Structural Preferences in Phosphanylthiolato Platinum(II) Complexes

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The transition-metal complexes of heterotopic phosphanylthiolato ligands are useful in various reactions which depend on the stereochemistry of the complexes. Bis-chelate complex [Pt(SCH₂CH₂PPh₂S)₂]₁ (1) was obtained in good yields by direct base-free substitution reaction of the corresponding phosphanylthiol (HSCH₂CH₂PPh₂) with K₂PtCl₄ or by oxidative addition of the same phosphanylthiol to Pt(PPh₃)₂. In agreement with the antisymbiosis rule, complex 1 shows a cis-P,S arrangement in solid state crystallizing in the monoclinic system (C2/c). Density functional theory (DFT) calculations on 1 reveal the right characteristics for the preferred cis-P,S arrangement, rationalizing its formation. Direct base-free reaction of [PtCl₂(1,5-cyclooctadiene)] with one equivalent of the same phosphanylthiol produce the trinuclear complex [PtCl₂(CH₂CH₂PPh₂S)₂]₂ (2) instead of the binuclear structure common in palladium and nickel derivatives. Crystals of 2 are triclinic (P₁) showing a sulfur-bridging edge-sharing cyclic trinuclear complex with square-planar coordination geometry around the platinum atoms and a Pt₃S₃ cycle in skew-boat conformation. This preference for the trinuclear structure was rationalized mechanistically and through conceptual DFT.

Introduction

The transition-metal complexes of heterotopic phosphanylthiolato ligands have been widely studied because of their applicability in some interesting reactions,[1] such as S-alkylation/S-dealkylations,[2,3] carbothiolations,[3] reductions,[4] copolymerizations,[5] or carboxylations.[6] These complexes also have relevance in desulfurization technologies[7] and in understanding the biological pathways of certain sulfur-containing metalloproteins.[8] For all these applications, the stereochemistry of these complexes has particular importance, as different stereoisomers could present different behavior in a given process.[9] Among all phosphanylthiolato ligands, we are particularly interested in 2-phosphanylalkylthiolato ligands because they can support a resolved chiral carbon in the chelate chain.[10] For group 10 metals (M=Ni, Pd, and Pt), the more abundant 2-phosphanylalkylthiolato complexes are the bis-chelates, [M(2-phosphanyl)ethanethiolato] analogues, [Ni(dppet)₂],...
with the chlorocomplexes, nickel has preference for the binuclear complex \([\text{NiC}l(\text{S}-\text{CH}_2\text{CH}_3\text{PPH}_2\text{X}^1\text{P}^2\text{S})]^+\),\(^{10,14}\) also observed for other phosphanylalkylthiolato ligands, both in solution and in solid state.\(^{10,14}\) Mononuclear \([\text{PdCl(dppet-X}^1\text{P}^2\text{S})(\text{PPH}_3)]\) proved to be stable in solution. No loss of \(\text{PPH}_3\) takes place, and no dimeric palladium complexes were ever detected.\(^6\) This complex shows in solution an equilibrium between the two geometric isomers strongly displaced to the \(\text{trans}-\text{PP}\) arrangement, but crystallization yields only the major stereoisomer. When an alkyl substituent is introduced in the chelate chain, as in the case of 1-(diphenylphosphanyl)butyl-2-thiolate derivative, dissociation of \(\text{PPH}_3\), and formation of the dimeric chlorocomplex, \([\text{PdCl}(_8\text{PPh}_{10}\text{X}^1\text{P}^2\text{S})]_2\), was described.\(^{11b}\) For platinum, only the mononuclear \(\text{cis}[\text{PtCl(dppet-X}^1\text{P}^2\text{S})(\text{PPH}_3)]\) was reported.\(^{11c}\)

As part of a project on the analysis of the ligand-based stereoelectronic effects that are determinant in the coordination conformations of phosphanylthiolato ligands around the metal,\(^6,16–12\) we now report new preparation methods, and the solid state structure, for bis-chelate 1 and for the unusual trinuclear complex \([\text{PtCl(} (_8\text{PPh}_{10}\text{X}^1\text{P}^2\text{S})_2\text{Cl}]_2\text{Pt}\text{PPh}_3\text{Cl}]).\(^2\) The structures obtained are also rationalized mechanistically and through conceptual DFT calculations.

### Results and Discussion

Complex 1 was first prepared in moderate yield (52%) from the reaction of \(\text{K}_2\text{PtCl}_4\) and Hdppet in the presence of \(\text{NEt}_3\) as a base.\(^{11c}\) The potential problems related to the use of the base,\(^{10a}\) together with the low yield of 1 with this method, prompted us to explore the direct, base-free, procedure. Thus, reaction of \(\text{K}_2\text{PtCl}_4\) with 2 equivalents of Hdppet in a mixture of methanol/water cleanly afforded bis-chelate 1, which was isolated in 92% yield (Scheme 1). Alternatively, 1 can be also obtained by oxidative addition of the phosphanylthiol to \(\text{Pt}(\text{PPH}_3)_4\) and subsequent reductive elimination of hydrogen. In this case, bis-chelate 1 was isolated in 70% yield (Scheme 1). According to the \(^{31}\text{P}([\text{H}])\) NMR spectrum, bis-chelate 1 exists as a single geometric isomer in solution, with a \(\delta_{\text{trans}}\) coupling constant of 2810.9 Hz which suggest a cis-PP arrangement.\(^{11c}\) The cis geometry of bis-chelate 1 in solid state was confirmed by the X-ray diffraction (XRD) crystal structure.

The XRD study was carried out on a crystal of 1 obtained from dichloromethane–hexane. Crystal data for the structure are given in Table 1. Selected bond lengths and bond angles are listed in the caption of Figure 1. The crystal structure reveals a mononuclear square-planar complex with \(\text{C}_2\) symmetry and the platinum atom placed on the rotation axis (Figure 1).

The Pt–S bond length is similar to those detected in other cis\(^{18}\) and trans-bis(phosphanylthiolato)\(^{13a}\) complexes of platinum(II), but the Pt–P is shorter than those observed in the \(\text{trans}\) geometries. The large \(\text{P}–\text{Pt}–\text{P}\) angle, nearly 105°, results from the cis orientation of the bulky \(\text{PPH}_3\) groups that compress the S–Pt–S angle to about 82°. The chelate angle, is in the order of those observed for mononuclear platinum(II) complexes.

### Table 1. Crystal data for 1 and 2

| Compound | 1 | 2 |
|----------|---|---|
| Formula  | \(\text{C}_8\text{H}_3\text{PtP}_2\text{S}_1\) | \(\text{C}_8\text{H}_3\text{PtP}_2\text{S}_1\) |
| Solvents | – | – |
| Formula weight | 685.65 | 1427.47 |
| Crystal size (mm\(^3\)) | 0.30 \(\times\) 0.20 \(\times\) 0.10 | 0.003 \(\times\) 0.003 \(\times\) 0.002 |
| Crystal color | yellow | yellow |
| Temp (K) | 153 | 153 |
| Crystal system | monoclinic | triclinic |
| Space group | \(\text{C}2/c\) | \(\text{P}1\) |
| \(\text{A (Å)}\) | 14.6909(3) | 12.2393(5) |
| \(\text{B (Å)}\) | 10.7332(2) | 13.4900(6) |
| \(\text{C (Å)}\) | 17.0890(3) | 15.4706(7) |
| \(\alpha (\text{deg})\) | 90 | 113.7590(10) |
| \(\beta (\text{deg})\) | 90 | 109.3020(10) |
| \(\gamma (\text{deg})\) | 90 | 113.7590(10) |
| \(\text{V (Å}^3\) | 2536.21(8) | 2195.42(17) |
| \(Z\) | 4 | 2 |
| \(\rho (\text{g cm}^{-3})\) | 1.796 | 2.159 |
| \(\mu (\text{mm}^{-1})\) | 5.839 | 10.000 |
| \(\delta_{\text{trans}} (\text{°})\) | 31.52 | 31.53 |
| Reflec. measured | 19126 | 30667 |
| Unique reflections | 3948 \([R_{\text{int}} = 0.0593]\) | 8180 \([R_{\text{int}} = 0.0821]\) |
| Absorp. correct. | \(\text{SADABS}\) | \(\text{SADABS}\) |
| Trans. min/max | 0.587/1.000 | 0.506/1.000 |
| Parameters/restraints | 206 | 647/834 |
| \(\text{R}1/\text{wR}2 \left[\text{all data}\right]\) | 0.0295/0.0709 | 0.0458/0.0998 |
| \(\text{R}1/\text{wR}2 \left[\text{all data}\right]\) | 0.0304/0.0716 | 0.0910/0.1008 |
| Goodness-of-fit (\(F^2\)) | 1.052 | 0.857 |
| Peak/hole (e/Å\(^3\)) | 1.993/–5.137 | 2.056/–3.358 |

### Scheme 1. Synthesis of bis-chelate 1. Reagents and conditions: a) Hdppet/MeOH, \(\text{K}_2\text{PtCl}_4\)/\(\text{H}_2\text{O}\), 30 min, rt, 92%; b) Hdppet (neat), \(\text{Pt}(\text{PPH}_3)_2\)/\(\text{CH}_2\text{Cl}_2\), 30 min, rt, 70%.

### Figure 1. ORTEP (Oak Ridge Thermal Ellipsoid Plot) figure (50%) of complex 1. H atoms are omitted for the sake of clarity; selected distances (Å) and angles (°): Pt–P 2.2705(6), Pt–S 2.3233(6), P–Pt–S 86.45(2), P–Pt–P 104.98(3), S–Pt–S 82.14(3), P–Pt–S 168.56(2). Symmetry transformation used to generate equivalent atoms: \(x, y, 1/2–z\).
plexes with the PPh₂ group of a chelated dppe ligand cis to a PPh₃.

The observed structural cis preference can be interpreted, in simple terms, on the basis of the antisymbiosis rule stating that two soft ligands in mutual trans positions have a destabilizing effect on each other when attached to a soft metal ion. To shed light into this preference for the cis conformation and get more detailed information, we envisaged density functional theory (DFT) calculations. For our study, we used the M06 exchange-correlation functional that includes dispersion corrections. M06/TZVP/M06/SVP calculations on complex I reveal a favorable energy difference of only 1.3 kcal mol⁻¹ for the cis isomer. This small difference can be the result of a low antisymbiotic effect (thiolates and phosphines are both soft bases; for example, hardness of CH₃S⁻ and PPh₂CH₃ are 61.8 and 65.9 kcal mol⁻¹, respectively) and the steric interactions that favor the trans isomer. When the thermal and entropic effects are not introduced, the energetic preference for the cis arrangement increases to 3.7 kcal mol⁻¹, which brings the computational results into much better agreement with experimental observations, and reveals a possible overestimation by our calculations of the entropic stabilization of the trans isomer as compared to the cis one. The large dipole moment of the cis isomer provides larger solvation energy in comparison with the nonpolar trans isomer. The chemical potential for the cis isomer of complex I is −70.5 kcal mol⁻¹ whereas it is −66.2 kcal mol⁻¹ for the trans conformation. In agreement with the maximum hardness principle, the chemical hardness of the cis conformation (41.5 kcal mol⁻¹) is somewhat higher than that of the trans conformation (41.3 kcal mol⁻¹).

Given the low energy difference between both isomers, we investigated the reaction pathway to get complex 1 from Pt(PPh₃)₄ (see Figure 2) in the cis and trans conformations to discern whether kinetic effects are responsible for the formation of exclusively the cis isomer. Formation of the cis isomer requires the generation of complex V in Figure 2. These complexes are generated by successive substitutions of phosphine by Hdppet ligands. The sequential dissociation of phosphine groups is not energy demanding, provided that at least two based phosphorous ligands remain bonded to platinum, either in the form of triphenylphosphines or phosphanylthiol ligands. Indeed the bis-phosphine structure is isoenergetic with the bis-Hdppet structure (compare complexes III and VII). This result concurs with the experimental fact that in the presence of a high concentration of Hdppet with respect to the Pt(PPh₃)₄ precursor, the PPh₃ groups are easily substituted. In any case the coordination of the phosphanylthiolato does not occur through the thiolate moiety, but through the phosphine group. Take for instance the coordination of the second molecule of Hdppet to species VIII, from which formation of complex X with the phosphine coordinated to Pt is 20.0 kcal mol⁻¹ more stable than the same complex coordinated through the thiol group. Once complex V is formed, the next dissociation of a phosphine ligand is not feasible without the oxidative addition of the S–H bond of the Hdppet ligand into the Pt center to form complex IX. Actually without removing the phosphine ligand, from complex V, this insertion takes places through a barrier of 11.5 kcal mol⁻¹. From IX, bearing the excess of Hdppet, the exchange of PPh₃ by Hdppet is favored by 1.6 kcal mol⁻¹, to form complex X. The final step that leads to complex 1 cis from species X takes places through a concerted transition state that involves a second oxidative addition and the reductive release of a hydrogen molecule in a process that requires 25.9 kcal mol⁻¹.

This rather high energy barrier is probably somewhat overestimated. The rate determining step (rds) for the formation of 1 cis corresponds to this last X to 1 cis transformation.

The trans conformation of complex 1 can be formed through different reaction pathways. First, it might be generated directly from the cis conformation, that is, complex 1 cis,

\[\text{Figure 2. Reaction pathways of the conversion of } \text{Pt(PPh₃)₄} \text{ to complex 1 (red: the values of the transition states, relative Gibbs energies in kcal mol⁻¹).}\]
however the barrier to isomerize to the trans conformation is 37.1 kcal mol$^{-1}$. Second, complex V can also evolve to VII through successive exchange of phosphines by Hdppet ligands. Two consecutive S–H oxidative additions followed by the reductive release of a hydrogen molecule in complex VII produce complex 1 trans in a process that has to surmount a Gibbs energy barrier of 26.8 kcal mol$^{-1}$. The XII to 1 trans process is the rds for the formation of complex 1 trans. This means that kinetically, the cis conformation is favored over the trans species by 0.9 kcal mol$^{-1}$. A final pathway to form complex 1 trans could be the isomerization of complex VIII to its trans conformation XI, that is, the rotation of the hydride by 90°. This transformation requires surpassing a barrier of 33.0 kcal mol$^{-1}$ with respect to I, being the trans isomer 6.4 kcal mol$^{-1}$ higher in energy. Therefore, this latter pathway can be ruled out. As a whole, our results show that formation of complex 1 cis is both thermodynamically and kinetically favored as compared to complex 1 trans formation. In both cases, the rds corresponds to the last step of the process that involves coordination of the phosphanylthiolato ligand and release of a H$_2$ molecule.

To further evaluate the preference for the cis isomer for complex 1, its phenyl groups were substituted by either methyl or tert-butyl (t-Bu) groups, and then the trans isomer was found to be lower in Gibbs energy by 0.8 and 15.2 kcal mol$^{-1}$, respectively. These energy values reveal that highly sterically demanding groups like t-Bu impedes the formation of the cis conformation, and the comparison between methyl and phenyl substituents indicates a major preference of the cis for the latter substituent because of the π–π stacking between its aryl groups. The structural deformation due to the substituents on the phosphorous is translated into the increase of the P–S–S angle, by 0.4 and 12.0° with methyl and t-butyl groups, respectively (see Figure 3).

To explore the possibility to obtain the dinuclear complex [PtCl($\mu$-SCH$_2$CH$_2$PPh$_3$-$\kappa$-S)]$_2$ similar to those observed for nickel$^{[15]}$ and palladium$^{[16]}$, the base-free reaction of [PtCl(COD)] (COD = 1,5-cyclooctadiene) with 1 equivalent of Hdppet in dichloromethane was performed, affording a quite insoluble material. According to the $^{31}$Pt($^1$H) NMR spectrum, this solid is formed mainly by two products in a 2/1 ratio. The minor component shows a singlet with a chemical displacement and a $^1$J$_{P-Pt}$ coupling constant similar to those observed for the bis-chelate complex 1. The major constituent of the mixture also shows a singlet, but at higher fields and with larger $^1$J$_{P-Pt}$ coupling constant. Slow evaporation of the NMR solutions of this mixture produces a microcrystal (3 x 3 x 2 μm$^3$) which was studied by XRD. Crystal data for the structure obtained, complex 2, are given in Table 1. Selected bond lengths and bond angles are listed in the caption of Figure 4.

The crystal structure reveals a sulfur-bridging edge-sharing cyclic trinuclear complex with square-planar coordination geometry around the platinum atoms (Figure 4). Related structures were found for aminoalkylthiolato, [PtBr($\mu$-SCH$_2$CH$_2$NM$_{2}$-$\kappa$-N,S)]$_2$ $^{[22]}$ phosphanylthiolato, [PtI($\mu$-SC$_3$H$_4$-2-PPh$_3$-$\kappa$-S)]$_2$ $^{[23]}$ and [PtI($\mu$-SC$_3$H$_4$-2-Pt1,1’-biphenyl)-$\kappa$-S)]$_2$ $^{[24]}$ and asarylnarylthiolato ligands, [PtI($\mu$-SC$_3$H$_4$-2-PAS$_2$-$\kappa$-As,S)]$_2$ $^{[25]}$ but complex 2 is, to our knowledge, the first example with phosphanylalkythiolato ligand.

The cis-Cl,P arrangement is in disagreement with the anti-symbiosis rule$^{[17]}$ but the cis-S,S geometry is necessary to build
The six-membered $\text{Pt}_3\text{S}_3$ cycle. This cycle adopts a skew-boat conformation (Figure 5) with each bridging sulfur atom showing one shorter and one longer Pt−S bond (Figure 4). Similar unsymmetrical bridging sulfurs were observed in related compounds. The $\text{S}–\text{Pt}–\text{S}$ angles are smaller than $\text{Pt}–\text{S}–\text{Pt}$ ones because of the restriction imposed by the metal square-planar coordination. Two of the three five-membered chelate cycles adopt a $\delta$ conformation with both phenyl radicals of the $\text{PPh}_2$ group in a pseudo equatorial position. The third chelate cycle shows a $\lambda$ conformation which locates one of the phenyl groups in axial position (Figure 6). On the face of the $\text{Pt}_3\text{S}_3$ cycle where this phenyl is placed, there is no other group that generates steric repulsions, resulting in the most favorable situation. Accordingly, the Pt−P and Pt−S distances are the shortest. The square-planar geometry around platinum is somewhat distorted with a chelate angle slightly reduced from the idealized value of 90°. Quite similar distortions from the idealized geometry are also observed in other platinum(II) complexes with chelated dppet ligands. The intramolecular Pt−Pt distances are greater than 3.65 Å suggesting no metal−metal covalent interactions.

Concerning the mechanism of the reaction, as we have observed in this work, the $^{195}\text{Pt}[\text{H}]$ NMR of the reaction mixture of one equivalent of the phosphanylthioarsine $\text{Ph}^2\text{AsSCH}_2\text{H}_2\text{PPh}_2$ with [PtI(COD)] shows initially the existence of a mixture of the bis-chelate and a second complex with chemical displacement at lower frequencies and larger $^{31}\text{P}–\text{Pt}$ coupling constant. The second compound resulted to be the trinuclear $[\text{Pt}(\mu-\text{SC}_2\text{H}_2\text{PPh}_2\cdot\text{k}^2\text{P}_2\text{S})]_3$. This parallelism, and the crystal structure obtained, allow us to assign the major component of our reaction mixture to complex 2. Regarding the reaction pathway, formation of the bis-chelate complex 1 has been postulated as the kinetically favored process, elapsing through a mononuclear intermediate (Scheme 2). The subsequent reaction of 1 with the mononuclear intermediate and unconverted starting product (path A) can generate a trinuclear intermediate that should isomerize to the final thermodynamic product 2.

This pathway is similar to that proposed for the formation of $[\text{Pt}(\mu-\text{SC}_2\text{H}_2\text{PPh}_2\cdot\text{k}^2\text{P}_2\text{S})]_3$, in which the trinuclear intermediate was identified, and the kinetic product, the bis-chelate, is totally transformed into the ultimate trinuclear complex.[23] In present work, the trinuclear intermediate has not been detected, and no interconversion between complexes 1 and 2 was observed, pointing to a quick association of the mononuclear intermediate to give trinuclear complex 2 (pathway B in Scheme 2).

To understand the trinuclear structural preference for complex 2, DFT calculations were carried for this complex and for the hypothetical binuclear intermediate $[\text{PtCL}(\mu-\text{SC}_2\text{H}_2\text{PPh}_2\cdot\text{k}^2\text{P}_2\text{S})]_2$, as well as for any moiety able to link complexes 1 and 2. First, the structural results on complex 2 showed good agreement between the experimental and theoretical data. The standard deviation for the bond distances is 0.053 Å and that for the angles is 1.3°,[22,28] thus providing confidence in the reliability of the chosen method to reproduce geometries of the studied complexes. Furthermore, although there is the experimental insight that both mononuclear and trinuclear species are diamagnetic, we performed calculations for neutral closed-shell singlet ground-state structures, but we also checked how far was the lowest-lying excited triplet state. In all cases, the triplet state presented a higher energy (the difference between these two states for 1 is 31.9 kcal mol$^{-1}$), indicating that the singlet states are the most favored. This is in agreement with the sharp peaks in the NMR spectra. Figures 7 and 8 map the paths B and A that drive [PtCl$_3$(COD)] to 2 and 1, respectively. The first step (a to b in Figure 7) involves the dissociation of the neutral COD ligand together with the coordination of a Hdppeet ligand. This process releases 17.0 kcal mol$^{-1}$. This new square-planar intermediate b might be in competition with the cationic moiety where the leaving group was a chloride instead of the COD.
Anyway chloride substitution is endergonic by 6.4 kcal mol\(^{-1}\), and, therefore, COD release is much more favorable. The next proton transfer from the thiol group to the chloride and release of HCl molecule requires 23.5 kcal mol\(^{-1}\) and drives to an unstable intermediate that trimerizes easily to complex 2. The formation of this trinuclear complex from complex d is found to be barrierless and quite exergonic (39.4 kcal mol\(^{-1}\)). Thus this result shows that pathway B involves relatively low-energy-demanding steps, and it is thermodynamically favored.

Alternatively, instead of the trinuclear interaction, intermediate d can interact with a new Hdpmpet substrate molecule to yield complex e (Figure 8). This complex can easily be transformed into f after overcoming a barrier of 8.5 kcal mol\(^{-1}\). Final release of an HCl molecule yields 1\(cis\) complex in a process that is 21.4 kcal mol\(^{-1}\) endergonic. On the other hand, from species d, the trans conformation of 1 might be also feasible, overcoming a barrier 17.0 kcal mol\(^{-1}\). Our results show that once complex d is generated, formation of 2 is kinetically and thermodynamically more favorable than obtaining any of the mononuclear species 1. This result is in agreement with the principle of maximum hardness since the chemical hardness for complex 2 is 7.8 kcal mol\(^{-1}\) higher than that of complex 1\(cis\).

The dimerization was also faced, instead of the trimerization. Although the process to get the dimeric structures, including...
either two chloride or sulfur bridges is barrierless, thermodynamically it is 30.2 kcal mol⁻¹ less favorable than the formation of the trinuclear structure. On the other hand, the other trinuclear structure proposed as an intermediate in path A (Scheme 2) was also investigated, but located to be 6.6 kcal mol⁻¹ higher in energy than 2. Despite its rather high stability, its formation requires the formation of complex 1 first, which is ruled out according to the mechanism proposed in Figure 8.

The substitution of the phenyl groups by methyl or tert-butyl groups on the phosphorous atoms did not change any qualitative trend, and quantitatively all barriers were nearly identical. Thermodynamically, the energy release with respect to the precursor [PtCl₄(COD)] in the formation of 2 is higher when the phenyl groups in the phosphines are substituted by methyl (13.2 kcal mol⁻¹) or tert-butyl (8.7 kcal mol⁻¹) groups. This confirms that the nature of phosphine substituents is not determining the feasibility of the formation of trinuclear species.

Conclusions

The transition metal complexes of heterotopic phosphanyl-thiolato ligands are important for their use in many interesting reactions. In this work, bis-chelate complex [Pt(SCH₂CH₂PPh₂)₂(S₂)] (1) has been obtained in good yields by direct base-free substitution reaction of the corresponding thiol with K₂PtCl₄ or by oxidative addition of the thiol to Pt(PPh₃)₄. The XRD studies of this complex 1 shows a cis-PP arrangement in agreement with the antisymbiosis rule. Density functional theory (DFT) calculations on 1 indicate that the cis geometry is preferred over the trans one for both thermodynamic and kinetic reasons. The rate determining step for the formation of complex 1 is the final step, which involves an oxidative addition of the S–H bond of a phosphanylthiol ligand into the Pt center and the reductive release of a hydrogen molecule. Direct base-free reaction of [PtCl₄(COD)] with one equivalent of the thiol produces the trinuclear complex [PtCl₂(SCH₂CH₂PPh₂)₂(S₂)] (2) with square-planar coordination geometry around the platinum atoms and a PtS₂ cycle in skew-boat conformation. Our DFT calculations show that formation of the trinuclear structure occurs through ClPt(dppe) complex d. Once this rather unstable intermediate is formed, the formation of the trinuclear structure is a barrierless and quite exergonic process. On the contrary, formation of the mononuclear and dinuclear species involves non-negligible energy barriers and leads to thermodynamically less stable products.

Experimental Section

Synthesis

General remarks: The complexes were synthesized using standard Schlenk techniques under N₂ atmosphere. The solvents were dried by standard methods and distilled and deoxygenated before use. The C, H, and S analyses were carried out using a Carlo–Erba microanlyser (Lakewood, USA). ¹H NMR spectra were recorded at 200 MHz on a Bruker DPX-200 spectrometer (Billerica, USA). Peak positions are relative to tetramethylysilane (TMS) as internal reference. ³¹P(¹H) NMR spectra were recorded on the same instrument operating at 81.0 MHz. Chemical shifts are relative to external 85% H₃PO₄, and downfield values are reported as positive.

[Pt(SC₃H₄PPh₂)₂(S₂)] (1). Method 1: Hdppe (30 mg, 0.12 mmol) in MeOH (2 mL) was added to a solution of K₂PtCl₄ (24.7 mg, 0.06 mmol) in deionized H₂O (3 mL). The mixture was allowed to react for 30 min at rt, the solvent is evaporated in vacuo down to 0.5 mL, and Et₂O (1 mL) is slowly added to precipitate an intense yellow microcrystalline solid. The product is separated by filtration, washed with Et₂O, and dried under current of N₂. Yielding complex 1 (24 mg, 92%). Method 2: neat Hdppe (112 mg, 0.44 mmol) was added to a solution of Pt(PPh₃)₄ (285 mg, 0.22 mmol) in CHCl₃ (8 mL). The mixture is allowed to react for 30 min at rt, and hexane (1 mL) is slowly added to precipitate 1 (105 mg, 70%). Completely dry complex 1 is stable in air, slightly soluble in CH₂Cl₂ and insoluble in CHCl₃, EtOH, MeOH, toluene, Et₂O, and hexane. ¹H NMR (200 MHz, CD₂Cl₂, TMS): δ = 2.52 (m, 4H, aliphatics), 7–8 ppm (m, 10H, aromatics). ³¹P(¹H) NMR (81 MHz, CD₂Cl₂, H₃PO₄): δ = 61.70 ppm (s, J_P,P₄ = 2810.9 Hz). The low solubility of 1 precluded the observation of a good-quality ¹³C NMR spectrum. Anal. calc'd for C₃₇H₃₂P₄Pt₂: S₈ 685.7: C 49.05, H 4.12, S 9.35; found C 49.29, H 4.30, S 9.65.

[PtCl₄(SCH₂CH₂PPh₂)₂(S₂)] (2): neat Hdppe (123 mg, 0.50 mmol) was added to a solution of [PtCl₄(COD)] (236.5 mg, 0.50 mmol) in CH₂Cl₂ (8 mL). The mixture was allowed to react for 1 h at rt, the solvent was evaporated in vacuo down to 3 mL, and Et₂O (5 mL) was slowly added to give a yellow precipitate. The product was separated by filtration, washed with Et₂O, and dried under a current of N₂, yielding a solid (189.7 mg) practically insoluble in CH₂Cl₂ and insoluble in CHCl₃, Et₂O, and hexane. The low solubility of this solid precluded the observation of good-quality NMR spectra. ³¹P(¹H) NMR (81 MHz, CD₂Cl₂, H₃PO₄): major product δ = 45.27 ppm (s, J_P,P₄ = ca. 3343 Hz), minor product δ = 62.18 ppm (s, J_P,P₄ = ca. 2771 Hz).

X-ray crystal structure determination

Yellow crystals of 1 were obtained by slow evaporation of CH₂Cl₂/hexane solutions at rt. Yellow crystals of 2 were obtained by slow evaporation of a CH₂Cl₂ solution. Measured crystals were prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation. Crystal data are presented in Table 1, and selected distances and angles in the captions of Figure 1 and 4.

Data collection: Crystal structure determinations for 1 and 2 were carried out using a Siemens P4 diffractometer (Munich, Germany) equipped with a SMART 1000 CCD area detector, a MAC Science Co. rotating anode with MoKα radiation, a graphite monochromator, and a Siemens low-temperature device (T = 120 C). Full sphere data collection was used with φ and ω scans. Programs used: Data collection SMART324; data reduction SAINT324 and absorption correction SADABS31.

Structure Solution and Refinement: Crystal structure solution was achieved using direct methods as implemented in SHELXTL320 and visualized using the program XP. Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on F² using all measured intensities was carried out using the program SHELX-93. All nonhydrogen atoms were refined including anisotropic displacement parameters.

Comments on the structures: Compound 1 crystallizes with a half molecule in the asymmetric unit showing C2 symmetry. Com-
Computational methods

All the DFT calculations were performed at the generalized gradient approximation (GGA) level with the Gaussian09 set of programs.[13] using the M06 functional of Truhlar.[14] The electronic configuration of the molecular systems was described with the standard split-valence basis set with a polarization function of Ahlrichs and co-workers for H, C, N, P, S, and Cl (SVP keyword in Gaussian).[15] For Pt we used the quasi-relativistic Stuttgart/Dresden effective core potential, with an associated valence basis set (standard SDD keywords in Gaussian09).[16] The geometry optimizations were carried out without symmetry constraints, and the characterization of the stationary points was performed by analytical frequency calculations. These frequencies were used to calculate uncoupled zero-point energies (ZPEs) as well as thermal corrections and entropy effects at 298 K and 1 atm by using the standard statistical-mechanics relationships for an ideal gas. Energies were obtained via single point calculations on the M06-optimized geometries with triple zeta valence plus polarization (TZVP keyword in Gaussian) using the M06 functional as well.[10] In these single point energy calculations, H, C, N, P, S, and Cl were described using the TZVP basis set, while for Pt, the SDD basis set was employed. On top of the M06/TZVP/M06/SVP energies, we added the ZPEs, thermal corrections obtained at the M06/SVP level. In addition, to calculate the reported Gibbs energies, we included solvent effects of a CHCl₃ solution estimated with the polarizable continuum model implemented in Gaussian09.[17] The chemical potential is a measure of the tendency of the electrons to escape from the system. It is calculated from the partial derivative of the electronic energy with respect to the total number of electrons. The hardness, η, is a measure of the resistance of a chemical species to change its electronic configuration, and it is defined as the second-order partial derivative of the total electronic energy with respect to the total number of electrons. Using a finite difference approximation and the Koopmans’ theorem, one obtains the expressions we have used for the calculation of the chemical potential and the hardness:

\[
\mu = \frac{E_{\text{LUMO}} + E_{\text{HOMO}}}{2},
\]

\[
\eta = \frac{E_{\text{LUMO}} - E_{\text{HOMO}}}{2},
\]

where \( E_{\text{LUMO}} \) and \( E_{\text{HOMO}} \) are the energies of the low unoccupied molecular orbital (LUMO) and the high occupied molecular orbital (HOMO), respectively.

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