (or CD_2Cl_2) coordination [24] in the place of CH_3CN; *iii*) dimerisation of the coordinatively unsaturated platinum species to give sulfur bridged dimers.

The possible coordination of the tetrafluoroborate in the place of acetonitrile has been ruled out by recording $^{19}F\{^1H\}$ NMR spectra (282 MHz) of **4** in CD_2Cl_2. The only signals present were ascribable to ionic free BF_4^- [δ = −152.98 (s, $^{10}BF_4^-$), δ = −153.02 ppm(s, $^{11}BF_4^-$)].

On the other hand, substitution of dichloromethane for a nitrile group, as already reported in a similar system,[23] should result in a significant increase of the ^1J(P,Pt). In our case, on the contrary, a slight decrease of the ^1J(P,Pt) is observed (Table 1).

The remaining hypothesis *iii*), (formation of the dimers), could be supported by the aforementioned small ^2J(P,Pt) coupling constants which is consistent with a P atom bound to a bridging sulfur and suggests the dimer structure [κ*P*,μ-κ*S*-(dppeS)Pt$(CH_3)]_2[BF_4]_2$ (**6**) (Scheme 1).

The presence of the two sulfur atoms in the coordination sphere of each platinum results in the downfield shift observed in the ^{31}P NMR spectrum for the P atoms directly bound to the Pt centre when comparing **4** with **6**.

In order to shift the dissociation equilibrium between the acetonitrile monomeric complex **4** and **6** to the right, we have heated solid **4** under vacuum. The reaction led quantitatively to the synthesis of **6** that, after crystallisation from CD_2Cl_2, could be submitted for the single-crystal XRD analysis.

The structure of **6** represents the first structurally characterised sulfur bridged bis(phosphanyl) monosulfide dimeric complex. An ORTEP view of its molecular structure in the crystal is given in Figure 2. The crystals contain two molecules of clathrated CD_2Cl_2 per complex molecule.

The asymmetric unit of **6** consists of half a centrosymmetric divalent cation, one tetrafluoroborate anion, and one solvent molecule, CD_2Cl_2. The coordination around platinum is that of a distorted square with angles ranging from 80.4° to 96.3°. Two neighbouring coordination sites are occupied by the two bridging sulfur atoms of the chelat-

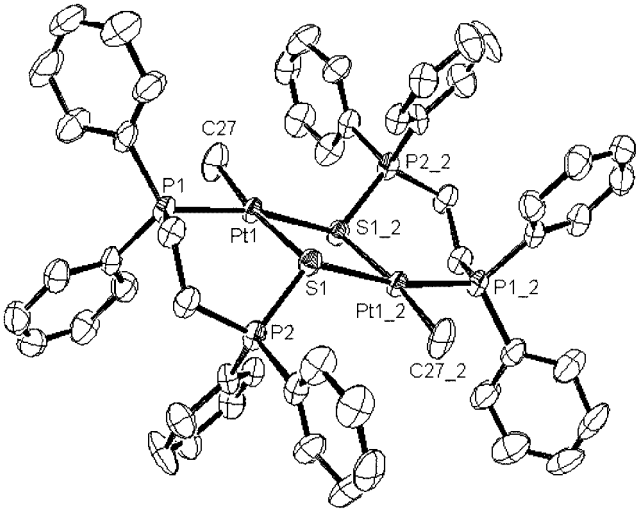


Figure 2. ORTEP drawing of **6**. Solvent molecules and counter anions were omitted for clarity; displacement ellipsoids are scaled to 40% probability

ing ligands; thus a four membered planar Pt_2S_2 ring around the crystallographic inversion centre is formed. The coordination sphere of each metal is completed by the methyl carbon and the donor phosphorus atom of the chelating ligand. The Pt−S bond lengths [2.402(3) and 2.427(3) Å] are similar to those [2.4094(17) Å and 2.4227(17) Å] observed for the related sulfur bridged complex $[Pt(C_6F_5)_2(\mu\text{-}SPPh_2C_5H_5)]_2$ [25] and are similar to that [2.4243(18) Å] observed for the parent complex **2** in which the sulfur atom is terminally bound.

The P−S distances of 2.043(4) Å are intermediate between the expected value for a P=S double bond and a P−S single bond, and the sulfur atoms are pyramidal, as indicated by the sum of the angles at the sulfur atom (320.4°).[25] Dihedral angles between the Pt_2S_2 plane and the phenyl rings range between 60.9(5)° and 76.7(5)°.

Owing to its bridging coordination mode, the P=S band in the IR spectrum was significantly red-shifted with respect to the monomeric cation **4** ($\tilde{\nu}_{(P=S)}$ changed from 586 cm^{-1} for **4** to 532 cm^{-1} for **6**).

In the case of **3**, the NMR spectra recorded in CD_2Cl_2 show the appearance of 45% of a new species different from the expected **6** homologue.

The $^{31}P\{^1H\}$ NMR spectrum of this new species consists of four signals with equal integrals: a doublet of doublets centred at δ = 22.3 and a doublet centred at δ = 52.1 ppm mutually coupled [^2J(P,P) 28 Hz], a doublet centred at δ = 12.8 and a doublet of doublets centred at δ = 52.0 ppm mutually coupled with a ^2J(P,P) 20 Hz. The further splitting observed in the signals at δ = 22.3 and δ = 52.0 corresponds to a mutual coupling of 4 Hz. The signals at δ = 22.3 and δ = 12.8 ppm, flanked by ^{195}Pt satellites from which ^1J(P,Pt) of 4469 Hz and 4724 Hz could be extracted are attributed to two chemically different Pt-bound P atoms. The partially overlapped signals at δ = 52.1 and δ = 52.0 ppm are ascribable to P atoms bound to coordinated sulfur. Both signals show broadening only at the base as unresolved ^{195}Pt satellites with a small ^2J(P,Pt) value. Moreover, the ^1H NMR spectrum shows, together with free CH_3CN (δ = 1.97 ppm) two peaks in the region of coordinated acetonitrile, one belonging to complex **3** at δ = 2.52 ppm and the other (δ = 2.54 ppm), having the same integration of the free CH_3CN, belonging to the new species.

All these spectroscopic features suggest that the species formed by partial CH_3CN dissociation on dissolving **3** in CD_2Cl_2, is the unsymmetrical dimer $[\{\kappa^2P,S\text{-}(dppmS)\}(CH_3)Pt\{\kappa P,\mu\text{-}\kappa S\text{-}(dppmS)\}Pt(CH_3)(CH_3CN)][BF_4]$ (**5**) depicted in Figure 3. The proposed structure is substantiated by ESI-MS analyses (vide infra) and by the observed ^3J(P,P) 4 Hz coupling constant between P^1 (bonded to Pt^1) and P^4 (bonded to the bridging sulfur).

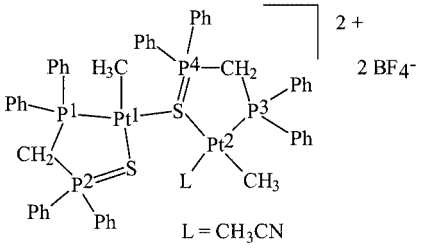


Figure 3. Alleged structure for complex **5**

The two methyl signals for **5** occurred in the ^1H NMR spectrum as doublets (with satellites) centred at δ = 0.74 ppm [^3J(H,P) = 3, ^2J(H,Pt) = 64 Hz, CH_3 *cis* to CH_3CN] and δ = 0.06 ppm [^3J(H,P) = 3.9, ^2J(H,Pt) = 66.9 Hz, CH_3 *cis* to bridging S]. Assignment of ^1H, ^{31}P, ^{13}C, ^{195}Pt NMR spectral features is reported in Table 1 and in the Exp. Sect.

The equilibrium between **3** and **5** or **4** and **6** (Scheme 1) completely shifts towards the acetonitrile species by adding CH_3CN to the $[D_2]$dichloromethane solutions.[26]

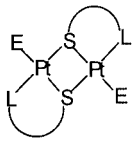
Heating solid **3** under vacuum for 8 h resulted in an enrichment of the equilibrium mixture in **5** (the dimer/monomer ratio passed from 0.82 to 3.0, based on total phosphorus, as assessed by ^{31}P NMR spectra in CD_2Cl_2). Attempts to shift the dissociation equilibrium between the acetonitrile monomeric complex **3** and **5** completely to the right, by prolonging the heating for 2.5 days, resulted in a complex mixture of products containing, according to ^{31}P integration data, ca. 43% of **5**.

It is interesting to note that the homologous cations $[\kappa^2P,S\text{-}(dppmS)Pd(CH_3CN)(CH_3)]^+$ and $[\kappa^2P,S\text{-}(dppeS)Pd(CH_3CN)(CH_3)]^+$, recently prepared by us,[17] are stable in CH_2Cl_2 solution as monomeric acetonitrile complexes.

The difference in behaviour between **3** and **4** observed in dichloromethane, i.e. the formation of the unsymmetrical or symmetrical dimers **5** or **6**, deserves a comment.

Theoretical calculations indicate that Pt_2S_2 rings adopt a planar conformation in Pt^{II} complexes of formulae *trans*-$[Pt_2(\mu\text{-}SR)_2L_2L'_2]$ or $[Pt_2(\mu\text{-}RS)_2L_4]$, and a hinged arrangement in Pt^{II} complexes of formula *cis*-$[Pt_2(\mu\text{-}RS)_2L_2L'_2]$.[27]

Moreover, given that the sulfur atom usually adopts a pyramidal geometry in bridging ligands like thiolates[28,29] and phosphino sulfides [25] with a Pt−S−Pt angle close to 100°,[30] a bidentate S L ligand must possess some specific structural features in order to form stable Pt^{II} complexes of structure:



In our case, where E = CH_3 and S^L = $Ph_2P(CH_2)_nPPh_2(S)$, the length of the methylene chain might be discriminating for the stability of the symmetrical dimer complexes. It seems, from our experimental data, that in the case of dppmS, only one sulfur bridge can be borne, because closing the Pt_2S_2 core with the second sulfur would result in a hinge distortion unfavourable for these types of compounds.[27]

On the contrary, the more flexible six-membered platinacycles of the symmetric dimer **6** obtained with dppeS, better fit into the geometrical constraints imposed by the planar core structure and the pyramidality of the bridging sulfur atom.

Such a hypothesis seems to be confirmed by studies carried out by Dervisi on Ni^{II}, Pd^{II}, Pt^{II} complexes of the related ligand 1-(diphenylphosphanyl)butane-2-thiolate (PS^-). It was found, in fact, that, under suitable conditions Ni^{II} and Pd^{II} formed sulfur bridged dimeric complexes of formula $[Ni(PS)Cl]_2$ and $[Pd(PS)Cl]_2$, both containing two five-membered metallacycles [31] whereas, attempts to prepare the analogous Pt^{II} complex were unsuccessful, leading only to the $[Pt(PS)_2]$ monomeric species.[32]

When CD_2Cl_2 solutions of **3** and **4** were exposed to an atmospheric pressure of carbon monoxide at room temperature, a fast reaction took place leading to carbonyl complexes **7a** and **8a** (Scheme 2) as evidenced by the appearance, in the IR spectra, of strong $\tilde{\nu}_{CO}$ bands at 2113 and 2112 cm^{-1}, respectively. The corresponding carbonyl resonances of **7a** and **8a** in the $^{13}C\{^1H\}$ NMR spectrum appear as doublets of doublets due to couplings with inequivalent P atoms, and are centred at δ = 177.7 and δ = 176.2 ppm, respectively.

The multinuclear NMR spectra of the reaction solution of **3** under CO ($P_{atm.}$) recorded every 2 days for one week showed the progressive isomerisation of **7a** into **7b** (Scheme 2). In fact the decrease of $^{31}P\{^1H\}$ NMR signals at δ = 25.3 and δ = 59.3 ppm attributed to the coordinated P and P(S) atoms of **7a,** respectively, was observed. Simultaneously new signals at δ = 31.2 and δ = 67.9 ppm [*J*(P,P) 72 Hz] appeared and were attributed to **7b**. The relatively low value of the ^1J(P,Pt) found for **7b** (1556 Hz) strongly supports the structure with the methyl group *trans* to the P atom. Comparable ^1J(P,Pt) are found for coordinated P atoms *trans* to CH_3 groups in complexes of formula $[(P\ P)Pt(Me)CO]^+$ [P P = 1,3-(diphenylphosphanyl)propane, ^1J(P,Pt) = 1593 Hz,[33] P P = BINAP, ^1J(P,Pt) = 1735 Hz .[19]]

The $^{13}C\{^1H\}$ NMR spectra of **7b** and **8b** show the carbonyl resonances at δ = 168.6 and δ = 167.9 ppm, respectively.

Figure 4 shows the $^{13}C\{^1H\}$ and $^{195}Pt\{^1H\}$ spectra of the CD_2Cl_2 reaction solution after carbonylation of **3** at two different times demonstrating the progressive enrichment in **7b**.

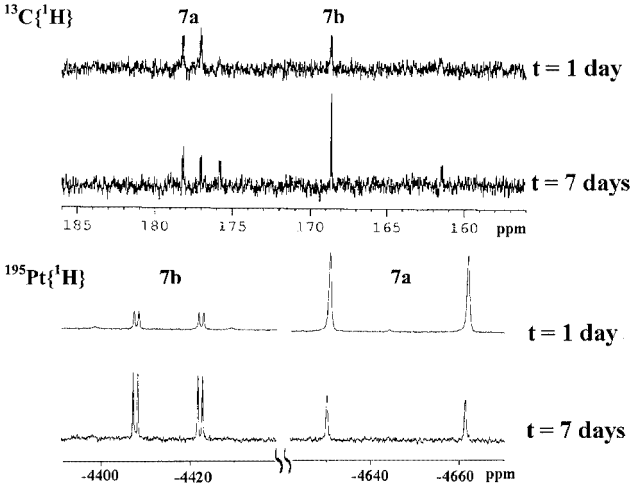
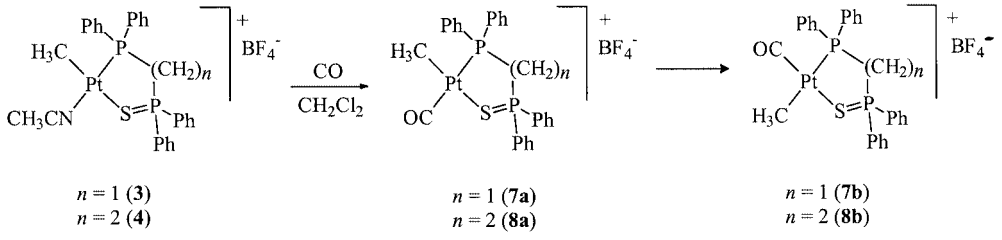


Figure 4. $^{13}C\{^1H\}$ (125 MHz) and $^{195}Pt\{^1H\}$ (107 MHz) NMR spectra (298 K, CD_2Cl_2) of the reaction solutions obtained by carbonylation of **3** recorded after 1 day (top traces) and after 7 days (lower traces)

An analogous behaviour was observed in the carbonylation of the cationic complex **4** which results in the immediate formation of **8a** that slowly isomerises into **8b** (Scheme 2). Table 3 summarises selected spectroscopic features of **7a**−**b** and **8a**−**b**.



n = 1 (**3**)
n = 2 (**4**)

n = 1 (**7a**)
n = 2 (**8a**)

n = 1 (**7b**)
n = 2 (**8b**)

Scheme 2. Carbonylation of **3** and **4**

Table 3. $^{31}P\{1H\}$ and $^{195}Pt\{1H\}$ NMR spectroscopic data (δ, ppm) of **7a**−**b** and **8a**−**b**

	δ(P)	δ[P(S)]	δ(Pt)	*J*(P,P) Hz	^1J(P,Pt) Hz	^2J(P,Pt) Hz
7a	25.3	59.3	−4646	33	3336	20
7b	31.2	67.9	−4415	72	1556	113
8a	13.8	43.1	−4560	[a]	3372	55
8b	3.6	40.8	−4328	31	1576	105

When acetonitrile solutions of **3** or **4** were exposed to CO at ambient conditions, the CH_3CN excess prevented the carbonylation reaction.

Conclusion

Methyl chloro platinum(II) complexes with the heteroditopic dppmS and dppeS ligands have been prepared and characterised. Chloride abstraction from the neutral complexes carried out in acetonitrile leads to the formation of the solvento species, which have been isolated in the pure state. Loss of acetonitrile, which leads to dimeric species, has been studied both in solution and in the solid state. In the case of the dppeS, the symmetric dimer **6** could be obtained by heating the corresponding acetonitrile complex under vacuum. This reaction represents an interesting example of clean solid state molecular rearrangement. The type of dimer formed in solution by loss of acetonitrile (mono bridged or dibridged) has been found to be strictly related to the number of the methylene groups in the ligand backbone. Carbonyl complexes obtained by substitution of acetonitrile with CO have also been synthesised and their isomerisation reactions, in solution, have been studied.

Experimental Section

General Remarks: All manipulations were carried out using standard Schlenk techniques under nitrogen as inert gas. Acetonitrile, dichloromethane, diethyl ether and *n*-hexane were dried and distilled under nitrogen; $AgBF_4$ and Celite™ were purchased from Fluka. NMR spectra in solution were recorded at 298 K on a Bruker AM 500 or a Bruker Avance DRX500 spectrometer (CARSO) or a Varian Mercury 300; frequencies are referenced to Me_4Si (^1H, ^{13}C), 85% H_3PO_4 (^{31}P), H_2PtCl_6 (^{195}Pt) and $CFCl_3$ (^{19}F). IR spectra were recorded with a Bruker Vector 22 FT instrument. C, H, N and S elemental analyses were carried out on a Eurovector CHNS-O Elemental Analyser. Cl elemental analyses were performed by potentiometric titration using a Metrohm DMS Titrino.

LC-MS analyses were performed with an Agilent HPLC system equipped with DAD, autosampler and MS systems (Agilent 1100 LC-MS SL series). All samples were dissolved in the same HPLC-grade solvent, which was used as eluent. The used interfaces were APCI or ESI for neutral complexes and ESI for cationic complexes. APCI conditions: negative ion mode, flow rate 0.5 mL/min, nitrogen as nebulizing and drying gas, nebulizer pressure 60 psi, vaporizer temperature 350 °C, corona current 25 μA, drying gas flow 5 L/min, drying gas temperature 300 °C (unless otherwise specified), capillary voltage 4000 V. ESI conditions: positive ion mode, flow rate 0.5 mL/min, nitrogen as nebulizing and drying gas, nebulizer pressure 30 psi, drying gas flow 13 L/min, capillary voltage 4000 V. The fragmentor voltage was varied from 0 to 400 V by 50 V increments in order to obtain clean and intense spectra. Other optimal conditions are specified below for each complex. Mass spectrometry data were acquired in the Scan mode (mass range m/z = 50−3000).

The ligands dppmS and dppeS have been prepared by the procedure described in ref.[17]

The complex [(cod)Pt(CH_3)Cl] was synthesised according to ref.[18]

Synthesis of [(P^P(S)Pt(CH_3)(Cl)] 1 and 2: A solution of bis(phosphanyl) monosulfide [hereafter denoted as P^P(S)] in CH_2Cl_2 was added to a CH_2Cl_2 solution containing an equimolar amount of [(cod)Pt(CH_3)Cl], kept under vigorous stirring at room temperature. After 3 h the solvent was evaporated to ca. one fifth of the volume and addition of *n*-hexane caused the precipitation of the desired complexes as white solids. Filtration followed by washings with 3 × 5 mL *n*-hexane and drying in vacuo afforded **1** and **2** in high yield. Scales and analytical data are given below.

Synthesis of [(P^P(S)Pt(CH_3)(CH_3CN)]BF_4 3 and 4: A solution of silver tetrafluoroborate in CH_3CN was added dropwise to a suspension containing an equimolar amount of [(P^P(S)Pt(CH_3)(Cl)] in CH_3CN kept under vigorous stirring at room temp. in the dark. The mixture was stirred for 10 minutes at room temp. and the suspension was then filtered through Celite™, obtaining a colourless solution which was evaporated to dryness in vacuo. The solid was washed with diethyl ether (2 × 10 mL) and dried in vacuo. Scales and analytical data are given below.

Synthesis of *af*-Dimethyl-*bd,ec*-bis{(diphenylphosphanylethyl-κ*P*)-diphenylphosphanyl Sulfide, μ-κ*S*)}diplatinum(II) Bis(tetrafluoroborate) [μ-(dppeS)Pt(CH_3)]$_2$[BF_4]$_2$ (6): Solid **4** (50 mg, 0.065 mmol) was heated under high vacuum in a Schlenk tube at 90 °C for 30 h obtaining a white solid (47 mg) consisting of pure dimer **6**. Crystallisation from slow evaporation of a CD_2Cl_2 solution gave colourless crystals suitable for XRD analysis. M.p. 169 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3056 (w), 2962 (w), 2886 (w), 1482 (m), 1437 (s), 1261 (m), 1060 (vs, br., BF_4^-), 997 (s), 803 (m), 750 (m), 692 (s), 532 (s, P=S), 488 (w) cm^{-1}. LC-MS: exact mass calcd. for the dication $C_{54}H_{54}P_4Pt_2S_2$: 1280.2 amu. ESI; found 1315 $[M + Cl]^+$, 640 $[M/2]^+$. $C_{54}H_{54}B_2F_8P_4Pt_2S_2$: calcd. C 44.58, H 3.74, S 4.41; found C 44.80, H 3.81, S 4.38. ^1H NMR (500 MHz, CD_2Cl_2): δ = −0.13 [d, ^3J(H,P) = 3.2, ^2J(H,Pt) = 66.4 Hz, 6 H, 2 CH_3], 3.21 [m, 4 H, P(S)CH_2CH$_2$P], 2.95 [m, 4 H, P(S)CH$_2$CH_2P], 7.45−8.18 (m, 40 H, $H_{arom.}$) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ = 1.9 [br. s, ^1J(C,Pt) = 624 Hz, CH_3], 21.1 [dd, ^1J(C,P) = 43, ^2J(C,P) = 6 Hz, P−CH_2CH$_2$−P(S)], 26.8 [br. d, ^1J(C,P) = 53 Hz, P−CH$_2$−CH_2−P(S)], 129.7 (s), 129.8 (s), 130.5 (s), 130.7 (s), 132.9 [d, ^2J(C,P) = 3 Hz], 133.4 [d, ^1J(C,P) = 11 Hz], 133.6 [d, ^2J(C,P) = 11 Hz], 135.7 [d, ^1J(C,P) = 3 Hz] ppm.

***a*-Chloro-*b*-methyl-*cd*-{(diphenylphosphanylmethyl)diphenylphosphanyl Sulfide-κ^2-*P*,*S*}platinum(II) (1):** Scale and yield: dppmS, (384 mg, 0.92 mmol) in 9 mL CH_2Cl_2; [(cod)Pt(CH_3)(Cl)], (326 mg, 0.92 mmol) in 3 mL CH_2Cl_2; yield: 570 mg (94%). M.p. 151 °C (dec). IR (KBr): $\tilde{\nu}$ = 3067 (m), 2966 (m), 2899 (m), 2798 (w), 1484 (m), 1434 (vs), 1100 (vs), 995 (m), 800 (s), 738 (vs), 725 (vs), 683 (vs) 585 (s, P=S str.), 536 (s), 503 (s), 494 (s), 276 (m, Pt-Cl) cm^{-1}. LC-MS: exact mass calcd. for $C_{26}H_{25}ClP_2PtS$: 661.05 amu; APCI;

found 697 [M + Cl]$^-$; 661 [M]$^-$. $C_{26}H_{25}ClP_2PtS{\cdot}CH_2Cl_2$: calcd. C 43.4, H 3.64, S 4.3; found C 43.6, H 3.53, S 4.4. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.42 [d, ^3J(H,P) = 3.9, ^2J(H,Pt) = 73.3 Hz, 3 H, CH_3], 3.87 [pseudo-t, ^2J(H,P) = 10.3, ^3J(H,Pt) = 44.8 Hz, 2 H, CH_2], 7.31 (m, 4 H_{meta} of Ph_2P-Pt), 7.34−7.41 [m, 4 H_{meta} of $Ph_2P(S)-Pt$ overlapped with 2 H_{para} of Ph_2P-Pt], 7.48 [m, 2 H_{para} of $Ph_2P(S)-Pt$], 7.58 (m, 4 H_{ortho} of Ph_2P-Pt), 7.68 [m, 4 H_{ortho} of $Ph_2P(S)-Pt$] ppm. ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ = −5.7 [d, ^2J(C,P) = 8, ^1J(C,Pt) = 628 Hz, CH_3], 42.8 [dd, ^1J(C,P) = 56, ^1J(C,P), CH_2], 128.8 (s), 128.9 (s), 129.4 (s), 129.5 (s), 131.6 [d, ^2J(C,P) = 2 Hz], 132.1 [d, ^1J(C,P) = 11 Hz], 133.3 [d, ^2J(C,P) = 3 Hz], 133.8 [d, ^1J(C,P) = 12, ^2J(C,Pt) = 38 Hz] ppm.

***a*-Chloro-*b*-methyl-*cd*-{(diphenylphosphanylethyl)diphenylphosphanyl Sulfide-κ^{2}P,S}platinum(II) (2):** Scale and yield: dppeS, (511 mg, 1.20 mmol) in 10 mL CH_2Cl_2; [(cod)Pt(CH_3)(Cl)], (425 mg, 1.20 mmol) in 4 mL CH_2Cl_2; yield: 738 mg (91%). M.p. 173 °C (dec). IR (KBr): ṽ = 3051 (m), 2936 (m), 2885 (m), 1482 (m), 1438 (vs), 1102 (vs), 1001 (m), 818 (s), 726 (vs), 670 (vs), 591 (s, P=S str.), 532 (s), 518 (s), 488 (m), 273 (m, Pt-Cl) cm^{-1}. LC-MS: exact mass calcd. for $C_{27}H_{27}ClP_2PtS$: 675.06 amu; APCI; found 710 [M + Cl]$^-$; 695 [M + Cl − CH_3]$^-$. ESI; found 681 [M − Cl + CH_3CN]$^+$, 640 [M − Cl]$^-$. $C_{27}H_{27}ClP_2PtS$: calcd. C 48.0, H 4.03, Cl 5.24, S 4.7; found C 49.1, H 3.96, Cl 5.11, S 4.3. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.39 [d, ^3J(H,P) = 4.6, ^2J(H,Pt) = 74.2 Hz, 3 H, CH_3], 2.65−2.85 [m, 4 H, CH_2-CH_2], 7.35−7.90 [20 H, $H_{arom.}$] ppm. ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ = −3.55 [d, ^2J(C,P) = 7, ^1J(C,Pt) = 649 Hz, CH_3], 22.4 [dd, ^1J(C,P) = 40, ^2J(C,P) = 4 Hz, P−CH_2CH_2−P(S)], 25.6 [d, ^1J(C,P) = 54 Hz, P−CH_2CH_2−P(S)], 128.7 (s), 128.8 (s), 129.4 (s), 129.5 (s), 131.2 [d, ^2J(C,P) = 3 Hz], 131.7 [d, ^1J(C,P) = 10 Hz], 133.1 [d, ^2J(C,P) = 3 Hz], 133.6 [d, ^1J(C,P) = 10, ^2J(C,Pt) = 34 Hz] ppm.

***a*-Acetonitrile-*b*-methyl-*cd*-{(diphenylphosphanylmethyl)diphenylphosphanyl Sulfide-κ^2-*P,S*)}platinum(II) Tetrafluoroborate (3):** Scale and yield: [(dppmS)Pt(CH_3)(Cl)], (528 mg, 0.80 mmol) in 30 mL CH_3CN; $AgBF_4$, (156 mg, 0.80 mmol) in 25 mL CH_3CN; yield: 494 mg (92%). IR (KBr): ṽ = 3069 (m), 2952 (s), 2869 (s), 2324 (w, CN), 2304 (w, CN), 1486 (m), 1432 (s), 1062 (vs, br, BF_4^-), 789 (vs), 736 (vs), 682 (vs), 580 (m, P=S str.), 545 (s), 490 (s), 360 (m) cm^{-1}. M.p. 163 °C (dec). LC-MS: exact mass calcd. for the cation $C_{28}H_{28}NP_2PtS$: 667.11 amu. ESI; found 667 [M]$^+$; 626 [M − CH_3CN]$^+$. $C_{28}H_{28}BF_4NP_2PtS$: calcd. C 44.6, H 3.74, N 1.9, S 4.2; found C 44.9, H 3.87, N 1.0, S 4.7, Cl absent. The following spectroscopic features refer to the exchange product obtained in CD_3CN. ^{1}H NMR (500 MHz, CD_3CN): δ = 0.36 [d, ^3J(H,P) = 3.4, ^2J(H,Pt) = 70.3 Hz, 3 H, CH_3], 4.23 [psudo-t, ^2J(H,P) = 11.3, ^3J(H,Pt) = 46.3 Hz, 2 H, CH_2], 7.30−7.75 [m, 20 H, $H_{arom.}$] ppm. ^{13}C{^{1}H} NMR (125 MHz, CD_3CN): δ = −7.6 [d, ^2J(C,P) = 6, ^1J(C,Pt) = 606 Hz, CH_3], 40.0 [dd, ^1J(C,P) = 52, ^1J(C,P) = 33 Hz, CH_2], 129.8 (s), 129.9 (s), 130.1 (s), 130.2 (s), 132.6 [d, ^2J(C,P) = 11 Hz], 133.1 (br. S), 134.5 (2 C overlapped) ppm. ^{31}P{^{1}H} NMR (202 MHz, CD_3CN): δ = 14.9 [d, ^2J(P,P) = 21, ^1J(P,Pt) = 4639 Hz Ph_2P], 53.0 [d, ^2J(P,P) = 21, ^2J(P,Pt) = 37 Hz, $Ph_2P(S)$] ppm. ^{195}Pt{^{1}H} NMR (107 MHz, CD_3CN): δ = −4532 [br. d, ^1J(P,Pt) = 4639 Hz] ppm.

***a*-Acetonitrile-*b*-methyl-*cd*-{(diphenylphosphanylethyl)diphenylphosphanyl Sulfide-κ^{2}P,S}platinum(II) Tetrafluoroborate (4):** Scale and yield: [(dppeS)Pt(CH_3)(Cl)]: (690 mg, 1.04 mmol) in 35 mL CH_3CN; $AgBF_4$: (202 mg, 1.04 mmol) in 30 mL CH_3CN; yield: 719 mg of **4** (90%). IR (KBr): ṽ = 3063 (m), 2938 (m), 2894 (m), 2330 (w, CN), 2300 (w, CN), 1484 (m), 1436 (s), 1038 (vs, br, BF_4^-), 812 (m), 751 (s), 697 (vs), 586 (s, P=S str.), 538 (vs), 495 (s) cm^{-1}. M.p. 138 °C (dec). LC-MS: exact mass calcd. for the cation $C_{29}H_{30}NP_2PtS$: 681.12 amu. ESI; found 681 [M]$^+$; 640 [M − CH_3CN]$^+$. $C_{29}H_{30}BF_4NP_2PtS$: calcd. C 45.3, H 3.94, N 1.8, S 4.2; found C 44.8, H 3.86, N 1.5, S 3.5, Cl absent. The following spectroscopic features refer to the exchange product obtained in CD_3CN. ^{1}H NMR (500 MHz, CD_3CN): δ = 0.24 [dd, ^2J(H,Pt) = 72.0, ^3J(H,P) = 3.5, ^4J(H,P) = 1.5 Hz, 3 H, CH_3], 2.96 (m, 4 H, CH_2CH_2), 7.45−7.85 (m, 20 H, $H_{arom.}$) ppm. ^{13}C{^{1}H} NMR (125 MHz, CD_3CN): δ = −5.3 [d, ^2J(C,P) = 6, ^1J(C,Pt) = 627 Hz, CH_3], 21.9 [dd, ^1J(C,P) = 44, ^2J(C,P) = 4 Hz, P−CH_2CH_2−P(S)], 25.1 [d, ^1J(C,P) = 55 Hz, P−CH_2−CH_2−P(S)], 129.6 (s), 129.7 (s), 130.2 (s), 130.3 (s), 132.0 [d, ^2J(C,P) = 10 Hz], 132.5 [d, ^2J(C,P) = 3 Hz], 134.0 [d, ^1J(C,P) = 11, ^2J(C,Pt) = 36 Hz], 134.2 [d, ^2J(C,P) = 3 Hz] ppm. ^{31}P{^{1}H} NMR (202 MHz, CD_3CN): δ = 6.8 [s, ^1J(P,Pt) = 4620 Hz, Ph_2P], 41.2 [s, ^2J(P,Pt) = 46, ^2J(P,Pt) = 55 Hz, $Ph_2P(S)$] ppm. ^{195}Pt{^{1}H} NMR (107 MHz, CD_3CN): δ = −4505 [br. d, ^1J(P,Pt) = 4614 Hz] ppm.

Spectroscopic Features of 5: See Figure 3 for atom numbering. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.06 [d, ^3J(H,P) = 3.9, ^2J(H,Pt) = 66 Hz, CH_3 *cis* to bridging S], 0.74 [d, ^3J(H,P) = 3.0, ^2J(H,Pt) = 64 Hz, CH_3 *cis* to CH_3CN], 2.54 (s, coord. CH_3CN), 4.88 [ps t, ^2J(H,P) = 11 Hz, CH_2 of the bridging dppmS], 4.11 [ps t, ^2J(H,P) 11 Hz, CH_2 of the non-bridging dppmS], 7.22−7.89 [m, $H_{arom.}$] ppm. ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ = −4.8 [br. s, ^1J(C,Pt) = 598 Hz, Pt^2-CH_3], −2.9 [br. s, ^1J(C,Pt) = 588 Hz, Pt^1-CH_3], 36.6 [dd, ^1J(C,P) = 49, ^1J(C,P) = 32 Hz, $P^3CH_2P^4$, 39.7 [dd, ^1J(C,P) = 51, ^1J(C,P) = 31 Hz, $P^1CH_2P^2$], 125−135 [$C_{arom.}$] ppm. ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ = 12.8 [d, ^2J(P,P) = 20, ^1J(P,Pt) = 4724 Hz, P^3], 22.3 [dd, ^2J(P,P) = 28, ^3J(P^1-P^4) = 4, ^1J(P,Pt) = 4469 Hz, P^1], 52.0 [dd, ^2J(P,P) = 20, ^3J(P^1-P^4) = 4 Hz, P^4], 52.1 [d, ^2J(P,P) = 28 Hz, P^2] ppm. ^{195}Pt{^{1}H} NMR (107 MHz, CD_2Cl_2): δ = −4502 [br. d, ^1J(P,Pt) = 4469 Hz, Pt^1]. δ = −4512 [br. d, ^1J(P,Pt) = 4724 Hz, Pt^2] ppm.

Carbonylation of 3 and 4: The complexes **3** and **4** were dissolved in CD_2Cl_2 (≈ 10 mg in 0.6 mL) in an NMR tube connected with a CO/vacuum manifold. The solution, kept at room temp., was exposed to an atmospheric pressure of carbon monoxide and followed for two weeks by multinuclear NMR spectroscopy.

^{31}P{^{1}H} and ^{195}Pt{^{1}H} NMR features for **7a**−**b** and **8a**−**b** are collected in Table 4.

LC-MS for **7**: Exact mass calcd. for the cations $C_{27}H_{25}OP_2PtS$: 654.07 amu. ESI; found 654 [M]$^+$, 626 [M − CO]$^+$.

LC-MS for **8**: exact mass calcd. for the cations $C_{28}H_{27}OP_2PtS$: 668.09 amu. ESI; found 668 [M]$^+$, 640 [M − CO]$^+$.

***a*-Carbonyl-*b*-methyl-*cd*-{(diphenylphosphanylmethyl)diphenylphosphanyl Sulfide-*P,S*}platinum(II) Tetrafluoroborate (7a):** IR (CD_2Cl_2): ṽ= 2113 (CO) cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.75 [d, ^2J(H,Pt) = 72.3, ^3J(H,P) = 6.4 Hz, 3 H, CH_3], 4.31 [m, 4 H, CH_2CH_2], 7.40−7.81 [m, 20 H, $H_{arom.}$] ppm. ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ = −10.1 [d, ^2J(C,P) = 5, ^1J(C,Pt) = 502 Hz, CH_3], 38.4 [dd, ^1J(C,P) = 52, ^2J(C,P) = 31 Hz, CH_2], 129.8 (2 C overlapped), 129.9 (2 C overlapped), 132.3 [d, ^2J(C,P) = 11 Hz], 133.2 [d, ^1J(C,P) = 3 Hz], 134.2 [d, ^2J(C,P) = 12, ^2J(C,Pt) = 28 Hz], 134.3 [d, ^1J(C,P) = 3 Hz,], 177.7 [dd, ^2J(C,P) = 145, ^3J(C,P) = 12, ^1J(C,Pt) = 1582 Hz, CO] ppm.

***a*-Carbonyl-*b*-methyl-*dc*-{(diphenylphosphanylmethyl)diphenylphosphanyl Sulfide-*P,S*}platinum(II) Tetrafluoroborate (7b):** IR (CD_2Cl_2): ṽ = 2090 (CO) cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.34 [dd, ^2J(H,Pt) = 57.7, ^3J(H,P) = 6.4, ^4J(H,P) = 0.6 Hz, 3 H, CH_3], 4.50 [m, 4 H, CH_2CH_2], 7.42−7.86 [m, 20 H, $H_{arom.}$] ppm. ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ = −7.3 [dd, ^2J(C,P) = 73, ^3J(C,P) = 15 Hz,^1J(C,Pt) = 381 Hz, CH_3], 34.1 [dd, ^1J(C,P) =

Table 4. Crystal data and structure refinement for **1**·CD_2Cl_2 and **6**·2CD_2Cl_2

	1·CD_2Cl_2	**6**·2CD_2Cl_2
Empirical formula	$C_{27}H_{25}D_2Cl_3P_2PtS$	$C_{56}H_{54}D_4B_2Cl_4F_8P_4Pt_2S_2$
Molecular mass	748.97	1628.28
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	8.8991(5)	10.966(5)
b (Å)	16.6324(9)	11.919(5)
c (Å)	20.1000(11)	12.984(5)
α [°]	90	79.459(9)
β [°]	102.4610(10)	65.545(10)
γ [°]	90	87.527(10)
Volume	2905.0(3) Å^3	1517.6(11) Å^3
Z	4	1
Density (calculated)	1.708 g/cm^3	1.782 g/cm^3
Absorption coefficient	5.303 mm^{-1}	5.016 mm^{-1}
F(000)	1456	792
Crystal size	0.36 × 0.25 × 0.13 mm	0.26 × 0.19 × 0.06 mm
θ range for data collection	1.60° ≤ θ ≤ 28.35°	2.04° ≤ θ ≤ 28.43°
Index ranges	−11≤ h ≤ 9, −21≤ k ≤ 22, −26 ≤ l ≤ 26	−14≤ h ≤ 14, −15≤ k ≤ 15, −17 ≤ l ≤ 17
Reflections collected	23079	21037
Independent reflections	7220 [R(int) = 0.0605]	7570 [R(int) = 0.1033]
Data/parameters	7220/308	7570/352
Goodness-of-fit on F^2	0.989	1.068
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0468	R_1 = 0.0745
Final wR_2 indices (all data)	wR_2 = 0.0842	wR_2 = 0.1594
Largest diff. Peak and hole	1.395 and −0.783 eÅ^{-3}	2.721 and −2.857 e·Å^{-3} (close to Pt)

51, ^2J(C,P) = 25 Hz, CH_2], 129.9 (s), 130.0 (2 C overlapped), 130.1 (s), 132.3 [d, ^2J(C,P) = 11 Hz], 133.0 [d, ^1J(C,P) = 3 Hz], 133.4 [d, ^2J(C,P) = 13, ^2J(C,Pt) = 14 Hz], 134.7 [d, ^1J(C,P) = 3 Hz,] 168.6 [d, J(C,P) = 8, ^1J(C,Pt) = 1815 Hz, CO] ppm.

***a*-Carbonyl-*b*-methyl-*cd*-{(diphenylphosphanylethyl)diphenylphosphanyl Sulfide-*P,S*}platinum(II) Tetrafluoroborate (8a):** IR (CD_2Cl_2): ṽ= 2112 (CO) cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.57 [dd, ^2J(H,Pt) = 74.3, ^3J(H,P) = 6.4, ^4J(H,P) = 1.0 Hz, 3 H, CH_3], 3.20 [m, 4 H, CH_2CH_2], 7.52−7.84 [m, 20 H, $H_{arom.}$] ppm. ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ = −8.0 [d, ^2J(C,P) = 5, ^1J(C,Pt) = 528 Hz, CH_3], 21.0 [dd, ^1J(C,P) = 40, ^2J(C,P) = 5 Hz, P−CH$_2$CH$_2$−P(S)], 25.1 [dd, ^2J(C,P) = 2 Hz ^1J(C,P) = 54 Hz, P−CH$_2$−CH$_2$−P(S)], 129.8 (s), 129.9 (s), 130.1 (s), 130.2 (s), 131.6 [d, ^2J(C,P) = 11 Hz], 133.0 [d, ^1J(C,P) = 3 Hz], 134.0 [d, ^2J(C,P) = 11, ^2J(C,Pt) = 25 Hz], 134.3 [d, ^1J(C,P) = 3 Hz,], 176.2 [dd, ^2J(C,P) = 148, ^3J(C,P) = 2 Hz; ^1J(C,Pt) = 1392 Hz, CO] ppm.

***a*-Carbonyl-*b*-methyl-*dc*-{(diphenylphosphanylethyl)diphenylphosphanyl Sulfide-P,S}platinum(II) Tetrafluoroborate (8b):** IR (CD_2Cl_2): ṽ = 2096 (CO) cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.28 [d, ^2J(H,Pt) = 55.4, ^3J(H,P) = 6.5 Hz, 3 H, CH_3], 3.40 [m, 4 H, CH_2CH_2], 7.46−7.89 [m, 20 H, $H_{arom.}$] ppm. ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ = 2.5 [dd, ^2J(C,P) = 75, ^3J(C,P) = 7 Hz,,^1J(C,Pt) = 358 Hz, CH_3], 21.2 [dd, ^1J(C,P) = 31, ^2J(C,P) = 5 Hz, P−CH$_2$CH$_2$−P(S)], 25.2 [d, ^1J(C,P) = 50, ^3J(C,Pt) = 17 Hz, P−CH$_2$−CH$_2$−P(S)], 130.0 (s), 130.1 (s), 130.3 (s), 130.4 (s), 132.1 [d, ^2J(C,P) = 11 Hz], 132.7 [d, ^1J(C,P) = 3 Hz], 133.1 [d, ^2J(C,P) = 12, ^2J(C,Pt) = 13 Hz], 134.7 [d, ^1J(C,P) = 3 Hz,], 167.9 [d, J(C,P) = 7 Hz; ^1J(C,Pt) = 1859 Hz, CO] ppm.

MS Analyses: All complexes were submitted for LC-MS analyses by using APCI and API-ES sources and positive and negative ionisation modes at different fragmentor voltages. The negative APCI spectrum of **1** in dichloromethane gave a very intense base peak at m/z = 697 [M + Cl]$^-$ (fragmentor voltage: 0 V). Increasing the fragmentor voltage the intensity of the [M + Cl]$^-$ ion decreased with the concomitant appearance of the [M]$^-$ ion (m/z = 661). At 200 V the base peak is represented by [M]$^-$ ion and the [M + Cl]$^-$ ion disappeared. The negative APCI mass spectrum of a dichloromethane solution of **2** displayed the [M + Cl]$^-$ ion (m/z = 710) and [M + Cl − CH_3]$^-$ (m/z = 695) at a fragmentor voltage of 100 V. Using CH_3CN as solvent and the ESI interface (positive ions) at a fragmentor voltage of 120 V the [M − Cl + CH_3CN]$^+$ (m/z = 681) and [M − Cl]$^+$ ions (m/z = 640, 100% relative abundance) were detected.

Complex **3** was first dissolved and analysed in acetonitrile. ESI-MS spectra were acquired in positive ion mode at a drying gas temperature of 300 °C. At a fragmentor voltage of 0 V the spectrum is dominated by a peak at m/z = 667 which corresponds to the cationic part of the complex [M]$^+$$BF_4^-$. A base peak at m/z = 626 was observed at fragmentor 200 V corresponding to the [M − CH_3CN]$^+$ ion due to the loss of a coordinated acetonitrile molecule. The use of dichloromethane as solvent (and eluent) for **3** and a fragmentor voltage of 350 V confirmed the presence of [M]$^+$ and [M − CH_3CN]$^+$ ions and showed the appearance of a new peak at m/z = 1287 attributable to the dimeric cation [2M − 2CH_3CN + Cl]$^+$. The latter ion may arise from complex **5,** which is formed by dissolving **3** in CH_2Cl_2, after substitution of a chloride for the coordinated acetonitrile. The relative abundance of the peak at m/z = 1287 passed from 5.0% to 10.0% lowering the 300 °C drying gas temperature down to 100 °C.

The mass spectrometric behaviour of **4** was similar to that of its homologue **3**. The base peak of ESI-MS spectra of **4** in acetonitrile was the [M]$^+$ ion (m/z = 681) at fragmentor voltages in the range

0−100 V. At 150 V the base peak was represented by the $[M - CH_3CN]^+$ ion (m/z = 640). The dichloromethane solution of **4** showed, in the 0−350V fragmentor voltage range, the m/z = 1315 ion corresponding to the cationic part of **6** (which is formed by dissolving **4** in CH_2Cl_2) plus a chloride ion.

The positive ESI-MS spectra of pure **6** were acquired in dichloromethane and were analyzed under the same conditions applied for **4**. The $[M + Cl]^+$ ion (m/z = 1315) was observed in the 0−350V fragmentor voltage range whereas the m/z = 640 peak, corresponding to the monocharged halfed dimer was the most intense peak in the fragmentor voltage range 0−100 V.

Chloride adduct formation is a consequence of the use of dichloromethane. No evidence of doubly charged ions was found: the strong tendency of the dicationic species to form single charged adducts in the presence of the above mentioned negative ions probably represents the optimal ionization pathway.

The positive ESI-MS spectra of dichloromethane solutions of carbonyl species **7** and **8** were acquired under the same conditions reported for **3** and showed intense $[M]^+$ ions (m/z = 654 for **7**, m/z = 668 for **8**) in the fragmentor voltage range 0−200 V. At 250 V the loss of the CO molecule gave the $[M - CO]^+$ ions (m/z = 626 for **7**, m/z = 640 for **8**) as base peaks.

X-ray Structure Determinations of 1·CD_2Cl_2 and 6·2CD_2Cl_2:[34] Single crystals were obtained by slowly evaporating solutions of the compounds in CD_2Cl_2. The stoichiometries of the resulting solvates were **1**·CD_2Cl_2 and **6**·2CD_2Cl_2. Data were collected at room temperature with a Bruker SMART D8 goniometer equipped with an APEX detector. The structures were solved by direct methods.[35] The final structure model with anisotropic displacement parameters for all non-hydrogen atoms and H atoms riding in idealized positions was refined on F^2.[36] Crystal data, parameters of data collection, and convergence results are compiled in Table 4. Table 2 summarises selected bond lengths and angles.

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