Extending The Reaction Landscape of the {Pt(μ-S)$_2$Pt} Core: From Metal Centers to Non-Metallic Electrophiles

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The outstanding nucleophilicity of the {Pt(μ-S)$_2$Pt} core in compounds [L$_2$Pt(μ-S)$_2$PtL$_2$] (L$_2$ = phosphane) accounts for their ability to act as metalloligands towards main group and transition metals, and thus for the high number of [{L$_2$Pt(μ$_3$-S)$_2$PtL$_2$}$_x$ML′$_y$]^z aggregates already described. However, the electronic and molecular features underpinning this behavior anticipate a landscape of comparable richness for the reactions of [L$_2$Pt(μ-S)$_2$PtL$_2$] with non-metal electrophiles. Exploration of the chemistry of [L$_2$Pt(μ-S)$_2$PtL$_2$] (L$_2$ = chelating diphosphane) towards various electron-acceptor species has been the aim of our research for the past years. In this microreview we survey the synthetic strategies of [L$_2$Pt(μ-S)$_2$PtL$_2$] compounds, their distinguishing electronic and molecular features, the dynamic processes and electron-donor properties of the {Pt(μ-S)$_2$Pt} core, and its binding ability towards metal centers. Moreover, particular attention is given to the reaction chemistry of [L$_2$Pt(μ-S)$_2$PtL$_2$] with organic electrophiles and protic acids, as well as to the influence of the {Pt(μ-S)$_2$Pt} core on the reactivity of inorganic or organic L′ ligands in [{L$_2$Pt(μ$_3$-S)$_2$PtL$_2$}$_x$ML′$_y$]^z aggregates.

Introduction

The outstanding ability of sulfur to bind heavy metals is not only evidenced by the enormous variety of metal sulfide minerals found in nature, but also by the occurrence of platinum group metals in mineral ores different from native deposits. One of these examples is cooperite, a platinum-bearing sulfide with the general formula Pt$_{0.6}$Pd$_{0.3}$Ni$_{0.1}$S, in which platinum(II) ions are coordinated by sulfide anions in a square-planar arrangement and these are tetrahedrally coordinated by four platinum ions.[1] In parallel to their

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Agustí Lledós (left) was born in 1955 in Barcelona. He received his BSc degree in Chemistry from the Universitat Autònoma de Barcelona in 1979, and his Ph.D. in 1984 at the same university, under the supervision of Juan Bertrán. After a postdoctoral stay at the Université de Paris-Sud (Orsay) with Yves Jean, he returned to the Universitat Autònoma in 1987 and created a research group devoted to the computational study of transition metal complexes. He was appointed Professor of Physical Chemistry in 1994. His research interests concern the computational modeling of transition metal systems, with focus on hydride complexes, σ-bond activation, bimetallic compounds and homogeneous catalysis.

MICROREVIEWS: This feature introduces the readers to the author's research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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abundance, the chemistry of metal sulfides has also been the object of extensive studies and still attracts great attention, mainly because of their structural diversity,[2] essential role in catalysis,[3] and rich solid-state and bioinorganic chemistry.[4] In contrast, platinum sulfide chemistry has received much less attention for many decades of the past century despite the fact that the first platinum-sulfur complex, $(NH_4)_2[Pt(\eta^2\text{-}S_5)_3]$, was isolated in 1903.[5]

A main hallmark in the field of platinum(II)−sulfur chemistry was established by Chatt and Mingos in 1970, who obtained several complexes of various nuclearities and structures.[6] Among them, $[(PMe_2Ph)_2Pt(\mu\text{-}S)_2Pt(PMe_2Ph)_2]$, followed by $[(PPh_3)_2Pt(\mu\text{-}S)_2Pt(PPh_3)_2]$[7] reported by Ugo et al. one year later, constitute the first examples of platinum(II) sulfide complexes containing the $\{Pt(\mu\text{-}S)_2Pt\}$ core. As a result of these studies, they also described the corresponding monoalkylated species $[L_2Pt(\mu\text{-}S)(\mu\text{-}SR)PtL_2]^+$ (L = PMe_2Ph, R = $PhCH_2$ [6] and L = PPh_3, R = CH_3 [7]) and the trinuclear $[Pt_3(PMe_2Ph)_6(\mu_3\text{-}S)_2]Cl_2$ complex,[6] whose formation provided the first evidence for the nucleophilicity of the bridging sulfido ligands in the $\{Pt(\mu\text{-}S)_2Pt\}$ core.

The evolution of the chemistry of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ (L = phosphane) has proceeded very rapidly over the past two decades. Thus, the significant number of known homo- and heterometallic derivatives of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ shows that this species is one of the most effective metalloligands identified to date. A summary of the historical milestones in platinum-sulfur chemistry leading to sulfide-bridged aggregates with the $\{Pt(\mu\text{-}S)_2Pt\}$ core, as well as the main developments in their synthesis, structure, and reactivity were excellently reviewed by Fong and Hor, who have made important contributions to this field.[8] Overall, the ability of the sulfido ligands in the $\{Pt(\mu\text{-}S)_2Pt\}$ core to extend their coordination mode from μ-S to μ_3-S accounts for the behavior of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ as building blocks for higher nuclearity complexes, and the flexible hinge angle between the two $Pt^{II}S_2$ planes for the varied coordination geometries at the heterometal M in the corresponding $[\{L_2Pt(\mu_3\text{-}S)_2PtL_2\}_xML'_y]^z$ aggregates.

Remarkably, the reaction chemistry of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ compounds towards nonmetallic electrophiles was not the object of systematic studies until much more recently. Combination of experimental results and theoretical calculations has allowed for a detailed knowledge of the cascade of reactions of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ in the presence of either organic electrophiles, such as CH_2Cl_2,[9] or the simplest electron-acceptor species, the proton.[10] In addition, the influence of $\{Pt(\mu\text{-}S)_2Pt\}$ core on the reactivity of L′ in $[\{L_2Pt(\mu_3\text{-}S)_2PtL_2\}_xML'_y]^z$ aggregates has been explored.[11] All these results promise to inspire new approaches that contribute towards the unveiling of the potential of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ compounds as nucleophilic agents.

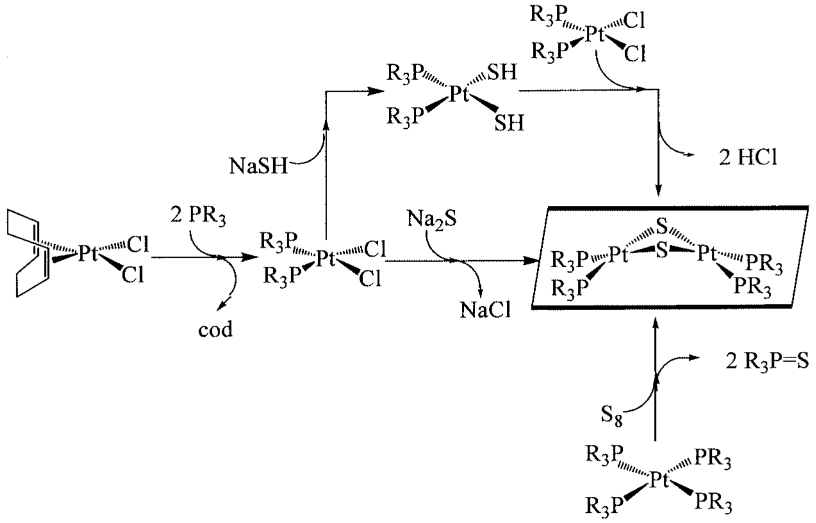
Understanding the rich and diverse chemistry of the $\{Pt(\mu\text{-}S)_2Pt\}$ core has been the aim of our research for the past several years. Our approach has focused on the use of chelating diphosphanes as terminal L ligands,[12] with an emphasis on the chemistry of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ with nonmetal electrophiles[9,10] and ML'_y fragments.[11] This report surveys the present knowledge on the nucleophilicity of the $\{Pt(\mu\text{-}S)_2Pt\}$ core in $[L_2Pt(\mu\text{-}S)_2PtL_2]$ compounds; the previous review by Fong and Hor is our starting point.[8] Thus, the peculiarities concerning the synthesis of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ compounds, their distinguishing electronic and molecular features, the dynamic processes and electron-donor properties of the $\{Pt(\mu\text{-}S)_2Pt\}$ core, and the reactivity of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ towards metallic and nonmetallic electrophiles will be summarized.

Synthesis, and Molecular and Electronic Structures of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ Complexes

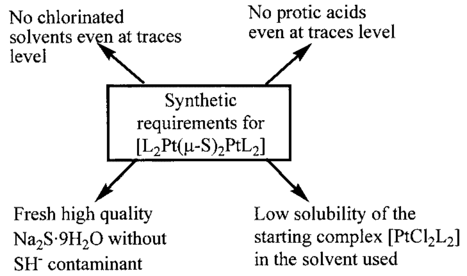
Synthetic Procedures

Despite their apparent simplicity, the synthetic routes reported for complexes with the formula $[L_2Pt(\mu\text{-}S)_2PtL_2]$ (Scheme 1) are not straightforward, often leading to mixture of products.[8] The most common procedure is based on the metathesis reaction between $[PtCl_2L_2]$ and $Na_2S{\cdot}9H_2O$,[6] for which only monometallic precursors with L = phosphane ligands have been used. These have generally been obtained by replacing 1,5-cyclooctadiene (cod) in $[PtCl_2(cod)]$ by the corresponding phosphane.[13] Other less direct routes entail the oxidation of $[PtL_4]$ with S_8, which affords phosphane sulfide as secondary product,[7] or, the reaction between $[PtCl_2L_2]$ and NaSH.[14] The latter involves the formation of $[Pt(SH)_2L_2]$ first and then its subsequent reaction with a second equivalent of $[PtCl_2L_2]$, thus yielding $[L_2Pt(\mu\text{-}S)_2PtL_2]$ plus two equivalents of HCl. However, as commented below, the presence of HCl is inconvenient as it can cause disintegration of the $\{Pt(\mu\text{-}S)_2Pt\}$ core.[10] Overall, the first pathway offers more advantages and becomes particularly adequate when the solubility of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ in the organic solvent used is high, and thus its separation from unreacted $Na_2S{\cdot}9H_2O$ and formed NaCl is feasible. This requirement is best accomplished by the chelating diphosphanes 1,2-bis(diphenylphosphanyl)ethane (dppe) or 1,3-bis(diphenylphosphanyl)propane (dppp) than by PPh_3.[9,15]

Our studies on the reactivity of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ (L_2 = dppe or dppp) towards nonmetal electrophiles[9,10] have provided information about the appropriate reaction conditions to obtain $[L_2Pt(\mu\text{-}S)_2PtL_2]$ from $[PtCl_2L_2]$ and $Na_2S{\cdot}9H_2O$ with maximum yield and purity (Scheme 2). To this end, the use of nonchlorinated solvents, the absence of protic acids in the reaction medium, and the purity of the reagent $Na_2S{\cdot}9H_2O$ are the main requirements. The choice of solvent is relevant so as to circumvent its reaction with $[L_2Pt(\mu\text{-}S)_2PtL_2]$, which occurs for L = PMe_2Ph, PPh_2py, PPh_3 and L_2 = dppf, dppe, dppp in the presence of CH_2Cl_2, as explained below. For the same reason, traces of CH_2Cl_2 that may be present in the $[PtCl_2L_2]$ starting complex should be eliminated. Similarly, the presence of protic acids should be avoided as they may cause protonation and subsequent disintegration of the $\{Pt(\mu\text{-}S)_2Pt\}$ core in the final $[L_2Pt(\mu\text{-}S)_2PtL_2]$ product.[10] Concern for the quality of the



Scheme 1. Common synthetic procedures for [L$_2$Pt(μ-S)$_2$PtL$_2$] complexes with unidentate or bidentate terminal phosphane ligands



Scheme 2. Optimum reaction conditions for obtaining [L$_2$Pt(μ-S)$_2$PtL$_2$] complexes from [PtCl$_2$L$_2$] and Na$_2$S·9H$_2$O

reagent Na$_2$S·9H$_2$O arises from the observation that [Pt(SH)$_2$L$_2$], whose formation requires the presence of hydrogen sulfide anions, is not an uncommon by-product in the synthesis of [L$_2$Pt(μ-S)$_2$PtL$_2$]. Finally, an additional factor that may hamper the synthesis of pure [L$_2$Pt(μ-S)$_2$PtL$_2$] is the formation of the trimetallic complex [{L$_2$Pt(μ$_3$-S)$_2$PtL$_2$}PtL$_2$]Cl$_2$ as a consequence of the coexistence in solution of the final product, [L$_2$Pt(μ-S)$_2$PtL$_2$], with one of the reagents, [PtCl$_2$L$_2$]. This undesirable process is minimized with the use of solvents in which [PtCl$_2$L$_2$] is very slightly soluble and, consequently, the [PtCl$_2$L$_2$]/[L$_2$Pt(μ-S)$_2$PtL$_2$] concentration ratio in solution during the reaction is very low.

All previous conclusions regarding the synthesis of [L$_2$Pt(μ-S)$_2$PtL$_2$] from [PtCl$_2$L$_2$] and Na$_2$S·9H$_2$O have been obtained by monitoring the reactions with L$_2$ = dppe or dppp over time by ^{31}P-NMR spectroscopy.[12] This technique is revealed to be very useful for the monitoring of the evolution of the products from the reagents, as well as for the determination of the reaction time that corresponds to the maximum yield.

Molecular and Electronic Structures

The core of [L$_2$Pt(μ-S)$_2$PtL$_2$] compounds consists of a four-membered {Pt(μ-S)$_2$Pt} ring, with the platinum(II) atoms in a square-planar arrangement. The main geometric parameters for complexes structurally characterized by X-ray diffraction are shown in Table 1.[9,14–17] A distinguishing structural feature within this family of compounds is the degree of hinging of the {Pt$_2$S$_2$} core, which is measured by the dihedral angle θ between the two PtS$_2$ planes. According to reported data, this angle is highly dependent on the nature of the terminal L ligands. Similar features have been found for complexes containing {M$_2$S$_2$}

Table 1. Main geometric parameters of the {Pt(μ-S)$_2$Pt} core in structurally characterized complexes; distances in angstroms and angles in degrees

Complex	Pt−S	Pt−P	Pt···Pt	S···S	Pt−S−Pt	S−Pt−S	P−Pt−P	θ[a]	Ref.
[Pt$_2$(PPh$_2$Py)$_4$(μ-S)$_2$]	2.33	2.28	3.55	3.01	99.6	80.4	102.9	180.0	[14]
[Pt$_2$(PPh$_3$)$_4$(μ-S)$_2$]	2.11[b]	2.22	3.17	2.69[b]	99.0	80.3	98.7	168.2	[16]
[Pt$_2$(dppe)$_2$(μ-S)$_2$]	2.35	2.24	3.29	3.13	88.9	83.7	86.2	140.2	[15]
[Pt$_2$(dppp)$_2$(μ-S)$_2$]	2.34	2.25	3.23	3.10	87.4	83.0	94.6	134.8	[9]
[Pt$_2$(PMe$_2$Ph)$_4$(μ-S)$_2$]	2.34	2.26	3.17	–	85.5	81.6	–	121.0	[17]

[a] Dihedral angle between the two PtS$_2$ planes. [b] Values of Pt−S and S···S distances could be indicative of experimental inaccuracy on localization of sulfur atoms in the structure.

cores, in which M = Ni[18] or Pd.[19] According to a theoretical and structural analysis on [$L_2M(\mu\text{-}X)_2ML_2$] complexes, in which M has a d^8 electronic configuration, the driving force for the hinging of the {M_2S_2} core arises from attractive metal···metal interactions between an occupied d_{z^2} orbital and an empty p_z orbital (Figure 1).[20] This interaction is modulated by the nature of the metal center, the terminal ligands, and the bridging atoms. Thus, the tendency to form bent structures increases with the diffuseness of the metal orbitals (i.e. going down the group of the periodic table), with the σ-donor ability of the terminal L ligands, and with decreasing electronegativity of the bridging X atoms. On the basis of these general rules it is clear that complexes with the formula [(phosphane)Pt(μ-S)$_2$Pt(phosphane)] are very well suited to adopt bent structures. However, steric interactions between terminal ligands can prevent the folding of the {M_2S_2} core, as observed for M = Pt and L = PPh_2py[14] or PPh_3,[16] where the resulting core is planar or almost planar, respectively. Moreover, the increase in the Pt−X distances from X = S to Te could account for the planar structures observed for the {Pt(μ-X)$_2$Pt} core with Se^{2-} or Te^{2-} bridging ligands (Table 2).[21−24] This increase involves elongation of the Pt···Pt distance, which thus becomes too long to allow for the attractive interactions that underlie the folding of the {Pt(μ-X)$_2$Pt} core.

The electronic structure of complexes containing the {Pt(μ-X)$_2$Pt} (X = S, Se or Te) core has been analyzed from a theoretical point of view in recent works.[25,26] Thus, DFT calculations for model complexes using simplified terminal phosphane ligands have revealed that in all cases the highest energy occupied molecular orbital (HOMO) consists of an antibonding combination of the chalcogen p_π orbitals (p_z). A 3-D plot of this molecular orbital calculated for the model compound [$(PH_3)_2Pt(\mu\text{-}S)_2Pt(PH_3)_2$] is shown in Figure 2. In addition, the orbital HOMO-1 consists essentially of a bonding combination of the same atomic orbitals. From this orbital analysis it can be inferred that a high electron density is located on the bridging chalcogenide ligand, which will thus be responsible for the nucleophilic character of [$L_2Pt(\mu\text{-}X)_2PtL_2$] compounds. The energy of the HOMO is a good criterion for the comparison of the relative Lewis basicity of complexes containing the {Pt(μ-X)$_2$Pt} core. The energy of the HOMO in [$Pt_2(\mu\text{-}Te)_2(PMe_3)_4$] (−3.46 eV) is considerably higher than that calculated for [$Pt_2(\mu\text{-}S)_2(H_2P(CH_2)_nPPH_2)_2$] ($n$ = 2, 3) (−3.89 eV), indicating that the lone electron pairs in the {Pt_2Te_2} core are more accessible than those in the sulfur analogue.[25] These energy values are consistent with the lower oxidation potentials found for {Pt_2Te_2} than for {Pt_2S_2} containing complexes.

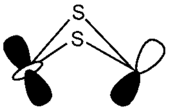


Figure 1. The driving force underlying the hinging of the {Pt(μ-S)$_2$Pt} core: $d_{z^2}-p_z$ metal to metal interactions

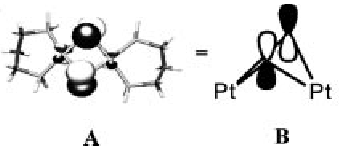


Figure 2. (A) 3D plot of the HOMO orbital in the model complex [{$PH_2(CH_2)_3PH_2$}Pt(μ-S)$_2$Pt{$PH_2(CH_2)_3PH_2$}]; (B) corresponding schematic drawing

The structural and electronic features of complexes [$L_2Pt(\mu\text{-}S)_2PtL_2$] reveal new perspectives for further studies. On the one hand, the different values found for the dihedral angle between the two PtS_2 planes in related [$L_2Pt(\mu\text{-}S)_2PtL_2$] compounds show the flexibility of the {Pt_2S_2} core and anticipate its involvement in dynamic processes. On the other hand, the high electron-density on the sulfide ligands in the above-mentioned core accounts for the electron-donor behavior of this family of complexes, which should be explored by means of electrochemical measurements. Both issues are considered in the following sections.

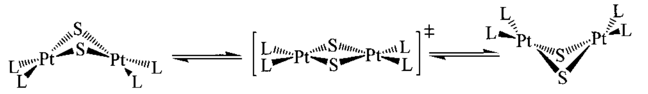
Dynamic Processes: The Flight of the Butterfly

Structural data on [$L_2Pt(\mu\text{-}S)_2PtL_2$] complexes show a wide range for the folding degree of the {Pt_2S_2} core, from strongly bent (θ = 121°, L = PMe_2Ph)[17] to planar (θ = 180°, L = PPh_2py)[14] rings (Table 1). In addition, theoretical calculations indicate that the energy cost for the hinging movement is low; the energy difference between bent and planar geometries is about 4−8 kcal/mol.[20,27] Interestingly, in theoretically studied model systems the planar geometry is not a minimum in the potential energy surface but, instead, it constitutes the transition state from a folded geometry to the corresponding reverse folding, as depicted

Table 2. Main geometric parameters of the {Pt(μ-X)$_2$Pt} (X = Se^{2-} or Te^{2-}) core in structurally characterized complexes; distances in angstroms and angles in degrees

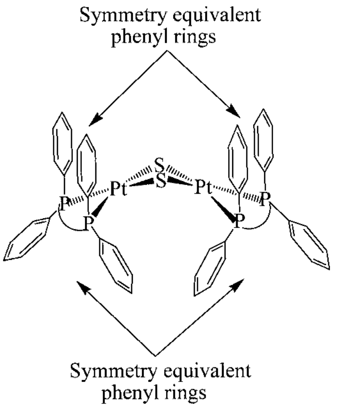
Complex	Pt−X	Pt−P	Pt···Pt	X···X	Pt−X−Pt	X−Pt−X	P−Pt−P	θ[a]	Ref.
[$Pt_2(PPh_3)_4(\mu\text{-}Se)_2$]	2.46	2.27	3.76	3.13	100.4	79.6	99.5	180.0	[21]
[$Pt_2(PPh_3)_4(\mu\text{-}Te)_2$]	2.62	2.30	4.10	3.25	102.7	76.9	100.4	180.0	[22]
[$Pt_2(PEt_3)_4(\mu\text{-}Te)_2$]	2.61	2.28	4.10	3.26	102.9	77.1	106.1	180.0	[23]
[$Pt_2(dppe)_2(\mu\text{-}Te)_2$]	2.63	2.25	3.96	3.46	97.7	82.3	86.0	180.0	[24]

[a] Dihedral angle between the two PtS_2 planes.



Scheme 3. Dynamic process arising from the flexibility of the $\{Pt(\mu\text{-}S)_2Pt\}$ core; the sign ‡ denotes a transition state

in Scheme 3. The low energy of the transition state is consistent with the hinging process that occurs at room temperature. Experimental evidence was obtained from ^{13}C NMR spectroscopic data on $[L_2Pt(\mu\text{-}S)_2PtL_2]$ complexes with the chelating phosphanes dppe or dppp as terminal ligands that showed the equivalence of all phenyl groups at room temperature in solution (Scheme 4). However, the hinged geometry of the $\{Pt_2S_2\}$ core in the corresponding X-ray structures[9,15] was inconsistent with NMR data unless a dynamic process enabled the phenyl rings to become symmetry-equivalent in solution. The fact that this equivalence is maintained even at low temperature is indicative of the low energy barrier of the bending process. In addition, it is worth noting that $[L_2Pt(\mu\text{-}S)_2PtL_2]$ complexes containing unidentate phosphane PR_3 do not allow for the distinguishing of the hinging process and the fast rotation along the Pt−P bond, which could account for the observed equivalence of all R groups in ^{13}C NMR measurements. Overall, the well-established term butterfly to designate $[L_2Pt(\mu\text{-}S)_2PtL_2]$ complexes appears particularly adequate on the basis of the dynamic properties of the $\{Pt_2S_2\}$ core.



Scheme 4. Asymmetry of the phenyl rings in a chelating phosphane considering a hinged geometry for the $\{Pt(\mu\text{-}S)_2Pt\}$ core

Other fast reversible intramolecular dynamic processes involving the $\{Pt_2S_2\}$ core have also been observed. One of them, consisting of the intramolecular S−H···S proton exchange in the complexes $[L_2Pt(\mu\text{-}S)(\mu\text{-}SH)PtL_2]^+$ (L_2 = dppe or dppp),[28] provided the first example of a fast S−H···S proton exchange in a metal complex. Experimental evidence came from VT-$^{31}P\{^1H\}$ NMR spectroscopic data (Figure 3), which showed the equivalence of the four phosphorus nuclei at 300 K in solution. However, the proton transfer between both sulfur atoms is frozen at 200 K and, consequently, the phosphorus nuclei in the *trans* and *cis* dispositions with respect to the bridging SH group show different chemical shift values. From the NMR data, $\Delta G^{\ddagger}$ of about 11 kcal/mol was estimated for the S−H···S proton-transfer process. Theoretical studies corroborated the feasibility of the S−H···S proton transfer process as well as its corresponding experimental energy. They also showed that the transition state involves a trigonal S−H−S arrangement, in which the partial rupture of the S−H bond is compensated by the partial formation of the new S−H bond (Scheme 5).

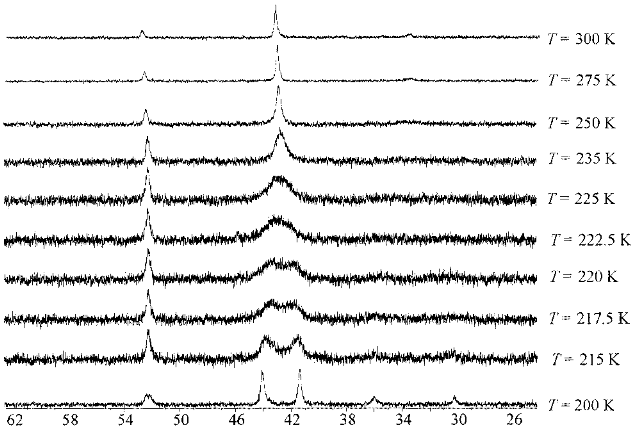
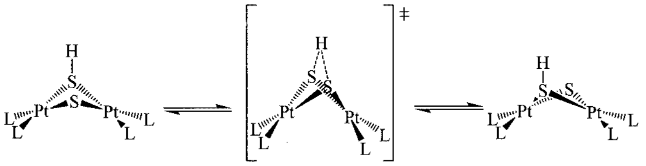


Figure 3. VT-$^{31}P\{^1H\}$ NMR spectra of complex $[Pt_2(dppe)_2(\mu\text{-}S)(\mu\text{-}SH)]ClO_4$

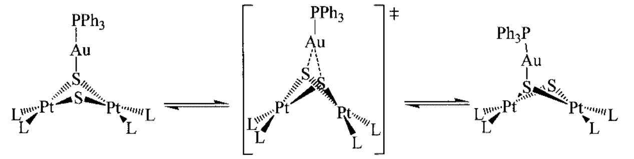


Scheme 5. Fast intramolecular S−H···S proton transfer in $[L_2Pt(\mu\text{-}S)(\mu\text{-}SH)PtL_2]^+$

It is worth mentioning the role played by the flexibility of the $\{Pt_2S_2\}$ ring in the process. Thus, the S···S distance is notably shorter in the transition sate (2.98 Å) than in the reactants (3.24 Å), the shortening of this distance is attained by increasing the degree of folding of the $\{Pt_2S_2\}$ ring (θ > 130° in the reactants and about 109° in the transition sate).

Remarkably, no proton transfer processes have been observed for $[L_2Pt(\mu\text{-}S)(\mu\text{-}SH)PtL_2]^+$ complexes in which PPh_3 replaces dppe or dppp.[29,30] One possible factor to account for these differences is the bulkiness of PPh_3 that could prevent the hinging of the $\{Pt(\mu\text{-}S)_2Pt\}$ fragment, thus disfavoring the folded transition state required for the intramolecular S−H···S proton transfer. Another explanation is the possible interaction of the S−H proton with a phenyl ring of PPh_3, thus stabilizing the $[L_2Pt(\mu\text{-}S)(\mu\text{-}SH)PtL_2]^+$ cation in relation to the transition state.

A similar transfer process has been observed in $[(PPh_3)_2Pt(\mu\text{-}S)\{\mu\text{-}S\text{-}Au(PPh_3)\}Pt(PPh_3)_2]^+$, closely related to $[L_2Pt(\mu\text{-}S)(\mu\text{-}SH)PtL_2]^+$, on the basis of the isolobal analogy of $[H]^+$ and $[AuPPh_3]^+$ fragments (Scheme 6).[31] It is noteworthy that in the former cation, the intramolecular exchange is observed even if the terminal ligand is PPh_3. Probably, the larger size of the gold atom, which in the transition state interacts with the two sulfur atoms of the $\{Pt(\mu\text{-}S)_2Pt\}$ core, provokes less important geometric constraints



Scheme 6. Fast intramolecular exchange of the $[AuPPh_3]^+$ group in the $[L_2Pt(\mu\text{-}S)\{\mu\text{-}S\text{-}(AuPPh_3)\}PtL_2]^+$ cation

in this core than the proton. In all, the lower flexibility of the $\{Pt_2S_2\}$ ring in $[(PPh_3)_2Pt(\mu\text{-}S)\{\mu\text{-}S\text{-}Au(PPh_3)\}\text{-}Pt(PPh_3)_2]^+$ is not an impediment for the observation of intramolecular exchange of the $[AuPPh_3]^+$ fragment.

The $\{Pt(\mu\text{-}S)_2Pt\}$ Core as Electron-Donor in Redox Processes

An immediate consequence arising from the electronic structure of the $\{Pt(\mu\text{-}S)_2Pt\}$ core is its ability to act as an electron-donor. The more direct way to observe this property is the study of the possible oxidation processes of the $[L_2Pt(\mu\text{-}S)_2PtL_2]$ complexes. Despite the potential interest of the redox properties of $[L_2M(\mu\text{-}X)_2ML_2]$ systems in the field of bioinorganic chemistry,[32−34] this feature had not been considered in the study of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ complexes until very recently. On the other hand, theoretical analysis has allowed to establish that bonding between antipodal atoms in binuclear complexes depends on the total number of electrons in the framework. Thus, qualitative rules anticipate that electrochemical oxidation of the $\{M_2X_2\}$ (M = d^8-metal) core induces formation of X−X or M−M bonds as a result of changing the number of electrons in the framework molecular orbitals.[20,27,32,35] However, experimental evidence showing variations in the connectivity of the atoms in the $\{M(\mu\text{-}X)_2M\}$ rings as a consequence of the redox processes are very scarce.

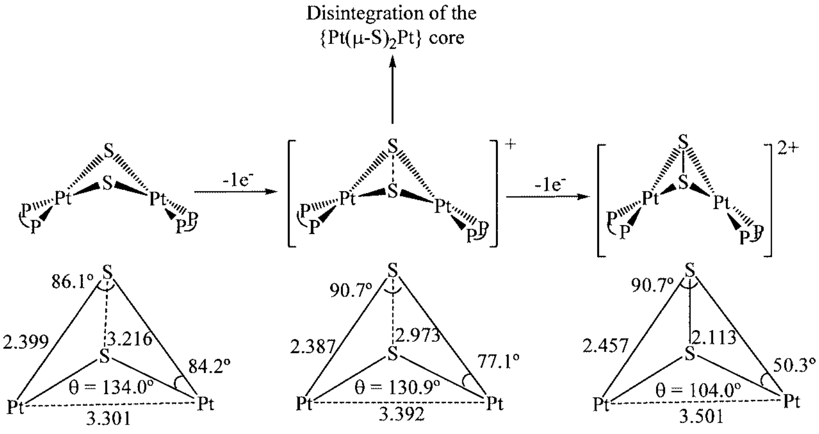
Recently, the energetic and structural consequences of the successive removal of two electrons from the $\{Pt(\mu\text{-}S)_2Pt\}$ core in $[L_2Pt(\mu\text{-}S)_2PtL_2]$ (L_2 = dppe or dppp) complexes have been studied by combining electrochemical measurements and DFT calculations. Assignment of the structure corresponding to the species involved in the cyclic voltammogram peaks relied on the theoretical calculations.[25] The cyclic voltammetric measurements were indicative of two consecutive monoelectronic oxidations. In addition, cyclic voltammetric data showed that the radical cation $[L_2Pt(\mu\text{-}S)_2PtL_2]^+$ is unstable and gives rise to the disintegration of the $\{Pt(\mu\text{-}S)_2Pt\}$ core. The stability of the oxidized $[L_2Pt(\mu\text{-}S)_2PtL_2]^+$ form is highly dependent on the nature of the terminal ligand, and is greater for dppp than for dppe.

Structural data obtained from theoretical calculations on the species $[L_2Pt(\mu\text{-}S)_2PtL_2]^{n+}$ (n = 0, 1, 2; L_2 = $H_2P(CH_2)_2PH_2$ or $H_2P(CH_2)_3PH_2$) show differences between neutral and monocationic species, the latter having slightly shorter S···S distances and smaller S−Pt−S angles, as well as longer Pt···Pt distances. These changes involve the formation of an incipient S−S bond. The abstraction of a second electron from the $\{Pt(\mu\text{-}S)_2Pt\}$ core enhances the structural tendencies found in the monoxidized complexes. These variations eventually lead to the formation of a S−S bond (S−S = 2.11 Å), with the concomitant lengthening of the Pt···Pt distance (Pt···Pt approximately 3.50 Å) and the larger folding along the S−S axis to give a highly bent geometry (θ = 104 °). In all, the oxidation of the $\{Pt(\mu\text{-}S)_2Pt\}$ core consists of two subsequent one-electron removals, thus giving rise to the bridging of the two metal centers by a disulfide S_2^{2-} ligand. The redox behavior of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ (L_2 = dppe or dppp) together with the main calculated structural features for neutral and oxidized forms in the model compound $[\{H_2P(CH_2)_2PH_2\}Pt(\mu\text{-}S)_2Pt\{H_2P(CH_2)_2PH_2\}]$ are depicted in Scheme 7. The evolution of the NPA (Natural Population Analysis) charges throughout the oxidation process agrees with the oxidation of the sulfur ligands.

With the aim of verifying that theoretical and experimental data were fully consistent, the redox potentials of the oxidation processes were calculated. The accurate calculation of redox potentials is still a very demanding problem, and only very recently the reduction potentials for some small organic molecules have been reported.[36] In large systems, with transition metal atoms, only semi-quantitative results can be expected. The methodology used for the theoretical estimation of the redox potentials involving the oxidation of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ compounds requires calculation of the Gibbs energy of the oxidation reaction in solution, $(\Delta G_{ox})_{sol}$, following the approach based on continuum solvent models.[37] The absolute redox potential can be calculated according to the following expression: $E_{ox} = (\Delta G_{ox})_{sol}/nF$.

To obtain the electrode potential value referenced with respect to a reference electrode it is necessary to calculate the difference between the calculated absolute potential and the absolute potential of the reference electrode. For this purpose, we used the value of +4.43 V assigned to the absolute reduction potential of the hydrogen electrode.[38] The closeness between the electrochemical data and DFT calculations confirmed that the experimentally observed abstraction of two electrons from $[L_2Pt(\mu\text{-}S)_2PtL_2]$ results in the formation of a S−S bond to give the disulfide containing complexes $[L_2Pt(\mu\text{-}S_2)PtL_2]^{2+}$.

Studies devoted to the redox behavior of complexes $[L_2Pt(\mu\text{-}X)_2PtL_2]$ (X = S, Se, Te) are very scarce in the literature. From a theoretical perspective, an early work demonstrated the ability of the $\{Pt(\mu\text{-}Se)_2Pt\}$ core to present a redox behavior similar to that observed for the $\{Pt(\mu\text{-}S)_2Pt\}$ core. Thus, Hartree−Fock calculations on $[(PH_3)_2Pt(\mu\text{-}Se)_2Pt(PH_3)_2]^{n+}$ (n = 0, 2) provided evidence for the formation of a Se−Se bond as a result of the oxidation of the $\{Pt(\mu\text{-}Se)_2Pt\}$ core.[21] The closest work to the study of the redox properties of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ complexes consists of the isolation and characterization of $[(PEt_3)_2Pt(\mu\text{-}Te)_2Pt(PEt_3)_2]$ and $[(PEt_3)_2Pt(\mu\text{-}Te_2)Pt(PEt_3)_2]^{2+}$.[23] Analogously to the $\{Pt(\mu\text{-}S)_2Pt\}$ core, chemical oxidation of $[(PEt_3)_2Pt(\mu\text{-}Te)_2Pt(PEt_3)_2]$ causes a decrease in the Te−Te distance from a nonbonding (3.263 Å) to a bonding dis-



Scheme 7. Redox behavior of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ (L_2 = dppe or dppp); calculated main structural parameters for $[Pt_2\{H_2P(CH_2)_2PH_2\}_2(\mu\text{-}S)_2]^{n+}$ (n = 0, 1 or 2) are included

tance (2.695 Å), indicating the formation of a Te−Te bond in the dication.

According to the experimental CV data, the difficulties found in determining all the species involved in the oxidation of the $\{Pt_2S_2\}$ core arise from the disintegration of the monocationic species, which leads to the well-known trimetallic $[\{L_2Pt(\mu_3\text{-}S)_2PtL_2\}PtL_2]^{2+}$ complex as the main product. Calculations of the thermodynamics of possible processes following disintegration of $[L_2Pt(\mu\text{-}S)_2PtL_2]^+$ show that the most favorable process involves the recombination of two $[L_2Pt(\mu\text{-}S)_2PtL_2]^+$ species to give the cited trimetallic complex and the neutral mononuclear $[L_2Pt(S_2)]$ complex.

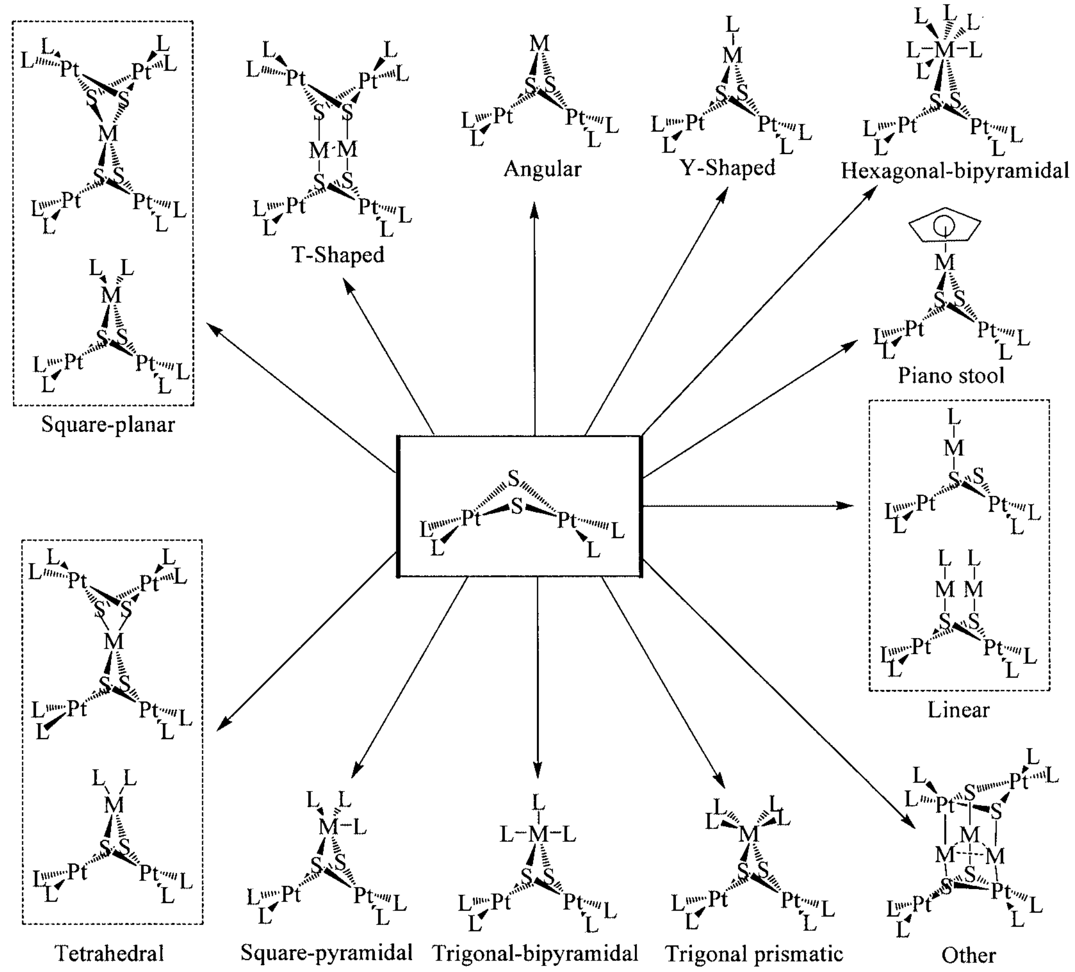
Complexes with functionalized $\{Pt(\mu\text{-}S)_2Pt\}$ cores are also able to show redox properties. In $[(PPh_3)_2Pt(\mu\text{-}S)(\mu\text{-}SHgR))Pt(PPh_3)_2]^+$, the observed process consists of the monoelectronic oxidation of the sulfide ligand that is not coordinated to the mercury atom.[39] However, the poor solubility of $[(PPh_3)_2Pt(\mu\text{-}S)_2Pt(PPh_3)_2]$ hampered comparison between the redox properties of the $\{Pt(\mu\text{-}S)_2Pt\}$ and $\{Pt(\mu\text{-}S)(\mu\text{-}SHg)Pt\}^+$ cores. Notwithstanding this, results obtained with the highly soluble $[L_2Pt(\mu\text{-}S)_2PtL_2]$ (L_2 = dppe or dppp) are consistent with the hypothesis presented by Hor et al., indicating that the sulfide ligands in the $\{Pt(\mu\text{-}S)_2Pt\}$ fragment are electroactive.

When the two sulfur atoms of the $\{Pt(\mu\text{-}S)_2Pt\}$ core act as electron-donors towards a metal center, a different redox activity is observed. Thus, electrochemical studies on the trimetallic clusters $[\{L_2Pt(\mu_3\text{-}S)_2PtL_2\}PtL_2]^{2+}$ (L_2 = dppm, dppe, dppp, dppb) have shown that the cationic core $\{Pt_3(\mu_3\text{-}S)_2\}^{2+}$ is able to accept one electron, as observed by means of cyclic voltammetric measurements.[40] These data indicate that the electron-donor properties of the $\{Pt(\mu\text{-}S)_2Pt\}$ core can be reversed, thus becoming an electron-acceptor, after coordination to a metal center. The electrochemical features of this family of trimetallic complexes are also highly dependent on the chelate ring size of the phosphane ligands.

Compounds $[L_2Pt(\mu\text{-}S)_2PtL_2]$ as Metalloligands to Metal Centers

Homo- and Heterometallic Derivatives of $[L_2Pt(\mu\text{-}S)_2PtL_2]$

The behavior of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ (L = phosphane) as a metalloligand to metal centers has prompted most of the research undertaken in this field of chemistry. The electronic and dynamic properties of the $\{Pt(\mu\text{-}S)_2Pt\}$ core, already explained, account for the outstanding ability of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ compounds to act as building blocks for higher nuclearity aggregates with the general formula $[\{L_2Pt(\mu_3\text{-}S)_2L_2\}_xML'_y]^z$. At the same time, the wide coordination environments offered by main group or transition metals together with the nature of their accompanying L′ species, either ligands or counter ions, enhance the structural diversity of this family of derivatives. As depicted in Scheme 8, aggregates of known structure include those with varied coordination geometries about the heterometal: linear,[41,42] angular,[43] T-shaped,[42,44] Y-shaped,[45] tetrahedral,[12,15,46] square planar,[12,47] square pyramidal,[48] distorted trigonal prismatic,[49] trigonal bipyramidal,[50] hexagonal bipyramidal,[51] "piano stool"[52] and others.[53,54] These aggregates also display the ability of the $[L_2Pt(\mu\text{-}S)_2PtL_2]$ metalloligand to function as a unidentate,[41] bridging,[53] or chelating ligand.[52] Concerning the nature of the heterometal M, a wide range of p- and d-block elements have been studied. Those included in $[\{L_2Pt(\mu_3\text{-}S)_2L_2\}_xML'_y]^z$ aggregates described subsequently to the earlier report by Fong and Hor,[8] are the following: V^{V},[51] Mo^{VI},[51] Re^{I},[50] Os^{II},[52] Rh^{III},[52] Ir^{III},[52] Zn^{II},[12,48] Cd^{II},[12,48] U^{VI},[51] and Sn^{IV}.[29] Moreover, it is remarkable that $[L_2Pt(\mu\text{-}S)_2PtL_2]$ metalloligands allow stabilization of oxidation states that are unstable in sulfur-thiolate environments as it occurs in tetrahedral $\{M^{II}(SR)_4\}^{2-}$, M = Co[55] or Cu,[15] complexes. Overall, on the basis of this formidable body of information, it seems that current knowledge on the wide family of the homo- and heterometallic deriva-



Scheme 8. Coordination environments at M in $[\{L_2Pt(\mu\text{-}S)_2PtL_2\}_xML'_y]^z$ aggregates

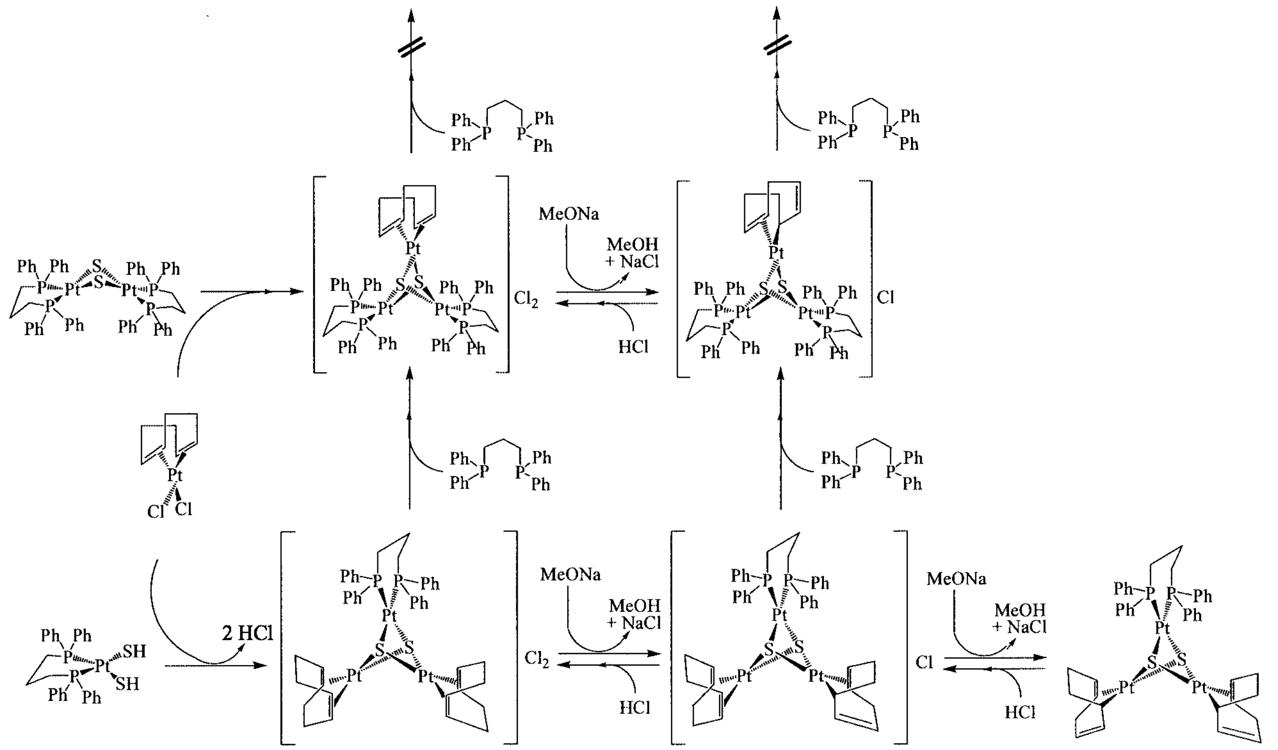
tives of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ compounds has achieved a considerable degree of maturity.

The suitability of electrospray mass spectrometry (ESI MS) to characterize charged inorganic species in solution has allowed its use for probing the reactivity of the $\{Pt(\mu\text{-}S)_2Pt\}$ core towards metal ions. This technique has proved very effective in providing a preliminary detection and characterization of the heterometallic aggregates predominant in solution as a result of a particular reaction. On the basis of the good correlation found between the ESI mass spectra and synthesis-scale reactions, the synthetic strategies can thus be focused on the synthesis of those aggregates that are supported by ESI MS evidence.[29,30]

Influence of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ on the Reactivity of ML′ Fragments

Significantly, despite the widespread attention devoted to the synthesis and characterization of $[\{L_2Pt(\mu_3\text{-}S)_2L_2\}_xML'_y]^z$ aggregates, studies on the influence of the $[L_2Pt(\mu\text{-}S)_2PtL_2]$ metalloligand on the reactivity of L′ remained unreported. In order to fill this gap, we recently described the synthesis and structural characterization of complexes $[\{(dppp)Pt(\mu\text{-}S)_2Pt(dppp)\}PtL']^z$ (L′ = cod,[11] z = 2+ or L′ = 2Cl, z = 0[56]), and studied the substitution reactions of cod and chloride ligands. Experimental results showed that cod was substitutionally inert towards dppp while chloride was easily replaced by dmso or phosphane ligands. These features were inconsistent with the common procedure used to obtain $[PtCl_2(dppp)]$ from $[PtCl_2(cod)]$ and dppp, and with the usual stability of $[PtCl_2(dppp)]$ in dmso solvent. Within this context, the influence of $[(dppp)Pt(\mu\text{-}S)_2Pt(dppp)]$ on the reactivity of the $\{Pt(cod)\}^{II}$ or $\{PtCl_2\}$ fragments deserved further consideration. Results obtained on the unusual reactivity observed for $[\{(dppp)Pt(\mu\text{-}S)_2Pt(dppp)\}Pt(cod)]^{2+}$ in the presence of $NaCH_3O$ are described below. Those concerning the substitution of chloride ligands in $[\{(dppp)Pt(\mu\text{-}S)_2Pt(dppp)\}PtCl_2]$ are given in the next section.

With the aim of exploring the influence of the $\{Pt(\mu\text{-}S)_2Pt\}$ core on the reactivity of the $\{Pt(cod)\}^{II}$ fragment, we obtained complexes $[\{Pt_2(\mu_3\text{-}S)_2(dppp)_2\}Pt(cod)]Cl_2$ and $[\{Pt_2(\mu_3\text{-}S)_2(cod)_2\}Pt(dppp)]Cl_2$ by reacting $[Pt_2(\mu\text{-}S)_2(dppp)_2]$ and $[PtCl_2(cod)]$ (1:1), and $[Pt(SH)_2(dppp)]$ and $[PtCl_2(cod)]$ (1:2), respectively.[11] In contrast with the general behavior of cationic olefin complexes of platinum,[57,58] the synthesized complexes did not undergo spontaneous loss of the unsaturated ligand and thus allowed exploration of their reactivity towards a strong nucleophile such as so-



Scheme 9. Reactivity of cod containing derivatives of $[L_2Pt(\mu\text{-}S)_2PtL_2]$

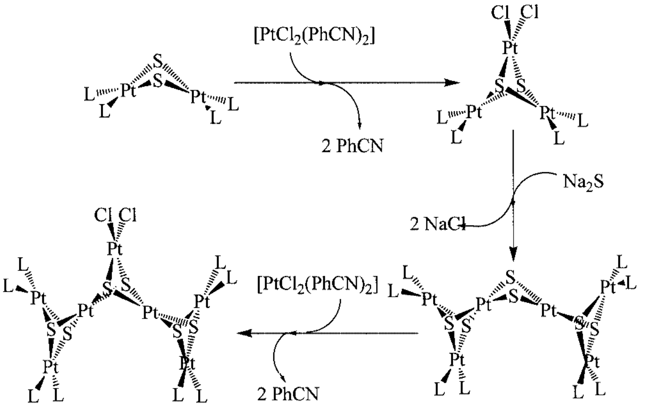
dium methoxide (Scheme 9). Remarkably, unlike previous reports on the attack of $NaCH_3O$ on the $\{Pt(cod)\}^{II}$ fragment,[59][60] the above reactions did not promote the nucleophilic attack of the methoxide anion, but only deprotonation of cod, thus leading to $[\{Pt_2(\mu_3\text{-}S)_2(dppp)_2\}Pt(C_8H_{11})]Cl$, $[\{Pt_2(\mu_3\text{-}S)_2(cod)(C_8H_{11})\}Pt(dppp)]Cl$ and $[\{Pt_2(\mu_3\text{-}S)_2(C_8H_{11})_2\}Pt(dppp)]$. Concerning the substitution of cod, in neutral or anionic form, by dppp, the five complexes obtained behaved differently. Those containing the $\{Pt_2(\mu_2\text{-}S)_2(dppp)_2\}$ moiety were substitutionally inert. By contrast, those based on the $\{Pt_2(\mu_2\text{-}S)_2(dppp)L\}$ moiety with $L = C_8H_{12}$ or $C_8H_{11}^-$ underwent the substitution reaction readily. However, DFT calculations indicated that thermodynamic factors were not responsible for the observed differences. Consequently, kinetic effects should account for the reluctance of the ligand cod to be replaced by dppp in $[\{Pt_2(\mu_3\text{-}S)_2(dppp)_2\}Pt(cod)]^{2+}$ and $[\{Pt_2(\mu_3\text{-}S)_2(dppp)_2\}Pt(C_8H_{11})]^+$, where the steric hindrance imposed by $\{Pt_2(\mu_2\text{-}S)_2(dppp)_2\}$ disfavors an associative pathway for the corresponding exchange reactions.

An interesting example to test the influence of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ on the properties of a $\{ML'_y\}$ fragment has recently been provided by Brunner et al.,[61] who synthesized the heterometallic trinuclear complex $[\{Pt_2(\mu\text{-}S)_2[\{(-)\text{-}diop]\}Rh(cod)]Cl$ by reacting the chiral $[Pt_2(\mu\text{-}S)_2\{(-)\text{-}diop\}]$ metalloligand with $[Rh(cod)Cl]_2$. However, its further use as a catalyst in enantioselective transformations afforded moderate results, which are mainly attributed to the reluctance of cod to be displaced from the trinuclear complex. This observation is consistent with the low tendency of cod in $[\{(PPh_3)_2Pt(\mu\text{-}S)_2Pt(PPh_3)_2\}Rh(cod)]^+$ to be substituted by H_2, CO, SO_2, and dppe, as reported by Briant et al. in 1985.[62] Overall, reported results fully confirm that the binding of the $[L_2Pt(\mu\text{-}S)_2PtL_2]$ metalloligand to $\{Pt(cod)\}^{2+}$ or $\{Rh(cod)\}^+$ causes profound alterations in the chemistry of such fragments. Extension of these findings to other fragments and studies on the influence of terminal L ligands on their properties may provide new perspectives within the area of organometallic chemistry.

$[L_2Pt(\mu\text{-}S)_2PtL_2]$ Compounds as Building Blocks

Further evidence of the influence of the $\{Pt(\mu\text{-}S)_2Pt\}$ core on the reactivity of bonded ML'_y fragments was recently provided by the lability of chloride ligands in $[\{(dppp)Pt(\mu\text{-}S)_2Pt(dppp)\}PtCl_2]$.[56] This became apparent through independent experimental data: (i) the partial or total loss of chloride ligands in some of the species identified in the characterization of this compound by ESI MS; (ii) the isolation of $[\{(dppp)Pt(\mu\text{-}S)_2Pt(dppp)\}PtCl(dmso)]Cl$ when the former complex is dissolved in dmso; and (iii) the displacement of chloride ligands by formation of $[\{(dppp)Pt(\mu\text{-}S)_2Pt(dppp)\}Pt(dppp)]Cl_2$ after addition of an stoichiometric amount of dppp. All these findings were in good agreement with previous reports on the lability of chloride ligand in the $[\{(PPh_3)_2Pt(\mu\text{-}S)_2Pt(PPh_3)_2\}PtCl(PPh_3)]^+$ complex.[63]

On the basis of the ability of the $\{Pt(\mu\text{-}S)_2Pt\}$ core to facilitate substitution of chloride ligands in $[\{Pt_2S_2\}PtCl_2]$ fragments, we designed a novel route to obtain multimetallic aggregates containing a $\{Pt_2S_2\}_n$ core (Scheme 10). The synthetic strategy involves first the expansion of the $\{Pt_2S_2\}$ ring to a $[\{Pt_2S_2\}PtCl_2]$ moiety. Replacement of chloride ligands by sulfide then causes the $\{PtCl_2\}$ fragment to form a $\{Pt_2S_2\}$ linking unit between two $\{Pt_2S_2\}$ rings, thus af-



Scheme 10. Synthetic strategy to obtain multimetallic complexes containing the $\{Pt(\mu\text{-}S)_2Pt\}_n$ core

fording a new $[\{Pt_2S_2\}_2\{Pt_2S_2\}]$ core. Its subsequent evolution into $[\{Pt_2S_2\}_3PtCl_2]$ lays the foundation for a new cycle.

According to the first step in Scheme 10, the reaction between $[(dppp)Pt(\mu\text{-}S)_2Pt(dppp)]$ and $[PtCl_2(PhCN)_2]$ afforded the unprecedented trinuclear $[\{(dppp)Pt(\mu\text{-}S)_2Pt(dppp)\}PtCl_2]$ complex, in spite of the fact that other nuclearities had been proposed for related complexes obtained under similar reaction conditions.[47,64] Another interesting feature as a result of the reactions depicted in Scheme 10 is that the characterization of the high nuclearity complexes $[\{Pt_2(\mu_3\text{-}S)_2(dppp)_2\}_2\{Pt_2(\mu\text{-}S)_2\}]$ and $[\{Pt_2(\mu_3\text{-}S)_2(dppp)_2\}Pt_2(\mu_3\text{-}S)_2PtCl_2\{Pt_2(\mu_3\text{-}S)_2(dppp)_2\}]$ was mainly achieved by means of MALDI-TOF mass spectrometry, which thus revealed its potential use in further studies.

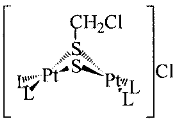
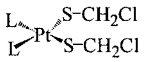
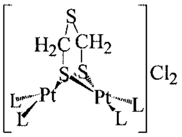
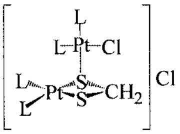
In all, while high nuclearity heterometallic derivatives of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ had been reported,[42,53] the systematic approach described above to obtain multimetallic derivatives is unprecedented. In fact, it demonstrates that the nucleophilicity of the $\{Pt(\mu\text{-}S)_2Pt\}$ core can be driven to build nuclearity-controlled multinuclear aggregates containing a $\{Pt_2S_2\}_n$ core. Extension of the same strategy to other metals with square-planar coordination may allow control of the size of metal chalcogenide compounds and thus of their properties and potential applications.

Reactivity towards Non-Metallic Electrophiles

Organic Electrophiles

The nucleophilicity of the sulfide bridges in the $\{Pt(\mu\text{-}S)_2Pt\}$ core towards organic electrophiles was established as a result of the reaction of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ (L = PMe_2Ph, PPh_3) compounds with $PhCH_2Br$[6] or CH_3I.[7] These reactions led to the corresponding monoalkylated cation $[L_2Pt(\mu\text{-}S)(\mu\text{-}SR)PtL_2]^+$ (R = Me or CH_2Ph), even if stoichiometric excess of the alkyl halide was present. Very recently, extension of the previous reaction to organic dihal-

Table 3. Complexes obtained upon exposure of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ in CH_2Cl_2

Complex	Terminal ligand	Experimental evidences	Ref.
	L = PPh_3 L_2 = dppf [a] L_2 = dppe [b] L_2 = dppp [c]	NMR	[68] [69] [9] [9]
	L = PMe_2Ph L = dppy [d] L_2 = dppe[b] L_2 = dppp[c]	NMR and X-ray diffraction	[70] [14] [9] [9]
	L_2 = dppf[a] L = PPh_3	NMR	[69] [71]
	L_2 = dppp[c]	NMR and X-ray diffraction	[9]
	L = PPh_3	NMR and X-ray diffraction	[46]

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[a] dppf = $[Fe(C_5H_4PPh_2)_2]$. [b] dppe = $Ph_2P(CH_2)_2PPh_2$. [c] dppp = $Ph_2P(CH_2)_3PPh_2$. [d] dppy = $PPh_2(C_5H_4N)$.

ides has allowed isolation of the dialkylated derivative $[(PPh_3)_2Pt(\mu\text{-}(SC_2H_4S)\text{-}S,S')Pt(PPh_3)_2]$ by reacting $[(PPh_3)_2Pt(\mu\text{-}S)_2Pt(PPh_3)_2]$ with 100-fold excess of 1,2-dichloroethane.[65] Similar double alkylations have been achieved in complexes containing the $\{Pt(\mu\text{-}Se)_2Pt\}$[66,67] or $\{Ni(\mu\text{-}S)_2Ni\}$[18] core.

A particular case of the previous reaction involving organic halides is the surprising progression of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ compounds when they are dissolved in chlorinated solvents, mainly CH_2Cl_2. Thus, in recent years, several different species have been characterized as a result of often unexpected reactions in this solvent (Table 3).[9,14,46,68–71] The first attempt to account for the apparent dispersion of the compounds obtained is due to Fong and Hor, who proposed a possible mechanism for the formation of various thiolato complexes from the disintegration of the $\{Pt(\mu\text{-}S)_2Pt\}$ core in CH_2Cl_2.[8] However, the lack of a systematic study prompted us to monitor the reaction of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ (L_2 = dppe, dppp) with CH_2Cl_2 by means of ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy, electrospray mass spectrometry, and X-ray data.[9] DFT calculations were also performed to obtain an energetic picture of the process. It is worth noting that the main information on both reactions was obtained by a series of $^{31}P\{^1H\}$ NMR spectra recorded as a function of time, as shown in Figure 4. These results allowed us not only to formulate all the steps involved from the initial to the final products (Scheme 11), but also to account for the nature and diversity of the compounds reported in closely related systems (Table 3).

The evolution of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ compounds with various phosphanes as terminal ligands (L = PMe_2Ph, PPh_2py, PPh_3; L_2 = dppf, dppe, dppp) upon exposure to the weak alkylating agent CH_2Cl_2 is depicted in Scheme 11. Thus, the first step of the reaction involves monoalkylation of the corresponding $\{Pt(\mu\text{-}S)_2Pt\}$ core to yield spectroscopically identifiable intermediates with the formula $[L_2\{Pt(\mu\text{-}S)(\mu\text{-}SCH_2Cl)Pt\}L_2]^+$,[9,68,69] whose energy is only slightly higher than that of the reactants. The monoalkylated intermediates subsequently undergo an internal self-alkylation process to afford $[L_2\{Pt(\mu\text{-}S_2CH_2)Pt\}L_2]^{2+}$ species, of elusive nature, but fully consistent with the double alkylation reported as a result of the reaction between $[(PPh_3)_2Pt(\mu\text{-}S)_2Pt(PPh_3)_2]$ and 1,2-dichloroethane. Calculations indicate that $[L_2\{Pt(\mu\text{-}S_2CH_2)Pt\}L_2]^{2+}$ are highly unstable species, that should decompose to give the monometallic complexes $[L_2PtCl_2]$ and $[L_2Pt(S_2CH_2)]$. Consistently, further pro-

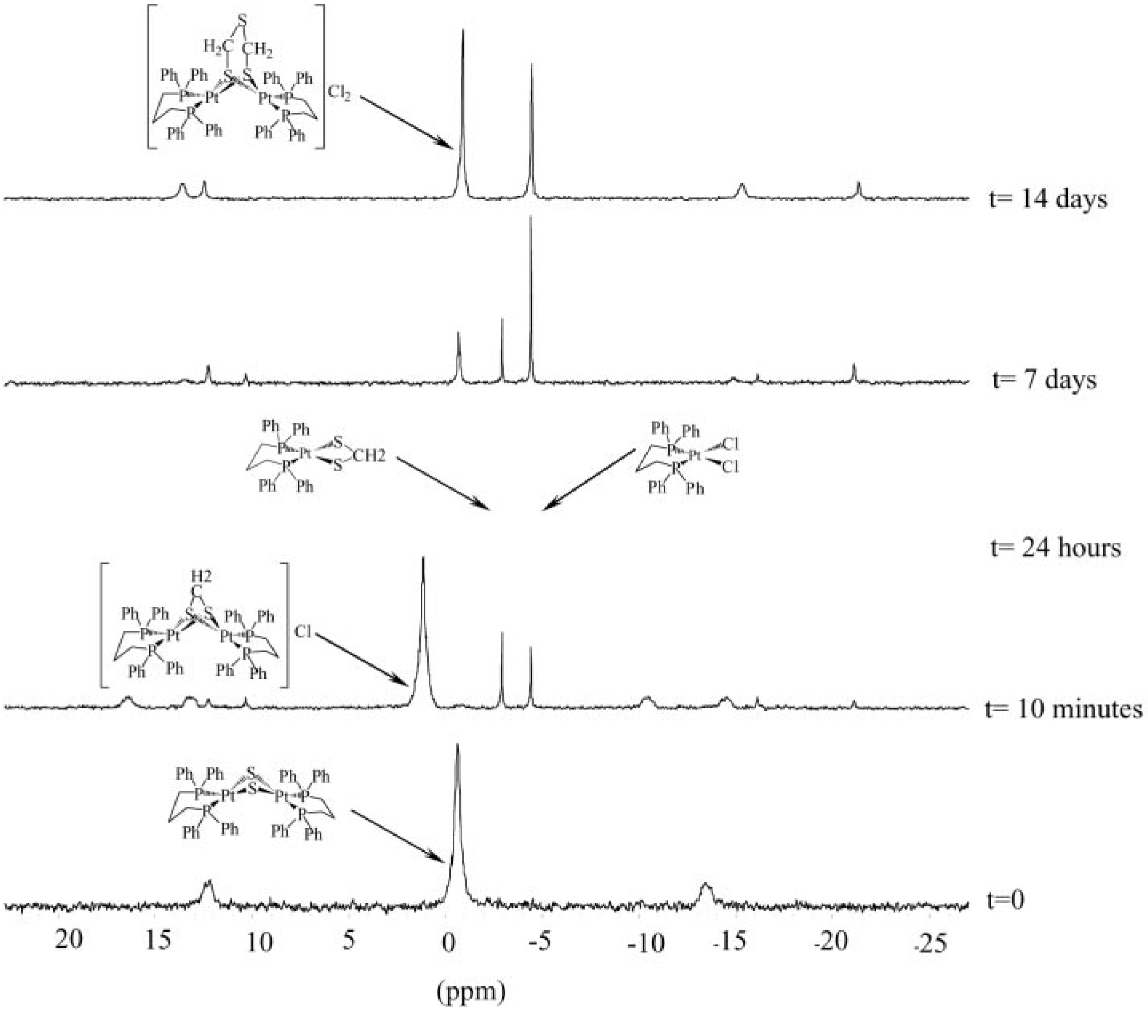
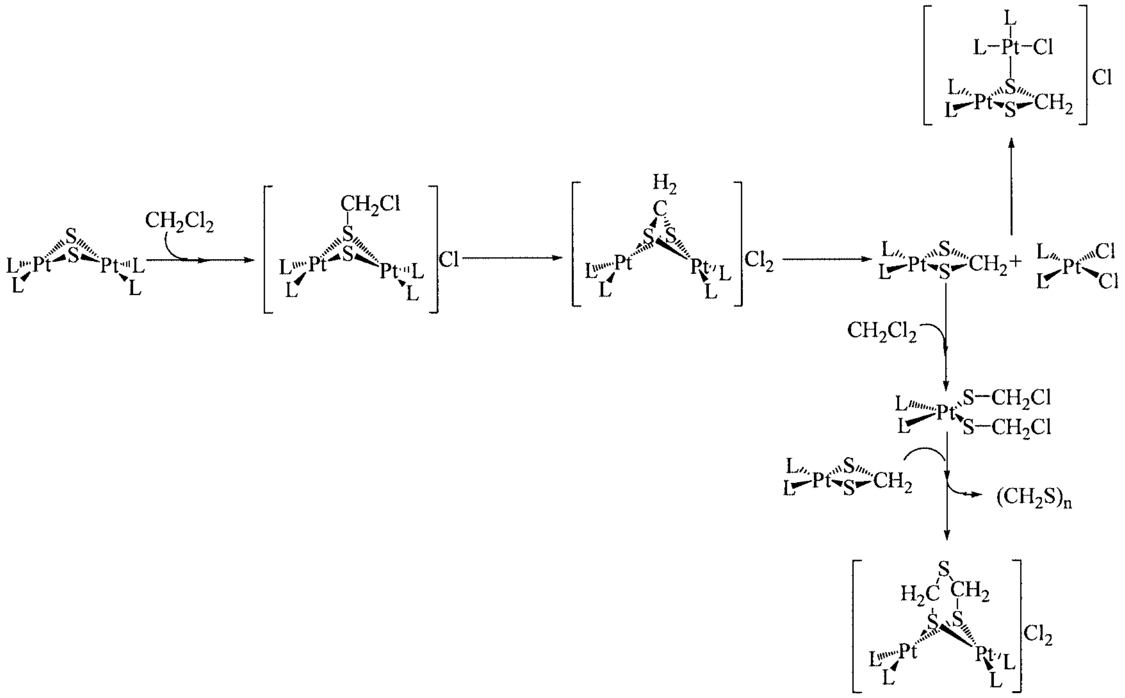


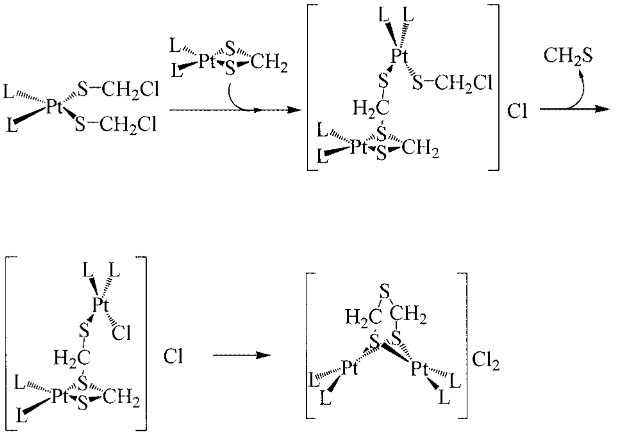
Figure 4. Progression of $[Pt_2(dppp)_2(\mu\text{-}S)_2]$ in CH_2Cl_2 as a function of time monitored by $^{31}P\{^1H\}$ NMR spectroscopy



Scheme 11. Reaction pathway corresponding to the evolution of compounds $[L_2Pt(\mu\text{-}S)_2PtL_2]$ in CH_2Cl_2; the nature of phosphane L ligands is given in the text

gression of $[L_2\{Pt(\mu\text{-}S_2CH_2)Pt\}L_2]^{2+}$ leads to a mixture of the above monometallic products. Compound $[L_2PtCl_2]$ is well-established in the literature for a wide range of terminal ligands, and $[L_2Pt(S_2CH_2)]$ has been fully characterized for L = PMe_2Ph,[70] dppy,[14] dppe,[9] and dppp[9] (Table 3). Remarkably, up to this stage, the reaction pathway is common for all $[L_2Pt(\mu\text{-}S)_2PtL_2]$ compounds (L = PMe_2Ph, PPh_2py, PPh_3; L_2 = dppf, dppe, dppp); further evolution is dependent on the nature of the terminal ligands. Thus, for PMe_2Ph, PPh_2py and dppe, the reaction of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ with CH_2Cl_2 does not progress any further after formation of the corresponding $[L_2PtCl_2]$ and $[L_2Pt(S_2CH_2)]$ compounds. Significantly, the latter species form faster for dppe- than for dppp-containing complexes.

Further evolution of the reaction mixture of $[L_2PtCl_2]$ and $[L_2Pt(S_2CH_2)]$ in CH_2Cl_2 depends on the nucleophilicity of the sulfur atoms in the latter compound. Hence, activation of a second molecule of CH_2Cl_2 yields complex $[L_2Pt(SCH_2Cl)_2]$, as observed for L_2 = dppf.[69] Subsequent activation of the C−Cl bonds in the latter compound by reaction with an additional molecule of $[L_2Pt(S_2CH_2)]$ leads to the bimetallic complex $[L_2Pt\{\mu\text{-}(SCH_2SCH_2S)\text{-}S,S'\}\text{-}PtL_2]Cl_2$, by means of the mechanism depicted in Scheme 12, as observed for L_2 = dppp.[9] Surprisingly, the evolution of $[L_2PtCl_2]$ and $[L_2Pt(S_2CH_2)]$ for L = PPh_3 has shown two different alternatives. On the one hand, analogously to that observed for L_2 = dppf, complex $[(PPh_3)_2Pt(SCH_2Cl)_2]$ was isolated.[71] However, in addition, the condensation reaction between $[(PPh_3)_2PtCl_2]$ and $[(PPh_3)_2Pt(S_2CH_2)]$ to afford $[(PPh_3)_2Pt(S_2CH_2)Pt(PPh_3)_2\text{-}Cl]Cl$ has recently been described.[46]



Scheme 12. Mechanism of the evolution from $[L_2Pt(SCH_2Cl)_2]$ to $[L_2Pt\{\mu\text{-}[S_3(CH_2)_2]\}PtL_2]Cl_2$ as observed for L_2 = dppp

Overall, the reactivity of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ towards CH_2Cl_2 provides evidence for the complex sequence of reactions triggered by the nucleophilicity of the sulfur atoms in the $\{Pt_2S_2\}$ core and shows the ability of the terminal phosphane ligands to tune such reactions. On the basis of the high number and different natures of the isolated species, it seems that the reaction of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ with organic electrophilic agents deserves further attention.

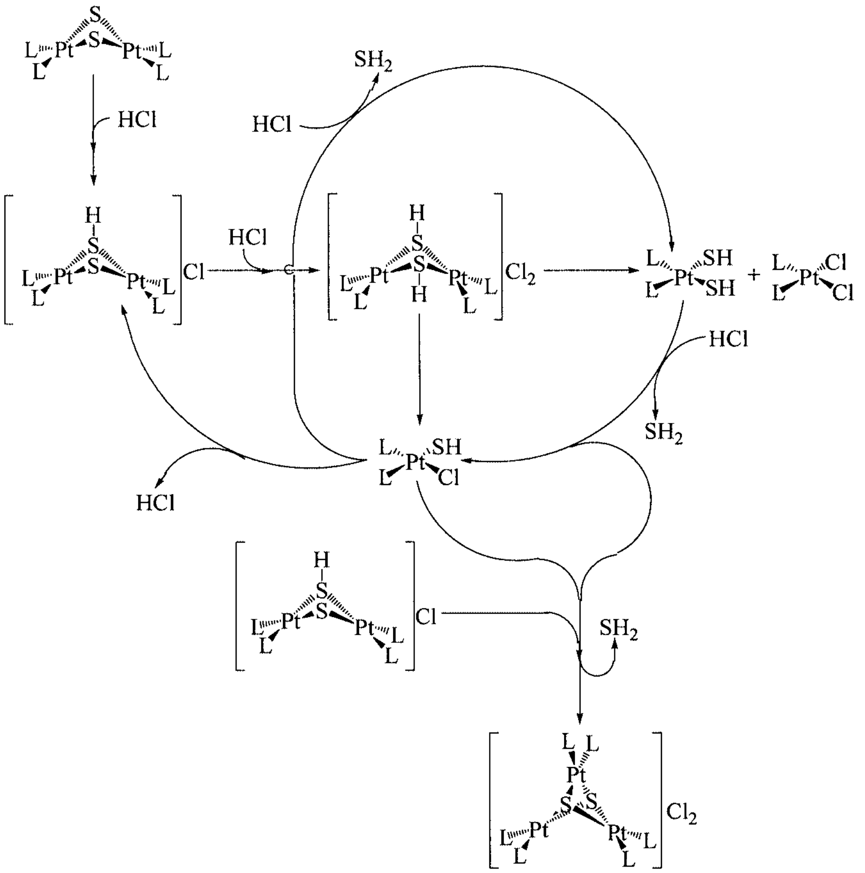
Protic Acids

A nice demonstration of the nucleophilicity of the sulfur atoms in the $\{Pt(\mu\text{-}S)_2Pt\}$ ring should be provided by the reaction of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ compounds with the simplest electron-acceptor species, i.e. the proton. In other words, the well-established reactivity of [$L_2Pt(\mu$-$S)_2PtL_2$] towards metal centers and organic electrophiles assures the basic character of such compounds in the presence of protic acids. Notwithstanding this, the systematic study of these properties had not been undertaken until very recently. As a result, the whole set of reactions ensuing the protonation of the {Pt(μ-S)$_2$Pt} core has been established for L_2 = dppe and dppp.[10]

The first evidence of the protonation of [$L_2Pt(\mu$-$S)_2PtL_2$] compounds were provided by Hor et al. who fully characterized the [$(PPh_3)_2Pt(\mu$-$S)(\mu$-$SH)Pt(PPh_3)_2$]$^+$ cation following its previous identification by ESI MS measurements.[29,30] However, consistently with the results obtained for L_2 = dppe and dppp,[10] the corresponding diprotonated [$(PPh_3)_2Pt(\mu$-$SH)_2Pt(PPh_3)_2$]$^{2+}$ complex was not isolated. Remarkably, the only example of a {Pt(μ-SH)$_2$Pt} core was found for L = $C_6F_5^-$, although in this case neither the monoprotonated nor the totally deprotonated precursors were described.[72] As opposed to the reluctance of the {Pt(μ-S)$_2$Pt} core to afford complexes [$L_2Pt(\mu$-$SH)_2PtL_2$]$^{2+}$ (L = phosphane), its [$(PPh_3)_2Pt(\mu$-$SeH)_2Pt(PPh_3)_2$]$^{2+}$ analog is the only species reported as a result of the protonation of the {Pt(μ-Se)$_2$Pt} core.[73]

The reaction pathways by which compounds [$L_2Pt(\mu$-$S)_2PtL_2$] (L_2 = dppe, dppp) react with protic acids were obtained by monitoring their titration with HCl (Scheme 13) or $HClO_4$ by $^{31}P\{H\}$ NMR spectroscopy and mass spectrometric techniques.[10] Characterization of all the species involved required previous isolation and structural characterization of [$Pt(SH)_2L_2$] and [{$L_2Pt(\mu$-$S)_2PtL_2$}PtL_2]$^{2+}$, for both dppe and dppp ligands. DFT calculations corroborated the thermodynamic feasibility of the reactions proposed on the basis of the experimental data. The first protonation step leads to the structurally characterized [$L_2Pt(\mu$-$S)(\mu$-$SH)PtL_2$]$^+$ cations, but the second step implies disintegration of the platinum-sulfur ring, thus giving rise to various mononuclear species. The subsequent evolution of some of these species allows regeneration of [$L_2Pt(\mu$-$S)(\mu$-$SH)PtL_2$]$^+$, while formation of complexes [$PtCl_2L_2$] and [{$L_2Pt(\mu$-$S)_2PtL_2$}PtL_2]$^{2+}$ is responsible for the cycles' dead end. Whereas the reaction pathway is essentially common for both phosphane ligands, dppe and dppp, the different coordinating ability of Cl^- or ClO_4^- determines the nature of the final products, a mixture of [$PtCl_2L_2$] and [{$L_2Pt(\mu$-$S)_2PtL_2$}PtL_2]Cl_2 or only [{$L_2Pt(\mu$-$S)_2PtL_2$}PtL_2]$(ClO_4)_2$.

The previous results show that the evolution of complexes [$L_2Pt(\mu$-$S)_2PtL_2$] (L_2 = dppe or dppp) in the presence of protic acids depends on several factors: (i) the concentration and nature of the protic acid, i.e. the coordinative features of the conjugate anion; (ii) the nature of the ter-



Scheme 13. Reaction pathway corresponding to the evolution of [$L_2Pt(\mu$-$S)_2PtL_2$] upon exposure to HCl as observed for L_2 = dppe or dppp

minal phosphane ligand, dppe containing species are more reactive than those with dppp; and (iii) the reaction medium used, the amount of $[Pt_3(\mu_3\text{-}S)_2(L_2)_3]^{2+}$ formed is directly related to the polarity of the solvent.

In summary, the reaction of compounds $[L_2Pt(\mu\text{-}S)_2PtL_2]$ (L_2 = dppe or dppp) with protic acids provides a new insight into the exceptionally rich chemistry arising from the nucleophilicity of the $\{Pt_2S_2\}$ core. On the one hand, protonation of the stable monoprotonated $[L_2Pt(\mu\text{-}S)(\mu\text{-}SH)PtL_2]^+$ complexes triggers a cascade of sequential reactions by which compounds $[Pt(SH)_2L_2]$ are formed. These are the keystone species for regenerating $[L_2Pt(\mu\text{-}S)(\mu\text{-}SH)PtL_2]^+$ complexes, and thus for the cyclical nature of the overall process. Remarkably, complex species containing the Pt−SH fragment, which is present in the above complexes, have been proposed as intermediates in the removal of sulfur as SH_2 from petroleum feedstock, known as hydrodesulfurization (HDS).[74−76] Both the cyclical nature of the processes described and the relevance of complexes containing the Pt−SH fragment in HDS provide additional interest to the results obtained with respect to their potential catalytic applications.

Concluding Remarks and Perspectives

The chemistry of compounds $[L_2Pt(\mu\text{-}S)_2PtL_2]$ (L = phosphane) is becoming increasingly important because of the exceptional ability of the $\{Pt_2S_2\}$ core to act as a powerful nucleophile towards virtually any electron-acceptor species. While its behavior as a metalloligand to metal centers has attracted unceasing attention, exploration of the chemistry involved in the reaction with nonmetal electrophiles has emerged in the recent years. The outstanding richness of this chemistry is witnessed by the cascade of reactions that the $\{Pt_2S_2\}$ core undergoes upon exposure to organic electrophiles and protic acids. The cyclical nature of some of these reactions as well as some of the intermediate species involved are promising for possible catalytic applications. In addition, the unusual reactivity of $\{ML'_y\}$ fragments in $[\{L_2Pt(\mu\text{-}S)_2PtL_2\}ML'_y]^z$ compounds has allowed taking advantage of the influence of the $\{Pt(\mu\text{-}S)_2Pt\}$ core to substantially modify the chemistry of either organic or inorganic L′ ligands. Because of this influence, an atypical C−H allylic activation for cod and an enhanced lability for chloride ligands have been established. The former allows envisaging further developments in organometallic chemistry. The latter has led to a novel route for the building of nuclearity-controlled multimetallic aggregates containing a $\{Pt_2S_2\}_n$ core that may be of use to obtain metal chalcogenide compounds of definite size and thus specific properties.

Our interest in exploring the chemistry of $[L_2Pt(\mu\text{-}S)_2PtL_2]$ compounds has been widely rewarded by its exceptional richness and diversity. Further developments will contribute to establish the still undefined limits of the nucleophilicity of the $\{Pt_2S_2\}$ core, as well as to find applications of this reactivity in main areas of chemistry. The potential of the $\{Pt_2S_2\}$ core to activate slightly polarized bonds involving carbon atom is the aim of our research for future studies.

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