DOI: 10.1002/ejic.201100943

Platinum(II) Complexes Bearing a Thiolate/Thioether Ligand – Hemilability vs. Dealkylation

Fabrice Guyon,*^[a] Michael Knorr,^[a] Aurélie Garillon,^[b] and Carsten Strohmann^[c]

Keywords: Platinum / S ligands / Coordination modes / C-S activation

Substitution of the chloro ligands of cis-[Pt(PEt₃)₂Cl₂] by 4methylthio-2-thioxo-1,3-dithiole-5-thiolate (L) leads to the thiolato complexes trans-[Pt(PEt₃)₂ClL] (2) and trans- $[Pt(PEt_3)_2L_2]$ (1), which have been characterised by X-ray crystallography. In the solid state, the square planar arrangement is capped by an endocyclic sulfur atom of L, which gives rise to distorted square-pyramidal and pseudooctahedral geometries for 2 and 1, respectively. Complex 1 coexists in solution with $[Pt(PEt_3)(\eta^1-L)(\eta^2-L)]$ (3), which results from the reversible dissociation of one phosphane ligand. The combination of $\eta^1\mathchar`-(thiolato)$ and $\eta^2\mathchar`-(thiolato/thioether)$ L in 3has been established by variable-temperature ¹H NMR spectroscopy and crystal structure determination. The n²-coordination mode of **L** is also observed in $cis-[Pt(PEt_3)_2L]^+$ (4), which results from the abstraction of the chloro ligand of 2 by excess TIPF₆. An S-demethylation reaction occurs when 1 is heated in acetonitrile to yield the structurally-character-

Introduction

Hemilabile ligands are polydentate ligands that contain one or several donor functionalities, which firmly bind to the metal centre, and at least one substitutionally-labile donor functionality, which allows a reversible opening-closing mechanism upon addition of a substrate. This class of ligands has found increasing use in the design of catalysts and chemosensors.^[1] For this purpose, ligands that combine hard and soft donor atoms, such as $P \cap O$ and $P \cap N$, have been studied extensively. However, the combination of identical atoms that lie in different environments, such as the thiolate/thioether association, may also confer hemilabile properties. For example, this behaviour has been studied for an oxorhenium(V) complex coordinated by edtMe ($edtH_2$ = 1,2-ethanedithiol).^[2] In continuation of our previous studies that concerned the coordination chemistry of dithiolene and dithioether ligands,^[3] we are interested in mixed thioether/thiolate derivatives with a tetrathioethylene skeleton

282

ised dithiolene complex $[Pt(PEt_3)_2(dmit)]$ (5) $(dmit^{2-} = 2$ thioxo-1,3-dithiole-4,5-dithiolate) and MeL. Treatment of cis- $[Pt(PPh_3)_2\mathrm{Cl}_2]$ with 2 equiv. of L leads to a mixture of $[Pt(PPh_3)_2(dmit)]$ (6) and $[Pt(PPh_3)(\eta^1-L)(\eta^2-L)]$ (7). Complex 7 predominates in solution over its parent compound, $[Pt(PPh_3)_2L_2]$. The identification of CH₃Cl by ¹H NMR spectroscopy proves that [Pt(PPh₃)₂ClL] is involved as an intermediate in the demethylation process. The reaction of L with platinum precursors that are blocked in a cis arrangement by chelation of 1,1-bis(diphenylphosphanyl)methane (dppm) and 1,1-bis(diphenylphosphanyl)ethane (dppe) leads to the formation of the thiolato complexes cis-[Pt(η^2 -dppm)L₂] (8) and cis-[Pt(η^2 -dppe)L₂] (9). The solid-state structure of 8 reveals the occurrence of an additional weak interaction between a thiomethyl group and the platinum centre (Pt-S 3.073 Å).

as potential hemilabile ligands (Scheme 1). Although these systems exhibit attractive features, the literature on this family of ligands is limited.^[4] Compared to the properties of edtMe, their chelating ability is expected to be strengthened due to the entropic factors that result from the use of a rigid ethylene bridge between the thiolate and the thioether groups. Moreover, multiple accessible oxidation states are expected in sulfur-rich ligands with the tetrathiafulvalene framework.^[5] In these redox-active thiolate/thioether ligands, the binding properties could change as a function of their oxidation state. Ligands that allow electrochemical control over the binding properties have been termed redoxswitchable hemilabile ligands.^[6] With potential applications in catalysis or materials science in mind, we have undertaken a study of the synthesis and properties of squareplanar complexes with mixed thiolate/thioether ligands that possess a tetrathioethylene core. This paper reports the preparation and reactivity of platinum(II) complexes with hemilabile 4-methylthio-2-thioxo-1,3-dithiole-5-thiolate (Medmit⁻ = L). The parent dithiolene ligand, 2-thioxo-1,3dithiole-4,5-dithiolate (dmit2-), is one of the most studied dithiolene ligands and has applications in conducting materials.^[7] The coordinating ability and structural aspects of L have been studied by Olk et al. with several other transition metals.^[4a,4b] Its coordination mode has been identified as monodentate through the thiolate sulfur atom in (Ph₃P)₃-

 [[]a] Institut UTINAM, UMR CNRS 6213, Université de Franche-Comté, Faculté des Sciences et des Techniques, 16 Route de Gray, 25030 Besançon, France E-mail: fabrice.guyon@univ-fcomte.fr

[[]b] SERAC – UT Špectro, Technopole Temis, 18 rue Alain Savary, 25000 Besançon, France

[[]c] Anorganische Chemie, Technische Universität Dortmund, Otto-Hahn-Strasse 6, 44227 Dortmund, Germany

AgL, $(Ph_3P)_2AuL$, Cp_2TiL_2 , $(tmeda)ZnL_2$ [tmeda = 1,2bis(dimethylamino)ethane] and $(dppe)PdL_2$ [dppe = 1,2bis(diphenylphosphanyl)ethane], whereas the mixed thiolate/thioether ligand acts as a bidentate ligand in $(Ph_3P)_2$ -CuL. Interestingly, both coordination modes coexist in $(dppe)NiL_2$. To develop this topic further, our contribution focuses on the complexation of L with platinum(II). We investigated the reactivity of the coordinated ligand and the influence of the nature of the ancillary ligand on the coordination mode.



Scheme 1.

Results and Discussion

Substitution of Chlorine by L in cis-[Pt(PEt₃)₂Cl₂]

The reaction of *cis*-[Pt(PEt₃)₂Cl₂] with 2 equiv. of CsL in dichloromethane yielded *trans*-[Pt(PEt₃)₂L₂] (1) as an ochre, air-stable powder (Scheme 2). Complex 1 is highly soluble in halogenated solvents, but poorly soluble in acetone and methanol. A cyclic voltammetry study performed in CH₂Cl₂ showed that 1 is irreversibly oxidised at ca. 0.8 V vs. AgClO₄/Ag (0.1 M in MeCN). The hydrogen atoms of the thiomethyl groups appear as a singlet at 2.44 ppm in the ¹H NMR spectrum, which excludes any coupling in solution between these protons and the metal. The ³¹P{¹H} NMR spectrum of 1 displays a singlet at 12.5 ppm, and the

Eurjic eliropean journal of horganic Chemi

coupling constant ${}^{1}J_{P,Pt}$ of 2372 Hz is consistent with the trans configuration of the ligands around the platinum centre.^[8] Modification of the nature of the solvent, for example MeOH or acetone, had no influence on the configuration of the resulting material. Monomeric complexes of the type $[Pt(PR_3)_2(SR)_2]$ have already been studied in the context of cis-trans isomerisation.^[9] The formation of trans species has been observed during the substitution of chloro ligands by thiolate^[8a,10] and in solution for an isolated *cis*-[Pt(PR₃)₂-(SR)₂] complex.^[11] To gain more information about the isomerisation process that occurs during the formation of 1, we reacted L with an equimolar amount of cis-[Pt(PEt₃)₂-Cl₂], which was solubilised in acetone with a relatively high dilution. After 1 h of reaction at ambient temperature, trans- $[Pt(PEt_3)_2LCl]$ (2) was extracted into hexane from the unreacted starting material along with a small amount of 1. Upon cooling, 2 was isolated as yellow crystals. The ${}^{31}P{}^{1}H$ NMR spectrum of 2 shows an unique signal at 14.5 ppm, which is flanked by two satellites with ${}^{1}J_{\rm P,Pt}$ of 2387 Hz. These data are in agreement with two magnetically equivalent phosphorus ligands in a trans arrangement. ¹H NMR analysis reveals the presence of a singlet at 2.41 ppm. The integration ratio between this signal and those of the ethyl groups fits with the stoichiometry of 2. The cis-trans isomerisation may occur at the first stage of the substitution to minimise the steric hindrance between the two PEt₃ ligands. The five-coordinate intermediate that results from the associative activation in square-planar substitution reactions favours the rearrangement, which takes place at ambient temperature. In contrast, in the reaction of PtCl₂ with 2 equiv. of tri-n-butylphosphane, which has approximately the same basicity and cone angle as PEt₃, isomerisation from the kinetic product, *cis*-[Pt(PBu₃)₂Cl₂],



Scheme 2.

to the thermodynamic product, trans-[Pt(PBu₃)₂Cl₂], requires a much higher temperature.^[12] Moreover, ³¹P NMR monitoring of the substitution evidences a singlet at 12.1 ppm (¹J_{Pt,P} 2895 Hz), the intensity of which decreases with time. This signal is tentatively assigned to a square-pyramidal intermediate of the type cis-[Pt(PEt₃)₂Cl₂L] (Scheme 2).

Crystallographic analysis of 1 confirms a centrosymmetric, *trans*-bis(thiolato) structure (Figure 1). The Pt atom displays a slightly distorted square-planar coordination with P–Pt–S angles of 86.415(15) and 93.585(15)°. The tetrathioethylene unit is perpendicular to the coordination sphere of Pt with a P–Pt–S(1)–C(1) dihedral angle of 100.5°. The Pt–P distance of 2.3339(5) Å and the Pt–S distance of 2.3345(5) Å are similar to those reported for other *trans*-[Pt(PEt₃)₂(thiolate)₂] compounds.^[8b,13] No interaction between the thiomethyl groups and the Pt atom is obvious in the solid state. In contrast, the Pt···S(2) contacts of 3.328 Å, which are slightly shorter than the sum of the corresponding Van der Waals radii, suggest an incipient octahedral geometry for this complex, which is corroborated by the Pt–S(1)–C(1)–S(2) dihedral angle of 0.657°.



Figure 1. Molecular structure of 1. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt–S(1) 2.3345(5), Pt– P 2.3339(5), C(1)–S(1) 1.7377(18), C(1)–C(2) 1.352(2), C(2)–S(5) 1.7521(18), S(5)–C(4) 1.806(2), S(1)–Pt–P 86.415(15), S(1)–Pt–P# 93.585(15), Pt–S(1)–C(1) 106.00(6), C(2)–S(5)–C(4) 99.73(9).

The structure of **2** is shown in Figure 2. The thiolate ligand lies *trans* to the chloro ligand. The Pt–S(1) distance of 2.3011(15) Å is similar to that in **1** and is in accord with the weak thermodynamic *trans* influence exerted by the



Figure 2. Molecular structure of **2**. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cl–Pt 2.3619(15), P(1)–Pt 2.3279(16), P(2)–Pt 2.3179(16), Pt–S(1) 2.3011(15), C(3)–S(1) 1.737(6), C(2)–C(3) 1.350(8), C(2)–S(2) 1.748(6), C(4)–S(2) 1.790(8), S(1)–Pt–P(2) 92.35(6), S(1)–Pt–P(1) 87.48(6), P(2)–Pt–P(1) 172.50(6), S(1)–Pt–Cl 176.73(6), P(2)–Pt–Cl 87.52(5), P(1)–Pt–Cl 92.23(5), C(3)–S(1)–Pt 103.1(2), C(2)–S(2)–C(4) 102.0(4). chloro ligand. In contrast, due to the more pronounced trans influence of the thiolato ligand, the Pt-Cl bond length of 2.3619(15) Å is significantly longer than that in trans-[Pt(PEt)₃Cl₂] (2.294 Å).^[14] The Pt-P bond lengths of 2.3279(16) and 2.3179(16) Å are in the same range as those of trans-[Pt(PEt)₃Cl₂] [2.300(19) Å] and 1. The coordination sphere of Pt involves two phosphorus atoms, a chloro ligand and a thiolato sulfur atom with cis angles lying between 87.48(6) and 92.35(6)°. Similar to the situation described in 1, the square-planar arrangement is capped by an endocyclic sulfur atom of L. However, the interaction is more pronounced in 2 as the Pt...S contact is shortened to 3.193 Å. Therefore, the coordination environment around the Pt centre in the solid state is best described as distorted square-pyramidal. In addition, molecules of 2 are organised in centrosymmetric dimers within the unit cell with a parallel orientation of the dmit core. The plane-to-plane separation is 3.45 Å, and the shortest S···S distance is 3.601 Å. This supramolecular assembly is not surprising as the ability of dmit to develop a network of intermolecular interactions through short S···S contacts is well documented.^[15]

Evolution of 1 in Solution – Hemilability vs. Demethylation

An additional weak peak with two satellites is observed at 16.5 ppm (${}^{1}J_{P,Pt} = 3348 \text{ Hz}$) in the ${}^{31}P{}^{1}H$ } NMR spectrum of 1 (Figure 3). This signal, and another singlet at 54.7 ppm, became more intense after the sample was stored for several days at 278 K. Concomitantly, the peak due to the phosphane ligands disappears. The nature of [Pt(PEt_3)(\eta^1-L)(\eta^2-L)] (3), which results from the transformation of 1, was established unambiguously by crystal structure determination after crystallisation by addition of hexane to a CDCl₃ solution (Figure 4).



Figure 3. ${}^{31}P{}^{1}H$ NMR spectra (CDCl₃ solution) of 1 (top) and 3 (bottom).



Figure 4. Molecular structure of 3. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt-S(4) 2.3052(10), Pt-S(9) 2.3278(10), Pt-S(5) 2.3418(10), Pt-P 2.2593(11), S(4)-C(8) 1.723(4). C(8) - C(9)1.332(5), C(9) - S(5)1.755(4).S(5)-C(10), 1.806(4), S(9)–C(12) 1.751(4), C(12)–C(13) 1.341(5), C(13)– S(10) 1.738(4), S(10)–C(14) 1.784(4), P–Pt–S(4) 92.40(4), P–Pt–S(9) 86.47(4), S(4)-Pt-S(9) 178.65(4), P-Pt-S(5) 177.89(3), S(4)-Pt-S(5) 89.51(4), S(9)-Pt-S(5), 91.63(5), Pt-S(4)-C(8) 101.10(13), S(4)-C(8)-C(9) 126.6(3), C(8)-C(9)-S(5) 121.2(3), C(9)-S(5)-Pt101.51(14), C(9)-S(5)-C(10) 102.77(18), C(10)-S(5)-Pt 104.38(15), Pt-S(9)-C(12) 106.67(13), S(9)-C(12)-C(13) 125.2(3), C(12)-C(13)–S(10) 122.7(3), C(13)–S(10)–S(14) 102.7(2).

Compound 3 bears only one phosphane ligand and the coordination demand of the Pt^{II} atom is satisfied by a supplementary strong dative interaction with one thiomethyl group. In solution, the two thiomethyl groups are equivalent at 293 K as only one signal is observed for these substituents in the ¹H NMR spectrum at 2.68 ppm (a poorly resolved doublet with ⁴*J*_{P,H} = 1.4 Hz) with satellites due to ³*J*_{Pt,H} of 14 Hz. In contrast, the exchange of the coordinated thiomethyl groups on platinum is slow at 223 K, and at this temperature, two singlets are found at 2.89 and 2.46 ppm (Figure 5). The evaluation of the coalescence temperature ($T_c = 240$ K) and Δv value in the low exchange limit allows the calculation of an activation energy ΔG^{\ddagger} of 47 kJ mol⁻¹ with the Eyring equation.

In the solid state, two types of L are clearly identified. The first is ligated to the platinum through a covalent Pt-S(thiolate) bond of 2.3278(10) Å. The second ligand chelates the metal with Pt-S(thiolate) and Pt-S(thioether) distances of 2.3052(10) and 2.3418(10) Å, respectively. As mentioned in the introduction, such a combination of η^{1} and η^2 -L ligands has already been observed in [Ni(dppe)- L_2]. However, in this case, the difference in strength of the interactions between the metal centre and the two types of sulfur atoms is much more pronounced.^[4b] Compared to the value measured in centrosymmetric 1, the Pt-P bond in 3, trans to Pt–S_{thioether}, is significantly stronger [2.2593(11)]vs. 2.3339(5) Å]. The distances measured for the trans Pt-P and Pt-Sthioether bonds compare well with those reported for cis-[(Et₃P)ClPt¹{S(MeS²)=C(S³Me)S}Pt²Cl(PEt₃)(Pt¹- $S^{3}(S^{2}-Pt^{2})$ [Pt-S 2.311(9) and 2.335(10) Å; Pt-P 2.267(10) and 2.249(10) Å].^[4c] Due to the hemilability of L, 1 and 3 coexist in solution in the equilibrium mixture $1 \Leftrightarrow 3 + PEt_3$ with a small equilibrium constant (Scheme 2). Indeed, from the integration of the signals at 2.68 (3) and 2.44 ppm (1) in the ¹H NMR spectrum of a pure sample of 1 in CDCl₃, the [1] to [3] ratio can be estimated to be 17:1. The complete transformation of 1 is a consequence of the



Figure 5. ¹H NMR spectra of **3** (CDCl₃ solution) recorded at 298 and 223 K.

oxidation of the triethylphosphane to its corresponding weakly-coordinating phosphane oxide (responsible for the signal at $\delta = 54.7$ ppm in the ³¹P{¹H} NMR spectrum, see above), which displaces the balance in favour of **3**. No reaction is observed when **3** is treated with excess CsL.

The η^2 -coordination mode of L is also observed in $[Pt(PEt_3)_2(\eta^2-L)]^+$ (4), which resulted from the abstraction of the chloro ligand of 2 by excess $TlPF_6$ (Scheme 2). This reaction was monitored by ³¹P{¹H} and ¹H NMR spectroscopy. The spectra prove unambiguously that the vacant coordination site on platinum is electronically saturated by a strong interaction with the thiomethyl group, which provides a 16 electron count. Indeed, the ³¹P{¹H} NMR spectrum consists of two mutually coupled doublets at 13.3 and 9.4 ppm (${}^{2}J_{P,P}$ = 22 Hz), which indicates the nonequivalence of the two phosphanes. The high-field resonance exhibits a ^{1}J coupling of 2702 Hz to the 195 Pt nucleus, whereas the low-field resonance displays a ${}^{1}J_{Pt,P}$ coupling of 3048 Hz. In the ¹H NMR spectrum, the thiomethyl protons resonate at 2.95 ppm, which is similar to that observed in 3. The coupling constants ${}^{4}J_{P,H}$ and ${}^{3}J_{Pt,H}$ of 3.1 and 33 Hz, respectively, are significantly stronger in 4. These observations corroborate a strong η^2 -coordination mode of L and the rearrangement of the phosphane ligands from a trans to a cis conformation.

Heating a solution of **1** in acetonitrile overnight led to the formation of [Pt(PEt₃)₂(dmit)] (**5**) and liberation of 4,5bis(methylthio)-1,3-dithiole-2-thione, which indicates that a methyl migration from one sulfur ligand to the other occurs at high temperature (Scheme 2). The ³¹P{¹H} NMR spectrum of **5** consists of a singlet at 6.5 ppm, which is coupled to platinum (${}^{1}J_{P,Pt} = 2798$ Hz). An X-ray structure analysis

FULL PAPER

of 5 confirmed unambiguously that the demethylation reaction occurred. The coordination sphere of the Pt^{II} complex is square planar and consists of a chelating dithiolene and two cis PEt₃ ligands. The structure depicted in Figure 6 is very similar to those of other structurally characterised heteroleptic phosphane(dithiolene)platinum(II) complexes, particularly [Pt(PPh₃)₂(dmit)].^[16] In 5, the Pt-S bond lengths of 2.3408(16) and 2.3314(17) Å are also similar to those in 1. Great attention has been paid to metal-assisted C-S bond activation from synthetic, catalytic and bioinorganic standpoints. The C-S bond cleavage evidenced in 1 is not without precedent. The conversion of thioether complexes into thiolato compounds by dealkylation has been observed in numerous group VIII metal complexes of $N \cap S$, $P \cap S$, $As \cap S$ and $S \cap S$ donor chelates.^[17] Such alkyl extrusion may result from photoreactions,^[18] electrochemical reductions,^[19] reactions with nucleophiles^[20] or under hightemperature conditions.^[21] It should, however, be mentioned that boiling an acetone solution of trigonal-planar [Au(PPh₃)₂L] resulted not in C-S bond activation but in the dissociation of one of the phosphane ligands, which led to a linear, two-coordinate gold(I) centre in [Au(PPh₃)L].^[4a]



Figure 6. Molecular structure of **5**. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P(1)–Pt 2.2971(18), P(2)–Pt 2.2931(16), Pt–S(2) 2.3314(17), Pt–S(1) 2.3408(16), C(1)–S(1) 1.748(6), C(2)–S(2) 1.735(6), C(1)–C(2) 1.349(9), P(2)–Pt–P(1) 98.60(5), P(2)–Pt–S(2) 88.28(5), P(1)–Pt–S(2) 173.10(5), P(2)–Pt–S(1) 176.36(5), P(1)–Pt–S(1) 83.84(5), S(2)–Pt–S(1) 89.33(5), C(1)–S(1)–Pt 101.7(2), C(2)–S(2)–Pt 101.4(2), C(2)–C(1)–S(1) 122.6(5), C(1)–C(2)–S(2) 124.9(5).

Influence of the Nature of the Phosphane Ligand

i) PPh₃ vs. PEt₃

In order to evaluate the influence of the nature of the phosphane ligand on the reactivity described above, CsL was also reacted with the *cis*-[Pt(PPh₃)₂Cl₂]. The reaction was first studied in dichloromethane at ambient temperature using a 2:1 ligand-to-metal ratio. The ³¹P{¹H} NMR spectrum of the crude product mixture showed the formation of two complexes, which are characterised by singlets at 18.4 and 17.3 ppm with $J_{P,Pt}$ couplings of 2961 and 3585 Hz, respectively. The two complexes were separated by chromatography on silica gel. On the basis of the NMR spectroscopic data reported by Bereman et al., the low-field resonance is attributed to [Pt(PPh₃)₂(dmit)] (6).^[16,22] Concerning the species responsible of the chemical shift at 17.3 ppm, the strong value of the associated coupling constant compares well with that observed for **3** and suggests

the formation of $[Pt(PPh_3)(\eta^1-L)(\eta^2-L)]$ (7). This hypothesis is confirmed by the detection of the signal of free triphenylphosphane at -3.7 ppm in the ³¹P NMR spectrum of the crude product. Moreover, dynamic behaviour similar to that reported for 3 was observed in solution. The ¹H NMR spectrum recorded at 293 K displays one broad resonance at 2.61 ppm, which is split into two singlets at 2.95 and 2.27 ppm at low temperature. In contrast, heating the sample to 320 K gives rise to a sharp singlet with a ${}^{3}J_{Pt,H}$ coupling of 15 Hz. As in 3, the two sulfur ligands mutually exchange their coordination mode from η^1 -thiolato to a chelating one that involves both Pt-S(thiolate) and Pt-S(thioether) interactions (Scheme 3) with an activation energy ΔG^{\ddagger} of 46.1 kJ mol⁻¹ (at $T_c = 241$ K). By adding a large excess of triphenylphosphane to a CDCl₃ solution of 7, the resonance due to compound 7 disappears in the ${}^{31}P{}^{1}H$ NMR spectrum, and a new singlet at 19.8 ppm with a $J_{Pt,P}$ coupling of 3054 Hz arises. This signal, and that observed in the ¹H NMR spectrum at 2.23 ppm, indicates the formation of $[Pt(PPh_3)_2(\eta^1-L)_2]$. From these observations, we can conclude that the monophosphane complex is the main product in the equilibrium $[Pt(PR_3)_2(\eta^1-L)_2] \Leftrightarrow [Pt(PR_3)(\eta^1-L)_2]$ $L(\eta^2-L)$] + PR₃ (R = Ph), whereas the use of the more basic triethylphosphane stabilises the diphosphane complex. Complex 7 is not sensitive to the presence of acetonitrile even in excess. Single crystals of 7 were grown from CHCl₃/CH₃CN. Two independent [Pt(PPh₃)(η^1 -L)(η^2 -L)] molecules are located in general positions in the unit cell, which differ mainly in the orientation of the sulfur ligand that is coordinated in the η^1 mode. The molecular structure



Scheme 3.



	1	2	3	5	7 ^[a]		8
Pt-P	2.3339(5)	2.3279(16) 2.3179(16)	2.2593(11)	2.2971(18) 2.2931(16)	2.2459(10)	2.2504(10)	2.2504(10) 2.2415(10)
$Pt-S_{thiolate}$	2.3345	2.3011(15)	2.3052(10) 2.3278(10)	2.3314(17) 2.3408(16)	2.2892(9) 2.3379(9)	2.2937(9) 2.3359(9)	2.3622(10) 2.3689(10)
Pt-S _{thioether}			2.3418(10)		2.3303(9)	2.3217(9)	

Table 1. Pt-P and Pt-S bond lengths [Å] in the molecular structures determined in this work.

[a] Two independent molecules in the unit cell.

of **7** is similar to that of **3** with a square-planar environment around the platinum centre composed of one phosphorus atom, two thiolate sulfur atoms and one thioether sulfur atom (Figure 7). The nature of the phosphane (PPh₃ vs. PEt₃) does not significantly affect the Pt–P and Pt–S bond lengths (Table 1). The Pt–S_{thioether} bond *trans* to the phosphane is only slightly stronger with PPh₃ [2.3303(9) and 2.3217(9) vs. 2.3418(10) Å].



Figure 7. Molecular structure of 7 (only one of the two independent molecules of the unit cell is depicted). H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P(1)–Pt(1) 2.2459(10), Pt(1)–S(1) 2.2892(9), Pt(1)–S(1) 2.3303(9), Pt(1)–S(6) 2.3379(9), P(1)–Pt(1)–S(1) 93.41(3), P(1)–Pt(1)–S(2) 175.50(3), S(1)–Pt(1)–S(2) 90.55(3), P(1)–Pt(1)–S(6) 87.20(3), S(1)–Pt(1)–S(6) 178.54(4), S(2)–Pt(1)–S(6) 88.89(3). For the second molecule: Selected bond lengths [Å] and angles [°]: P(2)–Pt(2) 2.2504(10), Pt(2)–S(11) 2.2937(9), Pt(2)–S(12) 2.3217(9), Pt(1)–S(16) 2.3359(9), P(2)–Pt(2)–S(11) 91.95(3), P(2)–Pt(2)–S(12) 174.81(3), S(11)–Pt(2)–S(12) 90.26(3), P(2)–Pt(2)–S(16) 90.73(3), S(11)–Pt(2)–S(16) 176.98(3), S(12)–Pt(2)–S(16) 86.95(3).

The nature of the phosphane donor plays also a role in the rate of the demethylation reaction. As mentioned above, the formation of **7** was always accompanied by **6**, even when the substitution reaction was performed at 273 K. At first glance, the increase of the rate of formation of the dithiolene compound on going from PEt₃ to PPh₃ ancillary ligands is surprising because of the predominant species in solution (diphosphane vs. monophosphane complex). Indeed, we have shown above that $[Pt(PEt_3)_2(dmit)]$ was formed by heating a solution of $[Pt(PEt_3)_2L_2]$. In order to gain more information on the species involved in the dealkylation process when triphenylphosphane is coordinated to the platinum centre, we reacted CsL with an equimolar amount of cis-[Pt(PPh₃)₂Cl₂] solubilised in acetone in high dilution. The mixture immediately turned yellow, and, an ochre powder was isolated after workup. The ³¹P NMR spectrum revealed signals arising from 6 and 7 as well as a singlet at 15.5 ppm with $J_{Pt,P}$ equal to 3130 Hz, which is tentatively assigned to the complex resulting from the monosubstitution of a chloro ligand, [Pt(PPh₃)₂ClL] (Scheme 3). More informative is the evolution of the sample. After storage for one week at 278 K, only the resonance due to 6 was detected in the ³¹P NMR spectrum. The ¹H NMR spectrum exhibits an intense singlet at 3.01 ppm, which indicates the formation of CH₃Cl. Based on this observation, a mechanism for the demethylation reaction is proposed starting from [Pt(PPh₃)₂ClL]. The first step is the oxidative addition of the S-CH3 bond, which leads to a labile hexacoordinate Pt^{IV} species, [Pt(PPh₃)₂(dmit)ClMe]. This intermediate evolves to 6 by the reductive elimination of chloromethane. Thus, the reactivity and the coordinating mode of L in platinum complexes can be tuned by the nature of the ancillary phosphane ligands.

ii) Using Chelating Diphosphanes

The reaction of CsL with platinum precursors blocked in a *cis* arrangement with the chelating diphosphanes 1,1bis(diphenylphosphanyl)methane (dppm) and dppe allows the formation of the air-stable complexes cis-[Pt(η^2 -dppm)- L_2] (8) and *cis*-[Pt(η^2 -dppe) L_2] (9) (Scheme 3). The ³¹P{¹H} NMR spectra for 8 and 9 display singlet resonances with platinum satellites at -48.1 (¹ $J_{P,Pt}$ = 2585 Hz) and 47.1 ppm $({}^{1}J_{P,Pt} = 2974 \text{ Hz})$, respectively. In the ${}^{1}\text{H}$ NMR spectra, the resonance of the S-CH₃ groups gives rise to singlets at 2.34 ppm for 8 and 2.26 ppm for 9. Again, no interaction seems to occur in solution between the platinum centre and thiomethyl group(s). Complexes 8 and 9 were also isolated quantitatively by adding one equivalent of dppm or dppe to 7 (Scheme 3). The reactivity is somewhat different starting from 3. Indeed, addition of one equivalent of dppm to 3 resulted in the formation of an equimolar mixture of 8, [Pt(PEt₃)₂L₂] and unreacted dppm (see Supporting Information), whereas dppe displaces the triethylphosphane to give 9 almost quantitatively (Scheme 2). This example illustrates the higher stability of the five-membered metallacycle compared to the four-membered one. The molecular structure of 8 was determined by a single-crystal X-ray diffraction study. The cis arrangement of the L ligands in 8 with a S(1)-Pt-S(6) angle of 88.59(4)° is shown in Figure 8. The

FULL PAPER

P(1)-Pt-P(2) angle of 74.05(4)° and the Pt-P distances of 2.2504(10) and 2.2415(10) Å are typical of dppm chelated to platinum.^[23] Compared to the situation described above for *trans* 1 and 2, the platinum-thiolato bonds are slightly elongated to 2.3622(10) and 2.3689(10) Å (Table 1). Again, the coordination environment around the platinum centre is best described as distorted square-pyramidal as an additional short Pt···S contact of 3.073 Å is observed. In this case, the S(2) sulfur atom involved belongs to a thiomethyl group; for the other L ligand, the sulfur thiomethyl atom S(7) is located at 3.692 Å. The apical Pt···S distance of 8 approaches the values reported in platinum(II)-1,4,7-trithiacyclononane complexes (2.84-2.97 Å).[24] The molecular structure of 8 compares well with that reported for the analogous compound *cis*-[Pd(η^2 -dppe)L₂], in which a close Pd···S(thiomethyl) contact of 3.11 Å was pointed out.^[4b] The intermolecular interactions observed in the solid-state packing diagram of 8 along the bc plane are worth mentioning; the S···S contacts of 3.416 Å (S4···S8) and 3.421 Å (S3...S3) fall below the sum of the Van der Waals radii of two S atoms (3.70 Å) and give rise to a 2D supramolecular network (see Supporting Information).



Figure 8. Molecular structure of complex **8**. For clarity, H atoms are omitted and only C_{ipso} of the phenyl groups are represented. Selected bond lengths [Å] and angles [°]: P(1)–Pt 2.2504(10), P(2)–Pt 2.2415(10), Pt–S(1) 2.3622(10), Pt–S(6) 2.3689(10), S(2)–C(28) 1.794(5), C(25)–S(2) 1.743(4), C(25)–C(26) 1.354(5), C(26)–S(1) 1.726(4), C(29)–S(6) 1.737(4), C(29)–C(30) 1.331(6), C(30)–S(7) 1.753(4), C(32)–S(7) 1.788(4), P(2)–Pt–P(1) 74.05(4), P(2)–Pt–S(1) 172.75(4), P(1)–Pt–S(1) 98.69(4), P(2)–Pt–S(6) 98.66(4), P(1)–Pt–S(6) 172.65(4), S(1)–Pt–S(6) 88.59(4), C(26)–S(1) -Pt 105.48(14), C(25)–C(26)–S(1) 130.3(3), C(26)–C(25)–S(2) 125.6(3), C(25)–S(2)–C(28) 100.9(2), C(29)–S(6)–Pt 106.74(14), C(30)–C(29)–S(6) 127.2(3), C(29)–C(30)–S(7) 121.9(3), C(30)–S(7)–C(32) 102.9(2).

Complex 8 is also sensitive to demethylation upon heating. Indeed, after heating an acetonitrile solution of 8 overnight, NMR spectroscopy revealed the partial evolution of the bis(thiolate) complex to the dithiolene complex [Pt(η^2 dppm)(dmit)] (δ = 47.0 ppm with $J_{Pt,P}$ = 2429 Hz in the ³¹P{¹H} NMR spectrum) and formation of Me₂dmit (δ = 2.49 ppm in the ¹H NMR spectrum).

Conclusions

We have shown that thiolate/thioether L coordinates to diphosphane platinum(II) centres by a firm metal-thiolate link and an incipient metal-thioether interaction in [PtP₂L₂]-type complexes. The dative interaction leads to the displacement of a phosphane ligand (hemilabile behaviour) or to the activation of the C–SMe bond on the platinum centre to generate a dithiolene complex. These results are very encouraging for the purpose of extending our research to other thiolate/thioether–platinum complexes, especially by introducing a reversibly oxidisable ligand with a coordination mode determined by its oxidation state. In light of the reactivity of the Pt–H bond towards insertion reactions, we are currently probing the synthesis of platinum–hydride complexes that bear this thiolate/thioether ligand system.

Experimental Section

General: All manipulations were performed using Schlenk techniques in an atmosphere of dry oxygen-free argon. Elemental analyses were performed with a Leco Elemental Analyser CHN 900. ³¹P{¹H} NMR spectra were recorded at 300.13 MHz with a Bruker DRX 300 spectrometer. CsL,^[4b] *cis*-[Pt(PEt₃)₂Cl₂],^[25] *cis*-[Pt(PPh₃)₂Cl₂],^[26] [Pt(dppm)Cl₂]^[27] and [Pt(dppe)Cl₂]^[28] were prepared according to literature procedures.

trans-[Pt(PEt₃)₂(L₁)₂] (1): A CH₂Cl₂ (20 mL) solution of *cis*-[Pt(PEt₃)₂Cl₂] (0.240 g, 0.48 mmol) and caesium 4-methylthio-2thioxo-1,3-dithiole-5-thiolate (CsL, 2 equiv., 0.330 g, 0.96 mmol) was stirred overnight at room temperature. After filtration, the solution was concentrated under reduced pressure. Ochre single crystals were grown by the addition of hexane (245 mg, 60%). C₂₀H₃₆P₂PtS₁₀ (854.12): calcd. C 28.12, H 4.25, S 37.54; found C 27.84, H 4.05, S 37.20. ¹H NMR (CDCl₃, 298 K): $\delta = 2.44$ (6 H, S–CH₃), 2.02 (m, 12 H, P–CH₂–), 1.16 (m, 18 H, CH₂–CH₃) ppm. ³¹P{¹H} NMR (CDCl₃, 298 K): $\delta = 12.5$ (s, ¹J_{195Pt,³¹P} = 2372 Hz) ppm. IR (KBr): $\tilde{v} = 2961$, 2930, 1437, 1059 (C=S), 1032 (C=S), 1007, 890, 760, 729 cm⁻¹.

trans-[Pt(PEt₃)₂ClL] (2): To an acetone (30 mL) solution of *cis*-[Pt(PEt₃)₂Cl₂] (0.200 g, 0.40 mmol) was added dropwise CsL (0.135 g, 0.39 mmol) dissolved in acetone (10 mL). After stirring the mixture at room temperature for 3 h, the solution was filtered, and the filtrate was evaporated to dryness. The residue was then extracted into hexane (4 × 10 mL), and the combined extracts were concentrated in vacuo. Cooling the solution to 253 K precipitated yellow needles of **2** (95 mg, 36%). C₁₆H₃₃ClP₂PtS₅ (678.24): calcd. C 28.33, H 4.90, S 37.54; found C 28.58, H 5.03, S 36.87. ¹H NMR (CDCl₃, 298 K): δ = 2.41 (3 H, S–CH₃), 1.98 (m, 12 H, P–CH₂–), 1.16 (m, 18 H, CH₂–CH₃) ppm. ³¹P{¹H} NMR (CDCl₃, 298 K): δ = 14.5 (s, ¹J₁₉₅pt,³¹p = 2387 Hz) ppm.

[Pt(PEt₃)(\eta^{1}-L)(\eta^{2}-L)] (3): Complex 1 (0.043 g, 0.05 mmol) was dissolved in oxygenated CH₂Cl₂ (10 mL) and let for two weeks at 278 K. A layer of hexane was added, and 3 was afforded as dark crystals after a few days (30 mg, 82%). C₁₄H₂₁PPtS₁₀ (736.05): calcd. C 22.84, H 2.88, S 43.56; found C 22.48, H 2.65, S 43.07. ¹H (CDCl₃, 298 K): δ = 2.68 (d, ⁴J_{PH} = 1.4, ³J_{Pt,H} = 14 Hz, 6 H, S–CH₃), 2.08 (s, 6 H, P–CH₂–), 1.19 (m, 9 H, CH₂–CH₃) ppm. ³¹P{¹H} NMR (CDCl₃, 298 K): δ = 16.5 (s, ¹J₁₉₅_{Pt,³¹P} = 3348 Hz) ppm.

cis-[Pt(PEt₃)₂L]⁺ (4): Complex 2 (13.5 mg, 0.02 mmol), TlPF₆ (9 mg, 0.026 mmol) and CDCl₃ (0.5 mL) were mixed in a NMR tube (*Caution: Thallium and its compounds are extremely toxic and should be handled with great care*). The reaction was monitored by ${}^{31}P{}^{1}H{}$ and ${}^{1}H$ NMR spectroscopy. After a few minutes the ${}^{31}P{}^{1}H{}$ NMR spectrum showed the quantitative transformation



of **2** into **4**. ¹H NMR (CDCl₃, 298 K): $\delta = 2.95$ (d, ⁴ $J_{P,H} = 3.1$, ³ $J_{Pt,H} = 33$ Hz, 3 H, S–*CH*₃), 2.16 (s, 12 H, P–*CH*₂–), 1.20 (m, 18 H, CH₂–*CH*₃) ppm. ³¹P{¹H} NMR (CDCl₃, 298 K): $\delta = 13.5$ (d, ² $J_{P,P} = 22$, ¹ $J_{195pt,^{31}P} = 3048$ Hz), 9.4 (d, ² $J_{P,P} = 22$, ¹ $J_{195pt,^{31}P} = 2702$ Hz) ppm.

[Pt(PEt₃)₂(dmit)] (5): Heating a solution of 1 (0.100 g, 0.12 mmol) in acetonitrile (10 mL) to reflux overnight led to an equimolar mixture of **5** and Me₂dmit. A pure sample of **5** was synthesised according the following procedure: equimolar quantities (0.5 mmol) of *cis*-[Pt(PEt₃)₂Cl₂] and Na₂dmit^[29] were heated to reflux in CH₂Cl₂ (20 mL) overnight under argon. After filtration, hexane was added to the red solution, which resulted in the precipitation of **5** as a red-brown powder (170 mg, 54%). C₁₅H₃₀P₂PtS₅ (627.76): calcd. C 28.70, H 4.82, S 25.54; found C 28.91, H 4.89, S 25.02. ¹H NMR (CDCl₃, 298 K): δ = 2.09 (12 H, P–C*H*₂–), 1.18 (t, 18 H, CH₂– C*H*₃) ppm. ³¹P{¹H} NMR (CDCl₃, 298 K): δ = 6.5 (s, ¹*J*_{195pt,³¹p</sup> = 2798 Hz) ppm. IR (KBr): \tilde{v} = 2924, 2853, 1470, 1052 (C=S), 1027(C=S) cm⁻¹.}

[Pt(PPh₃)(η¹-L)(η²-L)] (7): A CH₂Cl₂ (10 mL) solution of *cis*-[Pt(PPh₃)₂Cl₂] (0.126 g, 0.16 mmol) and CsL (2 equiv., 0.110 g, 0.32 mmol) was stirred at room temperature for 3 h. After filtration, the solvent was removed under reduced pressure. The resulting orange powder was washed with ethanol to afford a solid (0.105 mg), which was identified as a mixture of **6**^[16] and **7**. Complexes **6** and **7** were separated by chromatography (SiO₂, CHCl₃), and pure **7** (50 mg) was recovered in the first fraction. C₂₆H₂₁PPtS₁₀ (880.22): calcd. C 35.48, H 2.41, S 36.43; found C 35.71, H 2.69, S 35.87. ¹H NMR (CDCl₃, 320 K): δ = 7.70–7.44 (m, 15 H, *Ph*), 2.60 (³J_{Pt,H} = 15 Hz, 6 H, S–CH₃) ppm. ³¹P{¹H} NMR (CDCl₃, 298 K): δ = 17.3 (s, ¹J₁₉₅_{Pt,³¹P} = 3585 Hz) ppm. **[Pt(dppm)L₂] (8):** An MeOH (10 mL) solution of [Pt(dppm)Cl₂] (0.085 g, 0.13 mmol) and CsL (2 equiv., 0.090 g, 0.26 mmol) was stirred 4 h. at 40 °C. After filtration, the solid was extracted into CH₂Cl₂ (10 mL). Evaporation under reduced pressure afforded an orange powder (60 mg, 46%). C₃₃H₂₈P₂PtS₁₀ (1002.24): calcd. C 39.54, H 2.82, S 31.99; found C 39.42; H 2.70, S 31.67. ¹H NMR (CDCl₃, 298 K): δ = 7.75–7.47 (20 H, Ph), 4.41(m, 2 H, P–CH₂–P), 2.35 (s, 6 H, S–CH₃) ppm. ³¹P{¹H} NMR (CDCl₃, 298 K): δ = -48.1 (s, ¹J₁₉₅_{Pt,³¹P} = 2585 Hz) ppm. IR (KBr): \tilde{v} = 3053, 2963, 1435, 1261, 1099, 1063 (C=S), 1028 (C=S), 874, 800 cm⁻¹.

[Pt(dppe)L₂] (9): Complex **9** was prepared in an analogous manner to **8** starting from [Pt(dppm)Cl₂] and CsL (50% yield). C₃₄H₃₀P₂PtS₁₀ (1016.27): calcd. C 40.18, H 2.98, S 31.55; found C 40.05, H 2.77, S 30.97. ¹H NMR (CDCl₃, 298 K): δ = 7.76–7.52 (20 H, Ph), 2.38 (m, 4 H, PCH₂–CH₂P), 2.26 (s, 6 H, S–CH₃) ppm. ³¹P{¹H} NMR (CDCl₃, 298 K): δ = 47.0 (s, ¹J_{195pt,³¹P} = 2974 Hz) ppm. IR (KBr): \tilde{v} = 2959, 2914, 1435, 1103, 1049 (C=S), 1028 (C=S), 878, 818, 750, 715 cm⁻¹.

Crystal Structure Determinations: Compounds 1 and 5: Stoe IPDS diffractometer; data collection: Expose in IPDS (Stoe & Cie, 1999), cell determination and refinement: Cell in IPDS (Stoe & Cie, 1999), integration: Integrate in IPDS (Stoe & Cie, 1999); numerical absorption correction: Faceit in IPDS (Stoe & Cie, 1999). Compounds 2, 3, 7 and 8: Bruker APEX diffractometer (D8 three-circle goniometer) (Bruker AXS); data collection, cell determination and refinement: Smart version 5.622 (Bruker AXS, 2011); integration: SaintPlus version 6.02 (Bruker AXS, 1999); empirical absorption correction: Sadabs version 2.01 (Bruker AXS, 1999).

A suitable crystal of each complex was mounted in an inert oil (perfluoropolyalkylether); the crystal structure determination was

Table 2. Crystallographic refinement data for 1, 2 and 3.

	1	2	3	
Formula	$C_{20}H_{36}P_2PtS_{10}$	C ₁₆ H ₃₃ ClP ₂ PtS ₅	$C_{14}H_{21}PPtS_{10}$	
Formula weight	854.12	678.24	736.06	
Temperature [K]	173(2)	173(2)	173(2)	
Wavelength [Å]	0.71073	0.71073	0.71073	
Crystal system	monoclinic	monoclinic	monoclinic	
Space group	PĪ	$P2_1/n$	$P2_{1}/c$	
<i>a</i> [Å]	8.6626(9),	10.4688(9)	10.7909(6)	
<i>b</i> [Å]	10.5196(11)	22.4622(10)	29.2394(11)	
<i>c</i> [Å]	10.8651(11)	11.2344(7)	7.6003(2)	
a [°]	61.1180(10)			
β [°]	87.101(2)	108.792(8)	98.731(3)	
γ [°]	69.5280(10)			
Volume [Å ³]	803.70(14)	2501.0(3)	2370.25(17)	
Ζ	1	4	4	
Density (calculated) [g cm ⁻³]	1.765	1.801	2.096	
Absorption coefficient [mm ⁻¹]	5.125	6.264	6.287	
<i>F</i> (000)	424	1336	592	
Crystal size [mm]	$0.30 \times 0.30 \times 0.20$	$0.30 \times 0.20 \times 0.10$	$0.40 \times 0.20 \times 0.20$	
Theta range for data collection [°]	2.16 to 27.00	2.25 to 27.00	2.03 to 27.00	
Index ranges	$-11 \le h \le 11,$	$-13 \le h \le 13,$	$-12 \le h \le 13,$	
	$-13 \le k \le 13,$	$-28 \le k \le 28,$	$-36 \le k \le 37,$	
	$-13 \le l \le 13$	$-14 \leq l \leq 14$	$-9 \le l \le 9$	
Reflections collected	19653	17987	23207	
Independent reflections	3506 [R(int) = 0.0295]	5421 [R(int) = 0.0627]	5041 [R(int) = 0.0411]	
Refinement method		Full-matrix least-squares on F^2		
Data/restraints/parameters	3506/0/156	5421/0/233	5041/0/240	
Goodness-of-fit on F^2	1.025	1.013	0.990	
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0123, wR2 = 0.0338	R1 = 0.0409, wR2 = 0.1063	R1 = 0.0272, wR2 = 0.0506	
<i>R</i> indices (all data)	R1 = 0.0123, wR2 = 0.0338	R1 = 0.0530, wR2 = 0.1094	R1 = 0.0396, wR2 = 0.0522	
Largest diff. peak and hole $[e Å^{-3}]$	0.925 and -0.883	4.170 and -1.734	0.988 and -2.435	

FULL PAPER

	5	7	8
Formula	C ₁₅ H ₃₀ P ₂ PtS ₅ , CH ₂ Cl ₂	C ₂₆ H ₂₁ PPtS ₁₀ , 0.5 CHCl ₃	$C_{33}H_{28}P_2PtS_{10}$
Formula weight	712.65	880.22	1002.18
Temperature [K]	173(2)	173(2)	173(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	PĪ
a [Å]	11.075(4)	13.3850(2)	7.9483(2)
b Å	17.921(6)	13.8880(2)	11.3708(3)
c [Å]	13.330(5)	19.6274(3)	20.6496(6)
		90.5060(10)	103.175(2)
β ^[°]	102.422(6)	97.8530(10)	94.626(2)
2 [°]		113.727(2)	91.375(2)
Volume [Å ³]	2593.7(16)	3300.63(9)	1809.51(8)
Z	4	4	2
Density (calculated) $[g \text{ cm}^{-3}]$	1.832	1.891	1.839
Absorption coefficient [mm ⁻¹]	6.168	5.074	4.569
F(000)	1400	1836	988
Crystal size [mm]	$0.30 \times 0.30 \times 0.20$	$0.20 \times 0.20 \times 0.20$	$0.40 \times 0.20 \times 0.10$
Theta range for data collection [°]	1.93 to 26.63	2.15 to 27.00	2.30 to 27.00
Index ranges	$-13 \le h \le 13,$	$-17 \le h \le 17,$	$-10 \le h \le 10,$
-	$-22 \le k \le 22,$	$-17 \le k \le 17,$	$-14 \le k \le 14,$
	$-16 \le l \le 16$	$-25 \le l \le 25$	$-26 \le l \le 26$
Reflections collected	47856	140362	26543
Independent reflections	5394 [R(int) = 0.0552]	14385[R(int) = 0.0519]	7854 [R(int) = 0.0382]
Refinement method		Full-matrix least-squares on F^2	
Data/restraints/parameters	5394/0/241	14385/0/725	7854/ 0/417
Goodness-of-fit on F^2	1.070	1.009	1.007
Final R indices $[I > 2\sigma(I)]$	R1 = 0.0378, wR2 = 0.1043	R1 = 0.0242, wR2 = 0.0567	R1 = 0.0279, wR2 = 0.0593
R indices (all data)	R1 = 0.0399, wR2 = 0.1057	R1 = 0.0357, wR2 = 0.0580	R1 = 0.0366, wR2 = 0.0603
Largest diff. peak and hole [eÅ-3]	2.454 and -1.240	1.445 and -1.494	4.138 and -0.764

Table 3. Crystallographic refinement data for 5, 7 and 8.

effected at 173(2) K. All structures were solved by applying direct and Fourier methods using SHELXS-97 and SHELXL-97.^[30,31] For each structure, the non-hydrogen atoms were refined anisotropically. All of the H atoms were placed in geometrically calculated positions and each was assigned a fixed isotropic displacement parameter based on a riding model. The crystallographic parameters are listed in Tables 2 and 3.

CCDC-842700 (for 1), -842701 (for 2), -842702 (for 3), -842703 (for 5), -842704 (for 7) and -842705 (for 8) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): ${}^{31}P{}^{1}H{}$ NMR spectrum of the result of the reaction between **3** and dppm, view of the 2D supramolecular network of **8**.

- [1] a) A. Bader, E. Lindner, *Coord. Chem. Rev.* **1991**, *108*, 27–110; b) C. S. Slone, D. A. Weinberger, C. A. Mirkin, *Prog. Inorg. Chem.* **1999**, *48*, 233–350; c) P. Braunstein, F. Naud, *Angew. Chem.* **2001**, *113*, 702; *Angew. Chem. Int. Ed.* **2001**, *40*, 680– 699; d) Z. Weng, S. Teo, T. S. A. Hor, *Acc. Chem. Res.* **2007**, *40*, 676–684; e) H. V. Huynh, C. H. Yeo, Y. X. Chew, Organometallics **2010**, *29*, 1479–1486; f) S. E. Angell, C. W. Rogers, Y. Zhang, M. O. Wolf, W. E. Jones Jr, *Coord. Chem. Rev.* **2006**, *250*, 1829–1841; g) S. M. Thompson, F. Stöhr, D. Sturmayr, G. Kickelbick, U. Schubert, *J. Organomet. Chem.* **2003**, *686*, 183– 191; h) For a discussion of the reactivity of heterobimetallic Fe–Pd complexes that bear a hemilabile μ_2 - η^2 -bound Si(OR)₃ ligand see: P. Braunstein, M. Knorr, T. Stährfeldt, *J. Chem. Soc., Chem. Commun.* **1994**, 1913–1914.
- [2] X. Shan, J. H. Espenson, Organometallics 2003, 22, 1250-1254.

- [3] a) F. Guyon, A. Hameau, A. Khatyr, M. Knorr, H. Amrouche, D. Fortin, P. D. Harvey, C. Strohmann, A. L. Ndiaye, V. Huch, M. Veith, N. Avarvari, *Inorg. Chem.* 2008, 47, 7483–7492; b) A. Hameau, F. Guyon, M. Knorr, M. Enescu, C. Strohmann, *Monatsh. Chem.* 2006, 137, 545–555; c) F. Guyon, D. Lucas, I. V. Jourdain, M. Fourmigué, Y. Mugnier, H. Cattey, Organometallics 2001, 20, 2421–2424; d) I. V. Jourdain, M. Fourmigué, F. Guyon, J. Amaudrut, Organometallics 1999, 18, 1834–1839; e) A. L. Ndiaye, F. Guyon, M. Knorr, V. Huch, M. Veith, Z. Anorg. Allg. Chem. 2007, 633, 1959–1963.
- [4] a) S. Zeltner, S. Jelonek, J. Sieler, R.-M. Olk, *Eur. J. Inorg. Chem.* 2001, 1535–1541; b) S. Zeltner, R.-M. Olk, P. Joerchel, J. Sieler, *Z. Anorg. Allg. Chem.* 1999, 625, 368–373; c) B. Cetinkaya, P. B. Hitchcook, M. F. Lappert, P. L. Pye, D. B. Shaw, *J. Chem. Soc., Dalton Trans.* 1979, 434–440; d) D. W. Allen, R. Berridge, N. Bricklebank, E. Cerrada, M. E. Light, M. B. Hursthouse, M. Laguna, A. Moreno, P. J. Skabara, *J. Chem. Soc., Dalton Trans.* 2002, 2654–2659.
- [5] a) D. Lorcy, N. Bellec, M. Fourmigué, N. Avarvari, *Coord. Chem. Rev.* 2009, 253, 1398–1438; b) I. V. Jourdain, F. Guyon, *Can. J. Chem.* 2000, 78, 1570–1574; c) M. Nomura, T. Fujii, M. Kajitani, *Organometallics* 2009, 28, 3776–3784.
- [6] T. B. Higgins, C. A. Mirkin, Inorg. Chim. Acta 1995, 240, 347– 353.
- [7] a) N. Sevenstrup, J. Becher, Synthesis 1995, 215–235; b) A. E. Pullen, R.-M. Olk, Coord. Chem. Rev. 1999, 188, 211–262; c) P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A. Clark, A. E. Underhill, Coord. Chem. Rev. 1991, 110, 115–160; d) R.-M. Olk, B. Olk, W. Dietzsch, R. Kirmse, E. Hoyer, Coord. Chem. Rev. 1992, 117, 99–131; e) M. Fourmigué, Coord. Chem. Rev. 1998, 178–180, 823–864.
- [8] a) W. Henderson, B. K. Nicholson, C. E. F. Rickard, *Inorg. Chim. Acta* 2001, 320, 101–109; b) S. Kato, O. Niyomura, Y. Kawahara, T. Kanda, *J. Chem. Soc., Dalton Trans.* 1999, 1677–



1686; c) F. Estudiante-Negrete, R. Redon, S. Hernandez-Ortega, R. A. Toscano, D. Morales-Morales, *Inorg. Chim. Acta* 2007, *360*, 1651–1660.

- [9] a) R. D. Lai, A. Shaver, *Inorg. Chem.* **1981**, *20*, 477–480; b) Q. Chen, F. Boeheim, J. Dabrowiak, J. Zubieta, *Inorg. Chim. Acta* **1994**, *216*, 83–87.
- [10] a) V. Cordero-Pensado, V. Gomez-Benitez, S. Hernandez-Ortega, R. A. Toscano, D. Morales-Morales, *Inorg. Chim. Acta* 2006, 359, 4007–4018; b) S. Miranda, E. Vergara, F. Mohr, D. De Vos, E. Cerrada, A. Mendia, M. Laguna, *Inorg. Chem.* 2008, 47, 5641–5648.
- [11] M. Alesi, S. Fantasia, M. Manassero, A. Pasini, *Eur. J. Inorg. Chem.* 2006, 1429–1435.
- [12] G. B. Kauffman, L. A. Teter, in: *Inorganic Syntheses*, 1963, vol. VII (Ed.: J. Kleinberg), McGraw-Hill Book Company, Inc., p. 245.
- [13] X. Chang, K.-E. Lee, Y.-J. Kim, S. W. Lee, *Inorg. Chim. Acta* 2006, 359, 4436–4440.
- [14] G. G. Messmer, E. L. Amma, Inorg. Chem. 1966, 5, 1775–1781.
- [15] See, for example, M. Fourmigué, B. Domercq, I. V. Jourdain, P. Molinié, F. Guyon, J. Amaudrut, *Chem. Eur. J.* 1998, 4, 1714–1723.
- [16] C. E. Keefer, S. T. Purrington, R. D. Bereman, B. W. Knight, D. R. Bedgood Jr, P. D. Boyle, *Inorg. Chim. Acta* 1998, 282, 200–208.
- [17] a) P. G. Eller, J. M. Riker, D. W. Meek, J. Am. Chem. Soc. 1973, 95, 3540–3548; b) L. F. Lindoy, S. E. Livingstone, T. N. Lockyer, Inorg. Chem. 1967, 6, 652–656; c) J. S. Kim, J. H. Reibenspies, M. Y. Darensbourg, J. Am. Chem. Soc. 1996, 118, 4115–4123; d) C. Huang, S. Gou, H. Zhu, W. Huang, Inorg. Chem. 2007, 46, 5537–5543; e) G. N. Schrauzer, H. N. Rabinowiz, J. Am. Chem. Soc. 1968, 90, 4297–4302; f) K. Wang, E. I. Stiefel, Science 2001, 291, 106–109.

- [18] S.-I. Ohkoshi, Y. Ohba, M. Iwaizumi, S. Yamauchi, M. Ohkoshi-Ohtnai, K. Tokuhisa, M. Kajitani, T. Akiyama, A. Sugimori, *Inorg. Chem.* **1996**, *35*, 4569–4574.
- [19] S. K. Ibrahim, C. J. Pickett, J. Chem. Soc., Chem. Commun. 1991, 246–249.
- [20] D. M. Roundhill, S. G. N. Roundhill, W. B. Beaulieu, U. Bagchi, *Inorg. Chem.* 1980, 19, 3365–3373.
- [21] S. Mandal, N. Paul, P. Banerjee, T. K. Mondal, S. Goswani, *Dalton Trans.* 2010, 39, 2717–2726.
- [22] C. E. Keefer, R. D. Bereman, S. T. Purrington, B. W. Knight, P. D. Doyle, *Inorg. Chem.* **1999**, *38*, 2294–2302.
- [23] a) C. Albrecht, C. Bruhn, C. Wagner, D. Steinborn, Z. Anorg. Allg. Chem. 2008, 634, 1301–1308; b) T. S. Lobana, P. Kaur, G. Hundal, R. J. Butcher, A. Castineiras, Z. Anorg. Allg. Chem. 2008, 634, 747–753.
- [24] T. W. Green, R. Lieberman, N. Mitchell, J. A. Krause Bauer, W. B. Connick, *Inorg. Chem.* 2005, 44, 1955–1965.
- [25] G. W. Parshall, in: *Inorganic Syntheses* (Ed.: R. W. Parry), 1970, vol. XII, McGraw-Hill Book Company, Inc., p. 27.
- [26] U. Nagel, Chem. Ber. 1982, 115, 1998–1999.
- [27] M. P. Brown, R. J. Puddephatt, M. Rashidi, K. R. Seddon, J. Chem. Soc., Dalton Trans. 1977, 951–955.
- [28] E. G. Hope, W. Lewason, N. A. Powell, *Inorg. Chim. Acta* 1986, 115, 187–192.
- [29] K. S. Varma, A. Bury, N. J. Harris, A. E. Underhill, *Synthesis* 1987, 837–838.
- [30] G. M. Sheldrick, SHELXS-90, University of Göttingen, Germany, 1990.
- [31] G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997.

Received: September 6, 2011

Published Online: December 7, 2011