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The $\{Pt_2S_2\}$ core—a butterfly that stings

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The recent developments in the syntheses, structures and reactivities of sulfide-bridged aggregates with the $\{M_2S_2\}$ core (M = Pd or Pt) are discussed. The nucleophilicity of the parent $\{Pt_2S_2\}$ core and its synthetic utility in the preparations of aggregates and clusters are emphasised. Other $\{M_2S_2\}$ systems are also described for comparison.

1 Introduction

The ubiquity of transition metal sulfur compounds in nature has been augmented by the synthesis of many transition metal co-ordination complexes and clusters. While the literature is replete with examples of these sulfur compounds,[1] their biological and industrial significance notwithstanding, the chemistry of sulfido complexes of platinum remained largely unexplored. This is somewhat stupendous, especially when one considers the richness of the individual chemistries of both platinum and sulfur. Hence there should be no compelling reasons why a diverse chemistry involving both elements cannot be developed. The tremendous versatility of sulfur as a ligand is demonstrated by its propensity to (i) extend its co-ordination from terminal (*e.g.* in $[Mo_2S_{10}]^{2-}$)[2] to an encapsulated form {*e.g.* in $[Rh_{17}(S)_2(CO)_{32}]^{3-}$ which consists of three stacked square antiprisms sharing faces with interstitial S atoms in outer antiprisms and Rh in the inner},[3] (ii) catenate giving rise to polysulfido ligands of the type S_n^{2-} (where $n = 1–5$) and (iii) stabilise a variety of clusters. More recently, we have also observed a rare case of a μ_6-sulfide ligand in a complex containing a novel $\{Pd_6S_4\}$ core.[4]

Although any venture into platinum sulfide chemistry should prove propitious, our knowledge of these compounds remain tenuous,[5] being hampered mainly by an inimical climate that can be ascribed to a lack of incentives in this research area. Unlike the Chevrel–Sergent compounds, $M'[Mo_6(\mu_3\text{-}S)_8]$ ($M' = Pb^{II}$, Cu^{II}, *etc.*),[6] which exhibit superconducting properties under low temperature conditions in the presence of high magnetic fields, and the $[Fe_4(\mu_3\text{-}S)_4]$ and $[Fe_3Mo(\mu_3\text{-}S)_4]$ "cubane" units that effectively model the respective biological enzymes, ferredoxins and nitrogenase,[7] there did not seem to be a comparable significance in platinum sulfide complexes to warrant extensive academic interest. However, there is a resurgence of interest in some of these complexes fueled by studies on the concentration-dependent nephrotoxicity associated with the use of antitumour platinum drugs. It has been suggested that this toxicity is a result of the binding of platinum to sulfur-functionalised protein residues.[8] This has thus provided the impetus for some extensive studies.[9]

In 1903, Hofmann and Höchlen[10] reported the isolation of the first platinum–sulfur complex, $[NH_4]_2[Pt(\eta^2\text{-}S_5)_3]$. This early study spawned some fervent work into these compounds of platinum and sulfur. A summary of the main historical milestones in the development of general Pt–S chemistry *en route* to the $\{Pt_2S_2\}$ system is provided in Table 1. The origins of $\{Pt_2S_2\}$ chemistry may be traced to the first report of $[Pt_2(PMe_2Ph)_4(\mu\text{-}S)_2]$ **1a** by Chatt and Mingos[11] in 1970, followed almost immediately by Ugo *et al.*[12] in a study of the reactions of zerovalent platinum phosphine complexes with H_2S and elemental sulfur yielding $[Pt_2(PPh_3)_4(\mu\text{-}S)_2]$ **1b**. Since then, interest in these complexes had centred around rudimentary structural characterisations[13] as well as their reactivities with common organic electrophiles.[14–16] A simplistic theoretical model[17] was also proposed to explain the nucleophilicity of the $\{Pt_2S_2\}$ core.

More recently, there has been a gradual shift of *Weltanschauung* towards using complex **1b** as a versatile metalloligand building block to various homo-,[18] hetero-[19,20] and intermetallic[21] sulfide aggregates. A facile method[22] was also developed to reductively excise one of the sulfur atoms using CO under mild pressures, thereby inducing the formation of a Pt–Pt bond. The synthetic value of this strategy was demonstrated when we successfully adopted it to synthesize a series of heterometallic clusters from their respective aggregates *via* a reductive desulfurisation procedure.[23] Concurrent studies in the analogous palladium sulfido complexes have also been enunciated.[4,24]

In all, it has taken nearly three decades for this field to mature, with much of the activities occurring only within the

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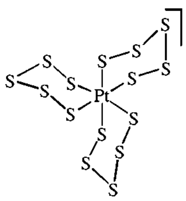
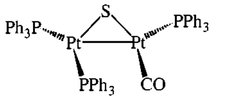
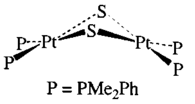
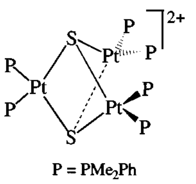
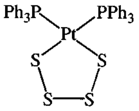
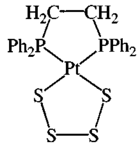
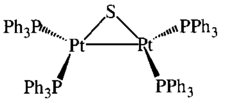
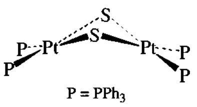
Andy Hor (b 1956, Hong Kong) joined the National University of Singapore in 1984 after graduating from Imperial College [B.Sc. (Hons.)], Oxford (D.Phil.) (with D. M. P. Mingos) and postdoctoral work at Yale (with R. D. Adams). He has authored 120 international papers on carbonyls, sulfide aggregates, ferrocene-based materials, and their catalysis. He was a fellow of Humboldt, Commonwealth Academic Staff, the Association of Southeast Asian Institutions of Higher Learning (ASAIHL) and the Japan Society for the Promotion of Science (JSPS). His major prizes include the Association of South-East Asian Nations (ASEAN) Achievement Award, the National Science and Technology Board (NSTB) Young Scientist & Engineer Award (Singapore), the Japanese Chamber of Commerce & Industry, Singapore (JCCI) Education Award and several teaching awards. A Singaporean and currently the vice-dean of the Faculty of Science, he is married with two children.

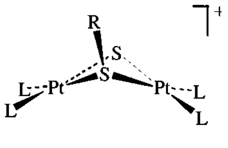
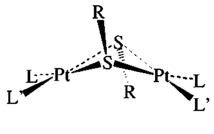
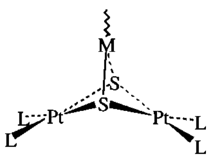
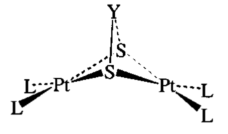
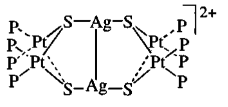
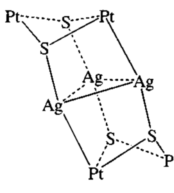
Table 1 Highlights in the development of general Pt–S chemistry *en route* to the $\{Pt_2S_2\}$ system

Author[a]	Molecular system	Structural class	Synthesis	Significance	Ref.
Hofmann and Höchlen (1903)[10]	$[Pt(\eta^2\text{-}S_5)_3]^{2-}$		$(NH_4)_2S + S_8 + H_2PtCl_6$[10] $H_2PtCl_6 + NH_3$ (aq) $+ H_2S + S_8$[49c]	First reported isolation of a η-pentasulfido complex of Pt First example of a purely inorganic chiral molecule (C_3 point group). Only the L enantiomer was isolated[49a] Structure of $[NH_4]_2[Pt(S_5)_3]$ solved by Jones and Katz (1967)[49b] Undergoes cyanide degradative reaction to give $[Pt(S_5)_2]^{2-}$,[49c] and reduction with PPh_3 in ethanol to give $[Pt(PPh_3)_2S_4]$[49d(i)]	10, 49
Baird and Wilkinson (1966)[50a]	$[Pt_2(CO)(PPh_3)_3(\mu\text{-}S)]$		$[Pt(PPh_3)_2(COS)]$ in refluxing CH_2Cl_2 or $CHCl_3$	First reported as the dinuclear Pt_2 complex $[Pt_2(CO)_2(PPh_3)_2(S)]$[50a] Reformulated as $[Pt_2(CO)(PPh_3)_3(\mu\text{-}S)]$ based on X-ray structural data (1969):[50b] a novel Pt–S–Pt triangle is thus established with the first unequivocal structural evidence of a Pt–Pt bond (2.647 Å) Robustness of the Pt_2S core demonstrated:[50c] the Pt–Pt bond resists insertion by CO, CH_3NC and C_2H_2, favouring substitution of the supporting ligands instead, *e.g.* $[Pt_2(PPh_3)_2(\mu\text{-dppm})(\mu\text{-}S)]$ is formed with dppm	50
Chatt and Mingos (1970)[11]	$[Pt_2(PMe_2Ph)_4(\mu\text{-}S)_2]$ **1a**		*cis*-$[PtCl_2(PMe_2Ph)_2]$ + $Na_2S\cdot 9H_2O$, EtOH[11]	Isolation of doubly bridged dinuclear complex $[Pt_2(PMe_2Ph)_4(\mu\text{-}S)_2]$ **1a**[11] Subsequent X-ray study by Mason *et al.*[13c] confirmed the structure and revealed that the two PtS_2 planes are hinged across the S···S bridge ($\theta = 121°$) with a non-bonding S···S distance of 3.06 Å Reacts with a variety of alkyl halides, notably $PhCH_2Br$ and MeBr, to yield $[Pt_2(PMe_2Ph)_4(\mu\text{-}S)(\mu\text{-}SCH_2Ph)]Br$ and *cis*-$[Pt(PMe_2Ph)_2Br_2]$ respectively[11]	11, 13(*c*)
	$[Pt_3(PMe_2Ph)_6(\mu_3\text{-}S)_2]Cl_2$		**1a** + *cis*-$[PtCl_2(PMe_2Ph)_2]$[11]	Chatt and Mingos proposed the structure of this white crystalline product based on ^1H NMR and analytical data. No M–M bonding was invoked since the square-planar Pt^{II} bridged by two S atoms can readily be accommodated[11] First example of a triplatinum complex using **1a** as a metalloligand towards a transition metal fragment. Structure solved by Bushnell *et al.* (1984)[13e]	11, 13(*e*)
	$[Pt(PPh_3)_2(\eta^2\text{-}S_4)]$		$[Pt(PPh_3)_4]$ + S (1:6) in benzene[11] $[Pt(S_5)_3]^{2-}$ + PPh_3 (1:3) or excess PPh_3, EtOH[49d(i),51a] *cis*-$[PtCl_2(PPh_3)_2]$ + Na_2S_n, EtOH[49d(i)]	First mononuclear tetrasulfido-complex reported[11] Independent work by Beck and co-workers (1972)[51a] and Schmidt and Hoffmann (1979)[49d(i)] also advocated the same product. However, limited solubility precluded NMR and X-ray investigations. Structure solved by Dudis and Fackler (1982)[51b]	11, 49(*d*), 51
	$[Pt(dppe)(\eta^2\text{-}S_4)]$		$[Pt(dppe)_2]$ + S (1:6) in benzene[11] $[Pt(S_5)_3]^{2-}$ + dppe, EtOH[49d(i)]	This complex was first proposed in 1970 and its structure only solved by Mingos and co-workers (1983)[20a] confirming that the S_4^{2-} adopts a η-tetrasulfido co-ordination mode and eliminated the alternative bis(η-disulfido) and *cyclo*-tetrasulfido structures proposed earlier[11]	11, 20(*a*), 49(*d*)
	$[Pt_2(PPh_3)_4(\mu\text{-}S)]$		*cis*-$[PtCl_2(PPh_3)_2]$ + excess Na_2S, ammoniacal EtOH	Proposed to have the Pt–S–Pt three-membered ring structure analogous to $[Pt_2(CO)(PPh_3)_3(\mu\text{-}S)]$[11]	11
Ugo *et al.* (1971)[12]	$[Pt_2(PPh_3)_4(\mu\text{-}S)_2]$ **1b**		$[Pt(PPh_3)_3]$ + S (1:1) or H_2S in benzene[12] *cis*-$[PtCl_2(PPh_3)_2]$ + excess Na_2S in benzene[12] $[Pt(SH)_2(PPh_3)_2]$ + NaOEt, EtOH–benzene (3:1)[49d(ii)]	Tetrameric $[\{PtS_2(PPh_3)\}_4]$ and dimeric $[\{PtS(PPh_3)_2\}_2]$ **1b** are proposed[12] Structure of **1b** purported to be similar to **1a** Complex **1b** reported to be reactive to a variety of electrophiles and nucleophiles[15,16]	12, 15, 16, 49(*d*)

[a] Indicates correspondence author(s) of work when first reported.

last 15 years, notably from the research groups of Mingos[16,20] and Adams[25] during the early 1980s, and in recent years, by our group.[19,21–24,26,27] González-Duarte and co-workers have also synthesized a series of μ-thiolato complexes with the $\{M_2S_2\}$ core (M = Ni, Pd or Pt)[28] as well as provided an *ab initio* MO study on the hinge distortion of the $\{Pt_2S_2\}$ ring.[29] A summary of some important developments in the $\{Pt_2S_2\}$ system is given in Table 2.

Table 2 Highlights in the development of selectively derivatised $\{\mathrm{Pt_2S_2}\}$ compounds with a hinged butterfly core

Structural class	Author[a]	Significance	Examples[b]	Ref.
	Chatt and Mingos (1970)[11]	Complex **1a** used as a nucleophile towards alkyl halides Nucleophilicity of the μ-sulfido groups established	$[\mathrm{Pt_2(PMe_2Ph)_4(\mu{-}S)(\mu{-}SCH_2Ph)]Br}$ **3**[11]	11, 12, 14, 16, 17
	Ugo *et al.* (1971)[12]	The nucleophilicity of **1b** is also confirmed through derivatisation using $\mathrm{PhCH_2Br}$ to give **4**	$[\mathrm{Pt_2(PPh_3)_4(\mu{-}S)(\mu{-}SCH_2Ph)]Br}$ **4**[12]	
	Morris and co-workers (1983)[14]	Confirmation of the earlier findings[11,12] in regard to the synthesis and nucleophilicity of **1b**	$[\mathrm{Pt_2(PPh_3)_4(\mu{-}S)(\mu{-}SMe)]X}$ (X = I **5a**, $\mathrm{PF_6}$ **5b** or $\mathrm{BPh_4}$ **5c**)[16]	
	Mingos and co-workers (1984)[16]	First fully dedicated study on the nucleophilicity of **1b** towards a series of alkyl halides	$[\mathrm{Pt_2(PPh_3)_4(\mu{-}S)(\mu{-}SR)]X}$ (R = $\mathrm{CH_2Cl}$ **6**[14,16] or $\mathrm{CHCl_2}$ **7**;[14] X = Cl, $\mathrm{PF_6}$ or $\mathrm{BPh_4}$)	
	Hor and Tan (1988)[17]	A simple qualitative MO model invoked to explain the nucleophilicity of the sulfur bridges of **1b** in terms of π interactions		
	Chatt and Hart (1960)[13a]	Chatt and Hart[13a] isolated the di-μ-thiolate complexes of $\mathrm{Pt^{II}}$; proposed the formation of an "inorganic aromatic ring" involving d_π–p_π interaction within the $\{\mathrm{Pt_2S_2}\}$ core Single-crystal analysis of **9** by Hall *et al.* (1972)[13b] Bird *et al.*[13d] advocated fusion *in vacuo* of complexes of type $[\mathrm{Pt(SR)_2(PR_3)_2}]$ as a facile route to **10**	*cis*-$[\mathrm{Pt_2(NO_2)_2(PPh_3)_2(\mu{-}SMe)_2}]$ **8**[16] $[\mathrm{Pt_2X_2(PR_3)_2(\mu{-}SR)_2}]$ (X = Cl or SR)[13a] *cis*-$[\mathrm{Pt_2Cl_2(PPr^n{}_3)_2(\mu{-}SEt)_2}]$ **9**[13b] *cis*-$[\mathrm{Pt_2(SCH_2Ph)_2(PMePh_2)_2(\mu{-}SCH_2Ph)_2}]$ **10**[13d]	13, 16
 M = Transition-metal fragment	Chatt and Mingos (1970)[11]	First example of a triplatinum complex **14** resulting from the use of **1a** as a metalloligand towards a transition metal fragment Structure of **14** solved by Bushnell *et al.* (1984)[13e]	$[\{\mathrm{Pt(PMe_2Ph)_2(\mu_3{-}S)}\}_2\mathrm{Pt(PMe_2Ph)_2}]^{2+}$ **14**[11,13e] $[\mathrm{(S{-}S)_2M}]^{n+}$ (*n* = 2, M = Pd **18** or Hg **24**;[20b] *n* = 1, M = Cu **25a**[19,27c]) $[\{\mathrm{(S{-}S)Pd}\}_2(\mu\mathrm{{-}Cl})_2]^{2+}$ **19**[20b] $[\mathrm{(S{-}S)ML_2}]^{n+}$ [$\mathrm{ML_2}$ = Pd(dppe) **20**,[20b] Rh(cod) **22**[20c] or $\mathrm{Rh(CO)_2}$ **23a**[20d]] $[\mathrm{(S{-}S)M(dppe)}]^{2+}$ (M = Ni **26**[19] or Hg **27**[20b]) $[\mathrm{(S{-}S)CoCl_2}]$ **28**[27a] $[\{\mathrm{(S{-}S)Cu}\}_2(\mu\mathrm{{-}dppf})]^{2+}$ **29**[19] $[\mathrm{Pt_2(PPh_3)_4(\mu{-}SMCl)_2}]$ (M = Ag **30a**[27e] or Au **31**[20f]) $[\mathrm{(S{-}S)M(PPh_3)}]^+$ (M = Cu **33a**,[27c] Ag **34**[20f] or Au **35**[20f])	11, 13(*e*), 19, 20, 22, 23, 27
	Mingos and co-workers (1983–1987)[20b–d]	Emergence of **1b** as a useful building block for heterometallic polynuclear complexes, functioning as a versatile metalloligand towards a wide array of transition metal fragments; co-ordination mode of the sulfido ligand changes from μ-S to μ_3-S The term "aggregates" was first coined by Mingos and co-workers[20b] to describe polynuclear structures in which no formal M–M bonding occurs		
	Hor and co-workers (1994–1997)[19,27b,c]	Novel use of X-ray photoelectron spectroscopy (XPS) to study heterometallic aggregates of **1b**; binding energies were related to the charge distribution and nucleophilicity of the sulfur centres. Allows for parallel studies of these polynuclear aggregates and other established inorganic solid systems[19]		
	Chin and Hor (1996)[22]	Establishment of a synthetic path involving facile reductive desulfurisation of the $\{\mathrm{Pt_2S_2}\}$ core to give Pt–Pt bonded $\{\mathrm{Pt_2S}\}$ triangle under mild CO pressure[22] Novel facile deheterometallation of a heterometallic aggregate **28** *via* carbonylative desulfurisation to yield $[\mathrm{Pt_2(CO)_2(PPh_3)(\mu{-}S)}]$[27a]		
	Hor and co-workers (1997)[23]	Induction of hetero-M–M bond formation by reductive desulfurisation using CO leading to a decapacitative transformation of a $\{\mathrm{Pt_2MS_2}\}$ aggregate to a $\{\mathrm{Pt_2MS}\}$ terahedral cluster		
 Y = Main-group fragment	Hor and co-workers (1993–1997)[21]	Emergence of **1b** as a versatile metalloligand toward various main-group Lewis acidic fragments to give "intermetallic" aggregates First intermetallic aggregates **42a** and **42b** reported with unusual "Mexican-hat-like" structure; presence of stereochemically active lone pair on Tl suppresses the electrophilicity of the complex[21a] Aggregates of differing local geometry at the heterometal Y, *viz.* bent $\mathrm{Tl^I}$ **42**, tetrahedral $\mathrm{Ga^{III}}$ **46** and $\mathrm{Bi^{III}}$ **47** and square-pyramidal $\mathrm{In^{III}}$ **49a** and $\mathrm{Bi^{III}}$ **48**, are synthesized[21a–d] Ligand transformation of analogous $[\mathrm{Pt_2(dppf)_2(\mu{-}S)_2}]$ **2a** in $\mathrm{CH_2Cl_2}$ to give $[\mathrm{Pt(SCH_2Cl)_2(dppf)}]$[21e] and reaction with $\mathrm{TlNO_3}$ to yield **43a**[21f]	$[\mathrm{(S{-}S)Tl}]\mathrm{NO_3}$ **42a**[21a] $[\mathrm{(S{-}S)Pb(NO_3)_2}]$ **44a**[21b] $[\mathrm{(S{-}S)Pb(NO_3)}]\mathrm{PF_6}$ **44b**[21b] $[\mathrm{(S{-}S)GaCl_2}][\mathrm{GaCl_4}]$ **46**[21c] $[\mathrm{(S{-}S)InCl_3}]$ **49a**[21c] $[\mathrm{(S{-}S)BiCl_3}]$ **48**[21d] $[\mathrm{(S{-}S)BiCl_2}]\mathrm{PF_6}$ **47**[21d] $[\mathrm{(S{-}S)Tl}]\mathrm{NO_3}$ **43a**[21f]	21, 26
	Tan *et al.* (1997)[26]	Structural peculiarities of intermetallics **42**, **44**, **46** and **49a** are investigated in a theoretical study[26]		
	Mingos and co-workers (1983)[20e]	First assembly of two $\{\mathrm{Pt_2S_2}\}$ moieties on a dimetal unit in the formation of a "giant" structure	$[\mathrm{(S{-}S)_2Ag_2}]^{2+}$ **32**[20e]	20(*e*)
	Yam *et al.* (1996)[36]	First synthesis of a heterometallic cluster based on the $\{\mathrm{Pt_2S_2}\}$ core with extensive M–M bonding	$[\{\mathrm{Pt_2(dppy)_4(\mu_3{-}S)_2}\}_2\mathrm{Ag_3}]^{3+}$ **36**[36]	36

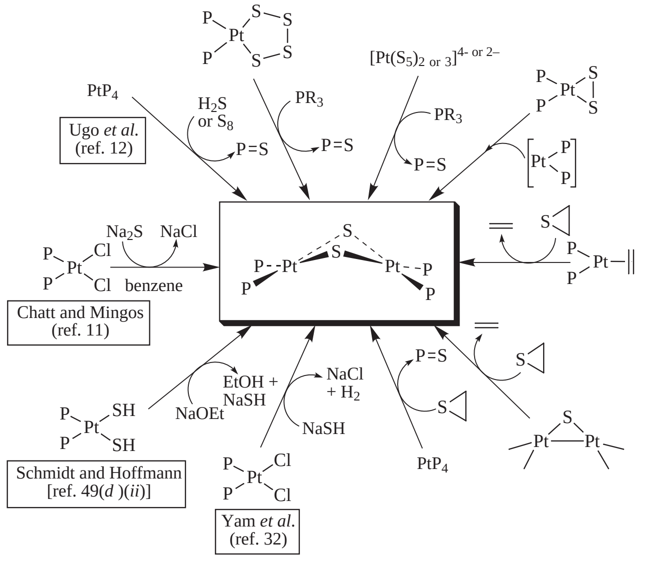
[a] Indicates correspondence author(s) of cited work. [b] S–S = $\mathrm{(Ph_3P)_4Pt_2(\mu{-}S)_2}$.

The chemistry of platinum sulfido aggregates and clusters was reviewed recently.[30] In this paper we shall broaden the scope to include other $\{M_2S_2\}$ complexes, highlight the latest developments and give a perspective view in this field.

2 Complexes with a hinged $\{Pt_2S_2\}$ core

The birth of a butterfly—synthesis of $\{Pt_2S_2\}$ precursors

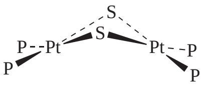
Complexes with a hinged $\{Pt_2S_2\}$ core are structured like a butterfly with the metal atoms at the wing-tip and sulfur at the hinge positions. The first of such complexes of platinum are $[Pt_2(L)_4(\mu\text{-}S)_2]$ (L = PMe_2Ph **1a**[11,13c] or PPh_3 **1b**[12]). The synthesis of **1a** is achieved through metathesis of *cis*-$[PtCl_2(PMe_2Ph)_2]$ with $Na_2S\cdot9H_2O$ in ethanol[11] while **1b** from oxidation of $[Pt(PPh_3)_n]$ ($n = 2$ or 3) with H_2S or S_8[12] or *via* metathesis of *cis*-$[PtCl_2(PPh_3)_2]$ with $Na_2S\cdot9H_2O$ in benzene.[15] The use of an inert solvent in these preparations is essential in view of the high nucleophilicity of the doubly bridging sulfido ligands. Complex **1b** is an orange solid, insoluble in all common non-chlorinated organic solvents, thereby hampering elucidation of its solid state structure. Little has been developed using **1a** as a precursor compared with **1b** presumably because of the ease in handling PPh_3 and the high crystallinity of its complexes. The analogous $[Pt_2(dppf)_2(\mu\text{-}S)_2]$ **2a** was similarly synthesized from either $[PtCl_2(dppf)]$ or $[Pt(MeCN)_2(dppf)][BF_4]_2$ with $Na_2S\cdot9H_2O$ in benzene.[21e] The recent structural elucidation of $[Pt_2(dppe)_2(\mu\text{-}S)_2]$ **2b** by Capdevila *et al.*[27d] also revealed the expected hinged $\{Pt_2S_2\}$ butterfly core. Another approach is demonstrated by Mitchell *et al.*[31] who used a base-assisted condensation reaction of $[PtCl_2(2,2'\text{-bipy})]$ with a model protein Cys residue, *e.g.* *N*-acetyl-L-cysteine (L-Haccys), to give $[Pt_2(2,2'\text{-bipy})_2(\mu\text{-L-accys-}S)_2]$. Yam *et al.*[32] have recently synthesized $[Pt_2(dppy)_4(\mu\text{-}S)_2]$ **1c** (dppy = 2-diphenylphosphinopyridine) from $[PtCl_2(dppy)_2]$ and NaSH and successfully used it as a synthetic precursor to some novel platinum sulfide clusters. Scheme 1 gives a summary of some known routes to the $\{Pt_2S_2\}$ core. The use of desulfurisation of polysulfide complexes by phosphines and oxidative sulfurisation of low-valent platinum complexes are strategies we have used but only with limited success.[33]



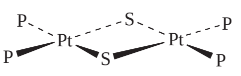
Scheme 1 Some established and projected pathways for the preparation of $[Pt_2(P)_4(\mu\text{-}S)_2]$ (P = phosphine).

Disfiguring a butterfly—reactions with organic electrophiles

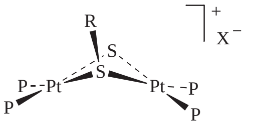
Chatt and Mingos[11] as well as Ugo *et al.*[12] independently demonstrated the nucleophilicity of the sulfur sites in complexes **1a** and **1b**. Complex **1a** reacts with a variety of organic electrophiles, *e.g.* MeI and $PhCH_2X$ (X = Cl or Br), to give the thiolate-bridged complexes $[Pt_2(P)_4(\mu\text{-}S)(\mu\text{-}SR)]X$ (P = PMe_2Ph, R = CH_2Ph, X = Br **3**;[11] P = PPh_3, R = CH_2Ph, X = Br **4**; P = PPh_3, R = Me, X = I **5**[12]). The sulfide ligand in **1b** is so nucleophilic that, upon exposure of **1b** to weak alkylating agents and chlorinated solvents like CH_3Cl and CH_2Cl_2, alkylation of the sulfide bridge rapidly occurs giving rise to $[Pt_2(PPh_3)_4(\mu\text{-}S)(\mu\text{-}SR)]X$ (R = CH_2Cl **6** or $CHCl_2$ **7**; X = Cl).[14,16] Further alkylation would result in bridge cleavage to give mononuclear thiolato complexes. Other examples of thiolate-bridged complexes supported by mixed ligands include *cis*-$[Pt_2(L)_2(X)_2(\mu\text{-}SR)_2]$ (L = PPh_3, X = NO_2, R = Me **8**;[16] L = PPr_3, X = Cl, R = Et **9**;[13b] L = $PMePh_2$, X = SCH_2Ph, R = CH_2Ph **10**[13d]).



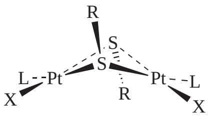
1a: P = PMe_2Ph
1b: P = PPh_3
2a: 2P = dppf
2b: 2P = dppe



1c: P = dppy



3: P = PMe_2Ph, R = CH_2Ph, X=Br
4: P = PPh_3, R = CH_2Ph, X = Br
5a: P = PPh_3, R = Me, X = I
5b: P = PPh_3, R = Me, X = PF_6
5c: P = PPh_3, R = Me, X = BPh_4
6: P = PPh_3, R = CH_2Cl, X = Cl
7: P = PPh_3, R = $CHCl_2$, X = Cl

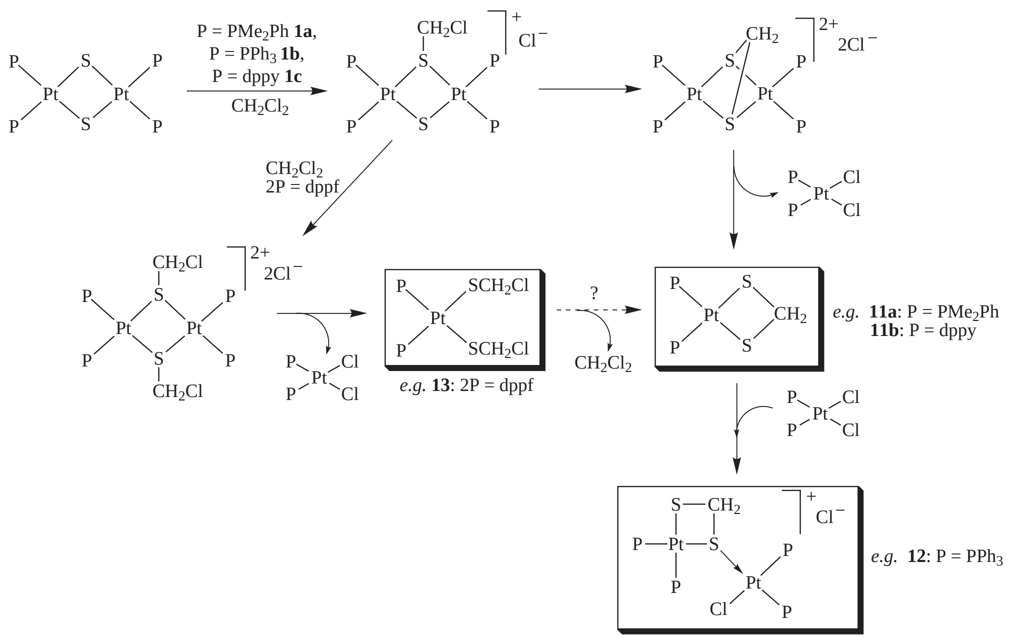


8: L = PPh_3, X = NO_2, R = Me
9: L = PPr_3, X = Cl, R = Et
10: L = $PMePh_2$, X = SCH_2Ph, R = CH_2

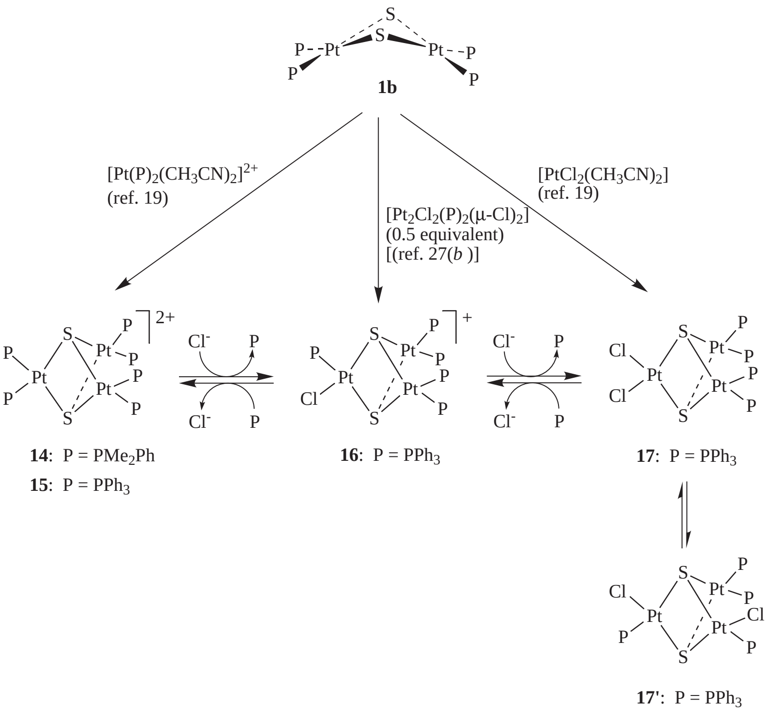
The first example of mononuclear complexes with the crystallographically proven $\{PtS_2CH_2\}$ ring is $[Pt(S_2CH_2)(PMe_2Ph)_2]$ **11a**, prepared by Shaver *et al.*[34] and the second is $[Pt(S_2CH_2)(dppy)_2]$ **11b** by Yam *et al.*[32] Both complexes are formed from the respective nucleophilic attack of the sulfide centres in **1a** and **1c** by the solvent molecules, *viz.* CH_2Cl_2. A recent structurally established example is provided by $[Pt_2Cl(PPh_3)_4(\mu\text{-}S_2CH_2)]PF_6$ **12** which is an unexpected product of $[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2Zn][PF_6]_2$ with CH_2Cl_2.[35] Similarly, $[Pt_2(dppf)_2(\mu\text{-}S)_2]$ **2a** in CH_2Cl_2 gives mononuclear $[Pt(SCH_2Cl)_2(dppf)]$ **13**,[21e] thereby showing a facile pathway to the formation of a terminal dithiolato complex from a di-μ-thio complex. Our characterisations of **12** by single-crystal X-ray diffractometry and **13** through NMR experiments provide some additional information as to the overall mechanism of disintegration of di-μ-thio complexes **1a**, **1b**, **1c** and **2a** in chlorinated solvents like CH_2Cl_2. This process involves alkylation at the highly nucleophilic sulfur to yield the substituted thiolato complexes. Monoalkylation would preserve the dinuclear core whilst dialkylation would lead to the collapse to mononuclear thiolato complexes. Further metallation could explain the formation of **12** (Scheme 2).

Spiking a butterfly—addition of d-block fragments and conversion of aggregates into clusters

Although derivatisation of complex **1a** to give the homometallic aggregate $[Pt_3(PMe_2Ph)_6(\mu_3\text{-}S)_2]Cl_2$ **14**[11,13e] had been known for some time, the synthetic usefulness of **1b** remained unexploited until the early 1980s when Mingos and co-workers synthesized a series of heterometallic complexes of general formula $[\{Pt_2(PPh_3)_4(\mu_3\text{-}S)_2\}_xML_y]^{n+}$ based on their Lewis acid–base reactions with a variety of transition metal fragments. The



Scheme 2 A possible mechanism for the formation of various thiolato complexes from the disintegration of the $\{Pt_2S_2\}$ core in CH_2Cl_2.



Scheme 3 Expansion of the $\{Pt_2S_2\}$ core in complex **1b** to a series of interconvertible homotriplatinum aggregates.

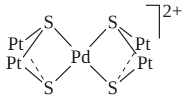
lack of active metal–metal bonds in these polynuclear structures prompted Mingos[20b] to describe them as sulfido "aggregates" (as opposed to "clusters"). The true value of sulfide ligands stems from their innate ability to form relatively strong bonds with nearly all the transition elements. They can also serve as bridging ligands with variable degrees of electron donation. Furthermore, in the case of the dinuclear complex **1b**, the flexibility of the hinge angle between the two PtS_2 planes, the variability of the S · · · S non-bonding separation together with the high nucleophilicity of the μ-sulfido ligands all serve to promote the stabilisation of a variety of these heterometallic aggregates. The nuclearity of these resultant aggregate complexes and the co-ordination modes of their sulfur centres are determined largely by the local geometry of the heterometal, M: square planar, *e.g.* $[(S–S)_2Pd]^{2+}$ **18**,[20b] $[(S–S)Rh(cod)]^+$ **22**,[20c] $[(S–S)Rh(CO)_2]^+[Rh(CO)_2Cl_2]^-$ **23a** or $[(S–S)Rh(C_2H_4)_2]^+$ **23b**;[20d] tetrahedral, *e.g.* $[(S–S)_2Hg]^{2+}$ **24**,[20b] $[(S–S)_2Cu]^+$ **25a**,[27c] $[(S–S)Ni(dppe)]^{2+}$ **26**[19] or $[(S–S)CoCl_2]$ **28**;[27a] linear, *e.g.* $[\{(S–S)Cu\}_2(\mu\text{-dppf})]^{2+}$ **29**,[19] $[(S–S)(AuCl)_2]$ **31**,[20f] $[(S–S)_2Ag_2]^{2+}$ **32**[20e] or $[(S–S)Au(PPh_3)]^+$ **35**[20f] [where (S–S) = $(Ph_3P)_4Pt_2(\mu\text{-S})_2$ **1b**]. A related copper(II) analogue of **25a**, *viz.* $[\{Pt_2(dppe)_2(\mu_3\text{-S})_2\}_2Cu]^{2+}$ **25b**, was also reported recently.[27d] Complex **1b** can also be expanded to the homotriplatinum complexes (*i.e.* $Pt_2 \longrightarrow Pt_3$) $[Pt_3(PPh_3)_6(\mu_3\text{-S})_2]^{2+}$ **15** and $[Pt_3Cl_2(PPh_3)_4(\mu_3\text{-S})_2]$ **17** through nucleophilic attack of $[PtCl_2(MeCN)_2]$ and $[Pt(MeCN)_2(PPh_3)_2]^{2+}$ respectively[19] (Scheme 3). The intermediate aggregate $[Pt_3Cl(PPh_3)_5(\mu_3\text{-S})_2]^+$ **16** has also been isolated.[27b] The related $\{PdPt_2\}$ aggregate has been assembled recently in a non-stoichiometric complex $[M_3Cl(PPh_3)_5(\mu_3\text{-S})_2]^+$ ($M_3 = Pd_{1.1}Pt_{1.9}$ or Pt_3).[27b] The introduction of a palladium(II) unit to **1b** gives rise to a series of isomers which are structurally isomorphous but differ only by the metal distribution on the triangular structure. Other d^8 fragments such as $[M(CO)(PPh_3)]^+$ (M = Rh or Ir) have also been successfully planted into the $\{MPt_2\}$ triangle.

Table 3 Selected structural parameters[a] (distances in Å, angles in °) of the heterometallic adducts of complex **1b** [S–S = $Pt_2(PPh_3)_4(\mu\text{-}S)_2$] with d-block transition metal fragments

Complex	d-Block metal ion M	Co-ordination geometry of M	Pt···Pt	S···S	Dihedral angle, θ^b/°	M···Pt	M–S	S–M–S	Ref.
18 $[(S\text{–}S)_2Pd]^{2+}$	Pd^{2+}	Square planar	[c]	[c]	[c]	[c]	2.348(2)	76.4(1)	20(*b*)
22 $[(S\text{–}S)Rh(cod)]^+$	Rh^+	Square planar	3.255(1)	3.004(4)	131.9	3.063(1) 3.040(1)	2.347(3)	79.6(1)	20(*c*)
23a $[(S\text{–}S)Rh(CO)_2]^+$	Rh^+	Square planar	3.269(1)	3.024(3)	132.0	3.048(1) 3.034(1)	2.356(3)	79.9(1)	20(*d*)
23c $[(S\text{–}S)Rh(Me_2C_6H_3NC)_2]^+$	Rh^+	Square planar	3.2907(6)	3.008(4)	112.1	3.0543(10)	2.365(2)	79.0(1)	20(*d*)
25b $[\{Pt_2(dppe)_2(\mu_3\text{-}S)_2\}_2Cu]^{2+}$	Cu^{2+}	Square planar	[c]	3.1	118.4 121.1	[c]	2.314(3)	83.60(9)	27(*d*)
28 $[(S\text{–}S)CoCl_2]$	Co^{2+}	Tetrahedral	3.197(4)	[c]	127.9(6)	3.066(1)	2.359(4)	80.0(1)	27(*a*)
30a $[(S\text{–}S)(AgCl)_2]$	Ag^+	Linear	3.569(2)	[c]	180	3.130(2) 3.060(2)	2.389(3)	173.4(2)[d]	27(*e*)
31 $[(S\text{–}S)(AuCl)_2]$	Au^+	Linear	[c]	[c]	180	3.111(1) 3.218(1)	2.692(7)	174.2(1)[d]	20(*f*)
32 $[(S\text{–}S)_2Ag_2]^{2+}$ (*Ag–Ag*)	Ag^+	Linear	3.350(2) 3.278(2)	3.06(1) 3.14(1)	[c]	[c]	2.389(9)	176.2(3)[e] 174.1(3)	20(*e*)
33a $[(S\text{–}S)Cu(PPh_3)]^+$	Cu^+	"Y-shaped"	3.279	[c]	137.5(5)	2.875(2) 2.864(2)	2.303(5) 2.269(5)	84.6(2)	27(*c*)
33b $[Pd_2Cu(PPh_3)_5(\mu_3\text{-}S)_2]^+$	Cu^+	"Y-shaped"	3.276(2)[f]	[c]	136.5	2.789(3)[g] 2.889(2)[g]	2.251(4) 2.266(5)	85.7(2)	45(*e*)
34[h] $[(S\text{–}S)Ag(PPh_3)]^+$	Ag^+	"Y-shaped"	3.351(2)	[c]	[c]	3.061(1) 3.066(1)	2.479(1) 2.585(1)	76.04(3)	23
34[h] $[(S\text{–}S)Ag(PPh_3)]^+$	Ag^+	"Y-shaped"	3.375(2)	[c]	[c]	3.240(1) 2.962(1)	2.607(2) 2.502(2)	74.33(7)	23
35 $[(S\text{–}S)Au(PPh_3)]^+$	Au^+	Distorted linear	3.279	[c]	135	3.314(1) 3.231(1)	2.345(2) 2.959(2)[i]	70.5(1)	20(*f*)

[a] Mean values are cited for chemically equivalent bonds and angles from previously published structures. [b] Dihedral angle between two $\{PtS_2\}$ (or $\{PdS_2\}$) planes. [c] Value not reported. [d] Angle S–Au–Cl given. [e] Angle reported for S atoms of opposing S–S since Ag is linear. [f] Pd···Pd distance. [g] M···Pd distance. [h] Exists as two polymorphic modifications. [i] Au–S contact distance.

A common structural feature among these compounds is the short non-bonding metal–metal separations. The metals are locked in close proximity chiefly by the capping sulfide ligands. Catalytic co-operation (*e.g.* in **23b**)[20d] and electrochemical communication (*e.g.* in **43a**)[21f] among the metals are subjects of our interest. The ability of **1b** to capture a variety of metal entities is partly attributed to the adjustable Pt···Pt and S···S non-bonding distances, as well as the dihedral angle θ between the PtS_2 planes. Some representative parameters are collated in Table 3.



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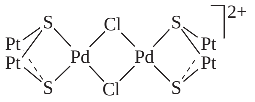

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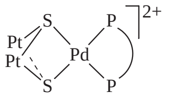
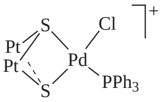


20: P_2 = dppe



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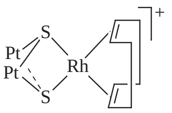

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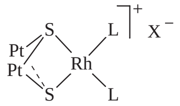
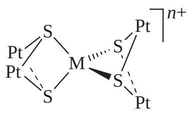


23a: L = CO, X = $[Rh(CO)_2Cl_2]$

23b: L = C_2H_4, X = Cl

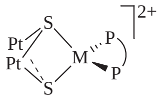
23c: L = 2,6-$Me_2C_6H_3NC$, X = PF_6



24: M = Hg, *n* = 2

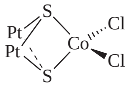
25a: M = Cu, *n* = 1

25b: M = Cu, *n* = 2



26: M = Ni, P_2 = dppe

27: M = Hg, P_2 = dppe



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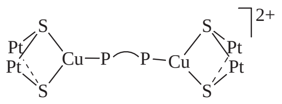
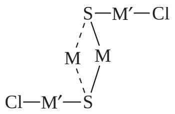


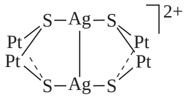
29: P_2 = dppf



30a: M = Pt, M′ = Ag

30b: M = Pd, M′ = Ag

31: M = Pt, M′ = Au



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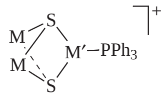


33a: M = Pt, M′ = Cu

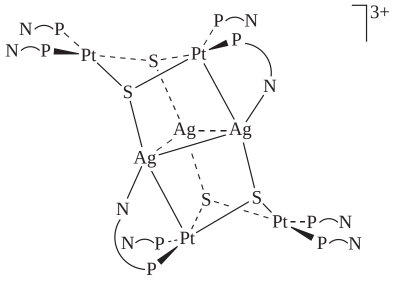
33b: M = Pd, M′ = Cu

34: M = Pt, M′ = Ag

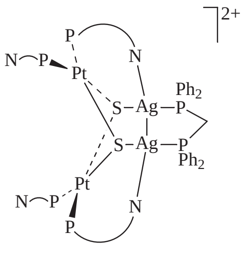
35: M = Pt, M′ = Au

We have recently provided a methodology for the sequential growth of heteropolymetallic Pt–Ag sulfide aggregates.[27e] Based on the early report of the Ag_2Pt_4 aggregate **32**,[20e] our recent isolation of the intermediate aggregates $[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2Ag_2Cl_2]$ **30a** and $[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2Ag(PPh_3)]^+$ **34** has provided clear evidence of the stepwise build-up of higher nuclearity aggregates, *viz.* from Pt_2 **1b** $\longrightarrow$ $AgPt_2$ **34** $\longrightarrow$ Ag_2Pt_2 **30a**

$\longrightarrow$ Ag_2Pt_4 **32**. The methodology developed was based on the reactivity of **1b** towards simple Ag^+ compounds. A similar approach by Yam *et al.*[36] using Ag^I on the analogous complex **1c** which bears a difunctional phosphine/pyridine ligand yielded some delightful polynuclear complexes with Pt–Ag bonds. Formation of $[\{(dppy)_4Pt_2(\mu_3\text{-}S)_2\}_2Ag_3]^{3+}$ **36** and $[(dppy)_4Pt_2(\mu_3\text{-}S)_2Ag_2(\mu\text{-}dppm)]^{2+}$ **37** from the reaction of **1c** with $[Ag(MeCN)_4]PF_6$ and $[Ag_2(dppm)_2(MeCN)_2][BF_4]_2$ respectively demonstrates that a pendant pyridine can help the sulfide in bringing the metals to close proximity. Complex **36** shows how an $\{Ag_3\}$ triangle can be sandwiched by two $\{Pt_2S_2\}$ moieties whereas in **32** the sandwich filling is made up of an Ag–Ag bond.[20e] In order to sustain the barrel-shaped structure in **36**, the planar $\{Pt_2S_2\}$ core in **1c** has to fold to 132.6°.

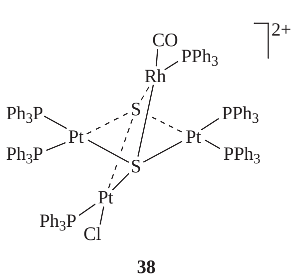


36: P⌒N = dppy



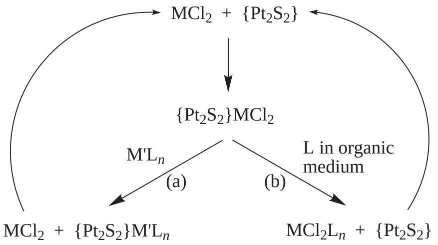
37: P⌒N = dppy

While the μ_3-thio ligand is well established in both hetero- and inter-metallic aggregates, the μ_4 co-ordination mode is less common but can be found in clusters such as $[Os_6(CO)_{16}(\mu_3\text{-}S)(\mu_4\text{-}S)]$,[37a] $[Os_6(CO)_{17}(\mu_4\text{-}S)]$,[37b,c] *etc.* The possibility of using the $\{M_3S_2\}$ as a synthon to make the $\{M_4S_2\}$ aggregate is being explored. Recent effort in our laboratory is directed at the synthesis of a complex like $[RhPt_3Cl(CO)(PPh_3)_6(\mu_4\text{-}S)_2]^{2+}$ **38**.[27b]



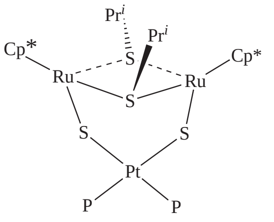
38

Recent results suggested that complex **1b** picks up binary metal halides like MCl_2 (M = Zn, Cd or Hg) to give simple adducts, $[Pt_2(PPh_3)_4(\mu\text{-}S)_2]\cdot MCl_2$.[27b] The prospect of using the $\{Pt_2S_2\}$ moiety as a "carrier" to introduce insoluble MCl_2 into an organic medium is enticing. This offers a possibility for a MCl_2-catalysed metal exchange reaction or $\{Pt_2S_2\}$ as a "phase-transfer catalyst" for metal halide reactions (Scheme 4).



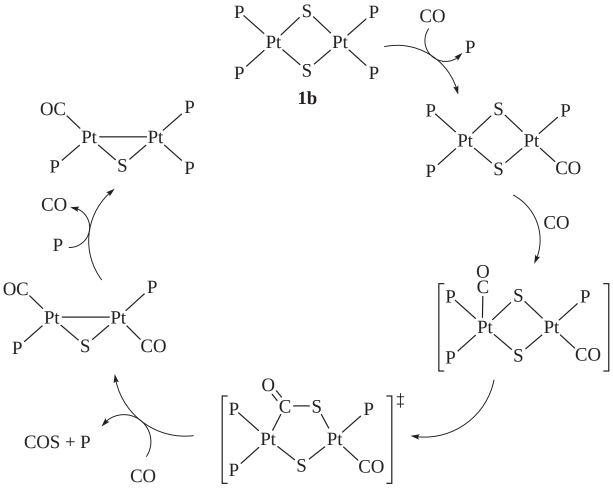
Scheme 4 Possible use of $\{Pt_2S_2\}$ complexes as a "carrier" for the MCl_2 species: (a) metal exchange reaction and (b) "phase transfer catalysis".

The use of complex **1b** as a precursor to heterometallic sulfide complexes offers a simple yet powerful strategy for the design of mixed-metal materials. Since almost any metal compound with some Lewis acidic character can be incorporated into the $\{Pt_2S_2\}$ core, the generality, simplicity and versatility of this method remains unrivaled by most other established routes in heteromultimetallic syntheses.[25c,30,38] A related but different approach is demonstrated by Hidai and co-workers[38c] in the use of $\{Ru_2S_2\}$ as a core for heterometallic synthesis. Insertion of a $[Pt(PPh_3)_2]$ fragment into an S–S bond of a disulfide complex $[Ru_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}S_2)(\mu\text{-}SPr^i)_2]$ yields $[PtRu_2(\eta^5\text{-}C_5Me_5)_2(PPh_3)_2(\mu\text{-}S)_2(\mu\text{-}SPr^i)_2]$ **39**. The absence of M–M bonds in this Pt^{II}/Ru^{III} aggregate is understood in a reaction best described as a reductive cleavage of a disulfide ligand to two μ-monosulfides. If one can direct the reduction to the metal instead of the sulfide sites a clusterification process can be envisaged. This approach is illustrated in our recent effort to introduce low-valent platinum(0) fragments, *e.g.* $[Pt(P)_2]$ ($P_2 = 2PPh_3$ or dppf),[39] to the $\{Pt_2S_2\}$ core. Given the nucleophilicity of the μ-thio ligands, the incoming metal group is expected to anchor onto the sulfur site or insert into the Pt–S bond, thereby creating a $\overline{Pt^{II}\text{–}Pt^{0}\text{–}Pt^{II}}$ triangle which should ease its electronic imbalance through Pt–Pt interactions.



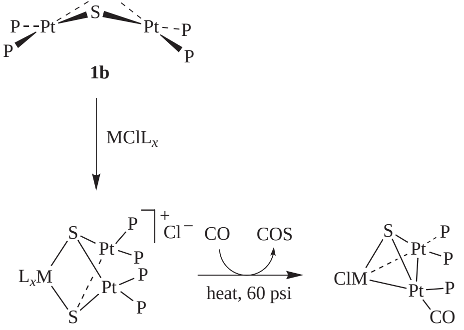
39: P = PPh_3

Recently, we showed that complex **1b** undergoes a facile reductive desulfurisation reaction under mild CO pressure (60 psi) to give $[Pt_2(CO)_n(PPh_3)_{4-n}(\mu\text{-}S)]$ (*n* = 1 or 2) with a strong Pt–Pt bond (Scheme 5).[22] The insertion of CO into the Pt–S bond and the formation of an intermediate bridging COS complex are exciting ideas which need substantiation. This is



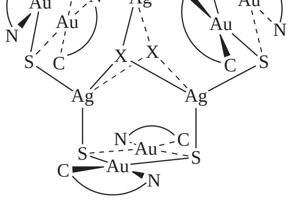
Scheme 5 Possible reaction mechanism of reductive desulfurisation of complex **1b** (P = PPh_3) under mild CO pressure.[22]

hitherto the only known route linking the $\{Pt_2S_2\}$ and $\{Pt_2S\}$ series. As already established in cluster synthesis, reduction and ligand removal are powerful means to induce metal–metal bond formation. Furthermore, it is significant that, after the removal of one sulfide bridge, the remaining sulfide is inert towards carbonyl attack even under higher CO pressure. This illustrates the selectivity of CO towards sulfide excision as well as its ability to reduce Pt^{II} to Pt^{I} without driving to the unstable platinum(0) state. On this basis, a simple, clean yet powerful method was recently developed for the conversion of heterometallic aggregates into clusters.[23] It involves an unprecedented series of concomitant processes: heterometallation, carbonylation, reductive desulfurisation and metal–metal bond formation (Scheme 6). These ideal qualities of CO serve very well to preserve any cluster framework formed. Indeed, no other common reagent can fulfill such a multifaceted role with such efficiency. An added advantage is the easy removal of the gaseous COS by-product. It remains an interesting possibility whether a similar strategy can be developed to convert other sulfur-rich complexes into their sulfur-poor counterparts.



Scheme 6 Direct conversion of heterometallic aggregates to clusters involving a series of concomitant processes, namely heterometallation, carbonylation, reductive desulfurisation and metal–metal bond formation; $MClL_x = CuCl$, $AgCl(PPh_3)$ or $RuCl_2(PPh_3)_3$.[23]

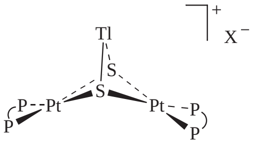
The isoelectronic $\{Au^{III}{}_2S_2\}$ analogue has emerged recently with the syntheses of $[Au_2Cl_4(\mu\text{-}SAuCl)_2]$,[40] $[(\{[C_6H_3(CH_2NMe_2)\text{-}2\text{-}(OMe)\text{-}5]Au(\mu\text{-}S)\}_2)_3Ag_3(\mu_3\text{-}Cl)_2]^+$ **40** and $[(\{[C_6H_4(CH_2NMe_2)\text{-}2]Au(\mu\text{-}S)\}_2)_3Ag_3(\mu_3\text{-}Br)_2]^+$ **41** from an unexpected thiourea desulfurisation reaction.[41] These novel Au–Ag aggregates were studied by electrospray mass spectrometry (ESMS). Although there are indications that parallel chemistry can be developed on these $\{Au_2S_2\}$ complexes, their metallacyclic chemistry appears to be different and unpredictable.



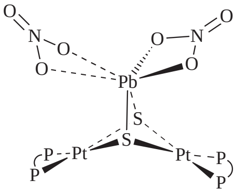
40: X = Cl, (N⌒C) = 2-dimethylaminomethyl-5-methoxyphenyl
41: X = Br, (N⌒C) = 2-dimethylaminomethylphenyl

From a butterfly to a hat—formation of intermetallics with p-block Lewis acids

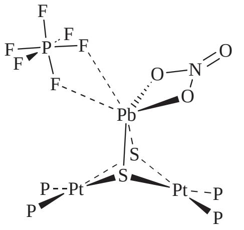
The nucleophilicity of the di-μ-thio groups in complex **1b** is also exploited when it functions as a bidentate ligand towards various main-group Lewis-acids.[21] The intermetallic complexes so obtained exhibit some unusual co-ordination geometries on the heterometal. For example, in $[Pt_2Tl(P\text{–}P)_2(\mu_3\text{-}S)_2]X$ (P–P = 2PPh$_3$, X = NO$_3$ **42a** or PF$_6$ **42b**;[21a] P–P = dppf, X = NO$_3$ **43a** or PF$_6$ **43b**[21f]), the Tl^+ is two co-ordinate, bent and exposes a non-participative (inert) lone pair. This results in a “Mexican hat-like” structure with the $\{Pt_2TlS_2\}$ core resembling the “Mercedes-Benz” insignia when viewed along the S···S axis. The sustainability of such structures by altering the peripheral phosphine (from PPh$_3$ to dppf, for example) offers an advantage in the design of electroactive multimetallic materials. The diverse chemistry of dppf[42] and its role in cluster chemistry[43] were recently reviewed. The presence of a ferrocenyl moiety in dppf is known to confer electroactivity to its complexes.[44] Although some cyclic voltammetric studies of **43a** and **43b** and the related complexes $[(dppf)_2Pt_2(\mu_3\text{-}S)_2Pb(NO_3)]NO_3$ **45** and $[(dppf)_2Pt_2(\mu_3\text{-}S)_2InCl_3]$ **49b** are not conclusive,[21f] the possibility for charge-transfer communication among the different metals and the ferrocenyl moieties serves as an incentive for further work. The ability to design a multimetallic architecture supported by electroactive ligands and connected by ligands that are known for charge distribution is an appetising prospect.



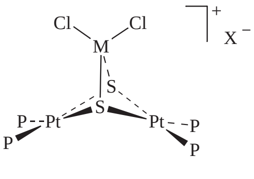
42a: $P_2 = 2PPh_3$, $X = NO_3$
42b: $P_2 = 2PPh_3$, $X = PF_6$
43a: $P_2 = dppf$, $X = NO_3$
43b: $P_2 = dppf$, $X = PF_6$



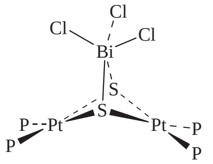
44a: $P_2 = 2PPh_3$
45: $P_2 = dppf$



44b



46: M = Ga, X = GaCl$_4$
47: M = Bi, X = PF$_6$



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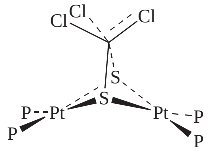


49a: $P_2 = 2PPh_3$
49b: $P_2 = dppf$

Other p-block metals also display some interesting properties when anchored on the $\{Pt_2S_2\}$ core. For example, Pb^{2+} shows a “vacant site” occupied by NO_3^- or PF_6^- in $[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2Pb(NO_3)]X$ (X = NO$_3$ **44a** or PF$_6$ **44b**[21b]), whereas Ga^{III} gives an ion-pair $[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2GaCl_2]^+[GaCl_4]^-$ **46** but In^{III} an almost perfect square pyramid in $[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2InCl_3]$ **49a**. The co-ordinatively exposed thallium(I) structures in **42** and **43** appear to be stabilised by some unusual $Tl^{I}\cdots Pt^{II}$ interactions as suggested by the short Tl···Pt distances and strong Pt–Tl coupling (^{195}Pt NMR). Some notable ligand dissociation and solution dynamics can also be found in the bismuth(III) adducts $[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2BiCl_2]PF_6$ **47** and $[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2BiCl_3]$ **48**. Both high and low co-ordination are found for the heterometal atom on the $\{Pt_2S_2\}$ core. All these data suggest that these intermetallics have rich and often surprising chemistry.[26,29] A

Table 4 Selected structural parameters[a] (distances in Å, angles in °) of the intermetallic adducts of complex **1b** [S–S = $Pt_2(PPh_3)_4(\mu\text{-}S)_2$] with p-block Lewis acidic fragments

Complex	p-Block metal ion Y	Co-ordination geometry of Y	Pt···Pt	S···S	Dihedral angle, θ[b]/°	Y–S	S–Y–S	Ref.
42b [(S–S)Tl]PF_6	Tl^+	Bent	3.293(2)	3.126(5)	135.7(1)	2.764(3)	68.9(1)	21(*a*)
44a [(S–S)Pb(NO_3)]NO_3	Pb^{2+}	Distorted trigonal prismatic	3.266(2)	3.060(4)	132.2(1)	2.718(4)	68.5(1)	21(*b*)
44b [(S–S)Pb(NO_3)]PF_6	Pb^{2+}	Distorted trigonal prismatic	3.290(2)	3.072(3)	133.5(1)	2.704(3)	69.2(1)	21(*b*)
46 [(S–S)$GaCl_2$][$GaCl_4$]	Ga^{3+}	Tetrahedral	3.220(1)	3.066(4)	123.1(3)	2.294(2)	83.9(1)	21(*c*)
47 [(S–S)$BiCl_2$]PF_6	Bi^{3+}	Distorted tetrahedral	[c]	[c]	130.7(2)	2.692(7)	70.1(2)	21(*d*)
48 [(S–S)$BiCl_3$]	Bi^{3+}	Distorted square-based pyramidal	[c]	[c]	128.8(3)	2.762(3)	66.6(1)	21(*d*)
49a [(S–S)$InCl_3$]	In^{3+}	Square-based pyramidal	3.253(2)	3.030(2)	128.3(2)	2.614(2)	70.8(1)	21(*c*)

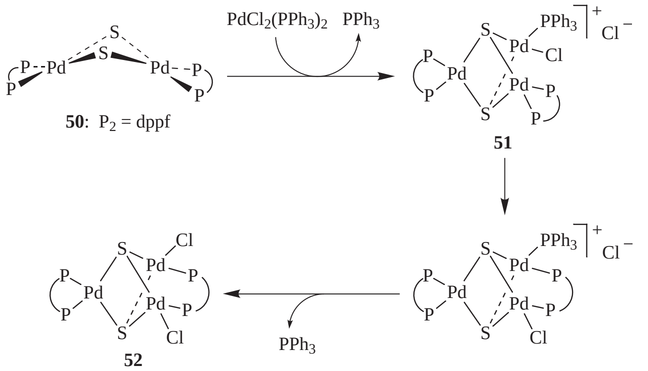
[a] Mean values are cited for chemically equivalent bonds and angles from previously published structures. [b] Dihedral angle between two PtS_2 planes. [c] Value not reported.

summary of selected structural data for these adducts is given in Table 4.

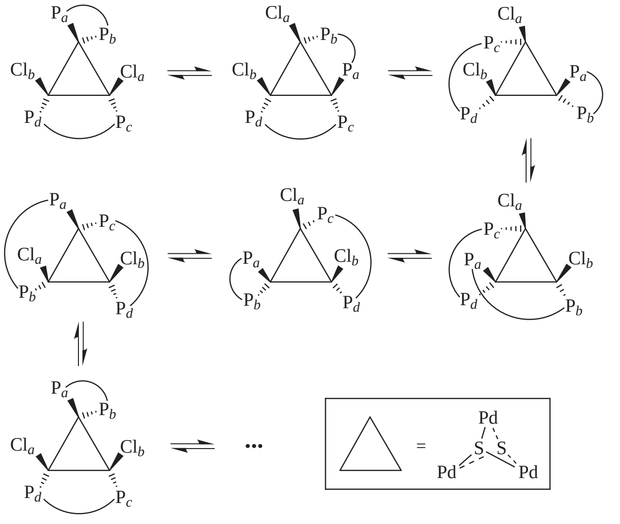
3 Complexes containing a tri-palladium core

The palladium analogue of complex **1b**, $[Pd_2(PPh_3)_4(\mu\text{-}S)_2]$, is poorly characterised[45] and its chemistry virtually unknown. Although its synthesis is plagued by the lability of the phosphine ligand, we circumvented the problem by replacing PPh_3 with the chelating diphosphine, dppf, yielding $[Pd_2(dppf)_2(\mu\text{-}S)_2]$ **50**.[24] The aggregate obtained on reaction between **50** and AgCl, *viz.* $[(dppf)_2Pd_2(\mu_3\text{-}S)_2Ag_2Cl_2]$ **30b**, is entirely analogous to **30a**, possessing a planar $\{Pd_2S_2\}$ core which openly bridges two AgCl moieties by the nucleophilic sulfur atoms. Its isolation has demonstrated the usefulness of **50** as a precursor to the heterometallic aggregates of Pd. It is also a clear indication that the rich heteropolymetallic chemistry based on the established $\{Pt_2S_2\}$ core aforementioned can be extended to the palladium system.

More recently, complex **50** was used as a metalloligand in the assembly of three triangular palladium sulfide aggregates with a $\{Pd_3S_2\}$ core,[24b] namely, $[Pd_3Cl(\eta^2\text{-}dppf)_2(PPh_3)(\mu_3\text{-}S)_2]X$ (X = Cl **51a** or NO_3 **51b**) and $[Pd_3Cl_2(\eta^2\text{-}dppf)(\mu\text{-}dppf)(\mu_3\text{-}S)_2]$ **52** (Scheme 7). The introduction of two diphosphine ligands on a Pd_3 core opens a range of possibilities for positional isomerism and fluxional mechanisms. The latter can involve a "creep-and-crawl" migration (Scheme 8 or Path *a* in Scheme 9) or a "wiper-screen" style of movement (Paths *b* and *c* of Scheme 9) of the phosphines. The former involves an interchange of chelating and bridging modes whilst the latter involves swinging of the phosphines around the metal atoms with the phosphines staying at the bridging mode. Both mechanisms are helped by the migratory movement of the chloride around the ring. The NMR evidence suggests that **52** shows the former type of fluxionality with an alternation of phosphine–phosphine and phosphine–chloride exchanges, *i.e.* Scheme 8, whereas **51** is stereochemically rigid because one of the chloride sites is replaced and blocked by a PPh_3 ligand. These migratory processes demonstrate the flexibility of dppf in the interchange of co-ordination modes and, very significantly, the stabilising role of the sulfide ligands in keeping the Pd_3 triangle intact while allowing the dissociation and migration of the peripheral ligands.



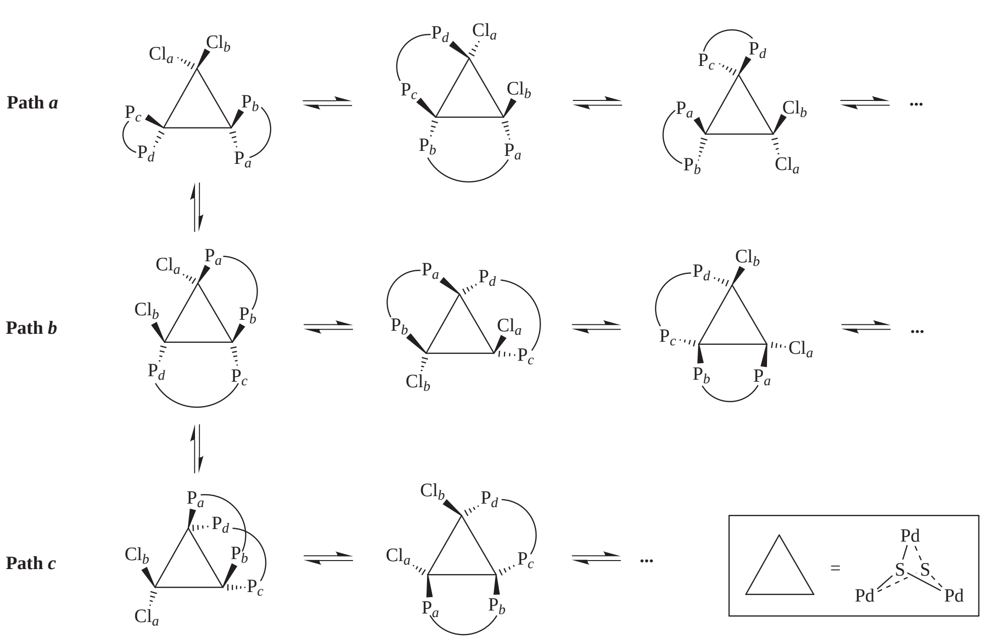
Scheme 7 Conversion of a $\{Pd_2S_2\}$ (**50**) to a $\{Pd_3S_2\}$ (**52**) core showing positional isomerism arising from ligand migrations [dppf = 1,1′-bis(diphenylphosphino)ferrocene].[24b]



Scheme 8 Possible migratory processes of two diphosphines on a $\{Pd_3S_2\}$ core supplemented by chloride and phosphine exchanges (P–P = dppf).[24b]

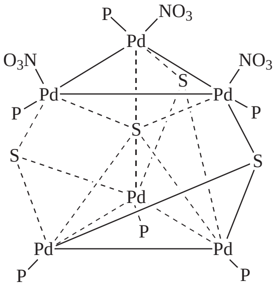
Other earlier work in $\{Pd_2S_2\}$ chemistry includes the syntheses of $[Pd_2(PPh_3)_4(\mu\text{-}S)_2]$,[45a] $[Pd_3Cl_2(PPh_3)_4(\mu_3\text{-}S)_2]$[45b] and $[Pd_3(PR_3)_6(\mu_3\text{-}S)_2]^{2+}$ (R = Me[45c] or Et[45d]). The recent isolation of $[(Ph_3P)_4Pd_2(\mu_3\text{-}S)_2Cu(PPh_3)]^+$ **33b** through a somewhat serendipitous approach from a mixture of $[Pd(PPh_3)_4]$ and $[Cu_2(PPh_3)_3(\mu\text{-}OS_3)]$ strongly suggests the thermodynamic stability of the $\{Pd_2MS_2\}$ core. It would not be surprising that, based on the isolation of **30b** and **33b**, other heterometallic complexes of Pd can be developed. The short Cu···Pd distances in **33b** (see Table 3) are not unusual when compared to those of other similar complexes.[45e]

We have recently isolated by accident $[Pd_6(NO_3)_3(PPh_3)_6(\mu_3\text{-}S)_3(\mu_6\text{-}S)]NO_3$ **53** from a mixture containing $[PdCl_2(PPh_3)_2]$, $Na_2S{\cdot}9H_2O$ and $AgNO_3$.[4] The complex has a $\{Pd_6S_4\}$ core which can be considered as an assembly of two $\{Pd_2S_2\}$ cores and two $Pd(NO_3)_2$ units or a fusion of two $\{Pd_3S_2\}$ cores with concomitant phosphine liberation and nitrate addition. The



Scheme 9 Possible migratory processes of two diphosphines in different co-ordination modes (either chelating or bridging), on a $\{Pd_3S_2\}$ core accompanied by Cl exchange (P–P = dppf).[24b]

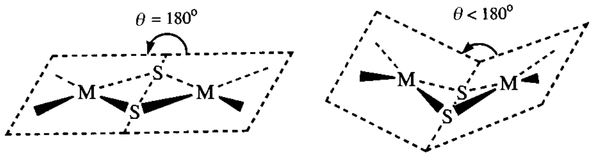
structure as a result consists of a prismatic Pd_6 core with an encapsulated sulfide and four μ_3-S each of which caps a face comprising two Pd atoms on the bottom planes and one Pd atom on the top plane. The nitrate ligands on the top Pd_3 plane are possible active sites for further metallation and hence cluster growth.



53: P = PPh_3

4 A flat or hinged butterfly—dihedral angle and some theoretical aspects of the $\{Pt_2S_2\}$ ring

Throughout the development of the $\{Pt_2S_2\}$ system there had been numerous studies on the possible determinants of ring folding, for example the role of the sulfido bridges and how their alkylation (or metallation) could affect the ring geometry. Initially, Chatt and Hart[13a] had ascribed the observed hinging to the formation of an "inorganic aromatic ring" involving d_π–p_π interaction within the $\{Pt_2S_2\}$ core. Based on this hypothesis, a simplistic MO model was used to explain how alkylation of one of the sulfur bridges would initiate such interactions and hence discourage further alkylation at the second sulfur atom.[17] There are sufficient examples among the platinum(II) sulfide and thiolato complexes which are known to adopt either a flat[31,46] ($\theta = 180°$) or hinged[13,16,46a,47] ($\theta < 180°$) conformation on the $\{Pt_2S_2\}$ ring (Scheme 10). This, coupled with the geometrical isomerism arising from *cis* and *trans* disposition of the ligands and the *syn* and *anti* conformation exhibited by the bridgehead R group [R = alkyl (or aryl) or metal residues], render the number of possible structures many and varied. Subtle changes in the ligands could affect the preferred conformations, just as a strong *trans*-influencing ligand could weaken the opposite Pt–S bond. Indeed, complexes based on a $\{Pt_2S_2\}$ ring characterised by single-crystal X-ray diffractometry show considerable structural diversity (see Tables 3, 4 and 5 for selected structural parameters). Generally, when both bridging groups are S^{2-} as in complexes **1a**, **1b** and **2a** or when either or both sulfide atoms are alkylated or metallated, there is pronounced hinging (*e.g.* $\theta = 121°$ in **1a**). A rare exception is the unsubstituted sulfide complex **1c** with a $\{Pt_2S_2\}$ core which is strictly flat.[32] However, when both sulfides are metallated to *different* groups, a hinged or flattened butterfly would result depending on the relative orientation of the R group (at *anti* or *syn* position) and *cis* or *trans* arrangement of the terminal ligand. When different supporting ligands such as 1,2-bis(diphenylphosphino)ethane (dppe = $Ph_2PCH_2CH_2PPh_2$) (*e.g.* in **54** and **55**) and 1,2-diaminoethane (en = $H_2NCH_2CH_2NH_2$) (*e.g.* in **56**, **57** and **58**) are used in place of unidentate phosphines or when the core metal is changed (*e.g.* Ni **54a**, Pd **54b** and Pt **54c**), a series of doubly substituted di-μ-sulfido complexes containing a globally planar central $\{M_2S_2\}$ ring is obtained.[28] Other examples of planar *trans*-$\{M_2S_2\}$ complexes are **60** to **63**. When compared with the hinged *cis*-$\{Pt_2S_2\}$ complexes **8** to **10**, it would seem that the *trans* complexes favour a planar $\{M_2S_2\}$ core while the *cis* favour the hinged form; subtle interplay between the *trans* influences of the various ligands appears to determine the most thermodynamically favoured ring conformation. Table 5 lists the available structural data for these variant $\{M_2S_2\}$ complexes.



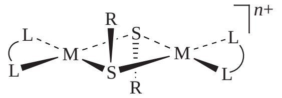
Scheme 10 Two possible geometrical forms adopted by the $\{M_2S_2\}$ ring.

A rigorous study into the hinge distortion in platinum(II) dimers with a $\{Pt_2S_2\}$ ring was recently provided by Capdevila *et al.*[29] After taking into account all possible determinants of the dihedral (hinge) angle in some representative complexes, it was concluded that electronic effects played a major role in governing the geometry about the central $\{Pt_2S_2\}$ ring; the amount of through-ring antibonding interaction between the in-plane sulfur p orbitals (which decreases upon ring folding)

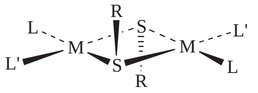
Table 5 Selected structural parameters[a] (distances in Å, angles in °) of some dinuclear μ-thiolato complexes possessing a central $\{M_2S_2\}$ (M = Ni, Pd or Pt) core

Complex	M–S$_b$[b]	M–L[c]	M···M	S$_b$···S$_b$	M–S$_b$–M	S$_b$–M–L[d]	S$_b$–M–S$_b$	L–M–L[e]	θ[f]/°	Ref.
1a $[\mathrm{Pt_2(PMe_2Ph)_4(\mu\text{-}S)_2}]$	2.340(8)	2.265(7)	3.175(2)	3.06(2)	85.5(4)	89.5(3)	81.6(4)	[g]	121	11, 13(*c*)
1c $[\mathrm{Pt_2(dppy)_4(\mu\text{-}S)_2}]$	2.333(1)	2.277(2)	3.555(1)	3.005(2)	99.58(6)	86.75(5)	80.42(6)	102.98(6)	180	32
2b $[\mathrm{Pt_2(dppe)_4(\mu\text{-}S)_2}]$	2.3496(12)	[g]	[g]	[g]	88.94(4)	[g]	83.67(4)	[g]	140.2	27(*d*)
5b $[\mathrm{Pt_2(PPh_3)_4(\mu\text{-}S)(\mu\text{-}SMe)]PF_6}$	2.320(8) 2.363(11)	2.269(5) 2.292(5)	3.306(1)	3.06(1)	88.9(2) 90.9(2)	90.0(2) 85.9(2)	81.6(2)	102.3(2) 99.0(2)	138	16
8 *cis*-$[\mathrm{Pt_2(NO_2)_2(PPh_3)_2(\mu\text{-}SMe)_2}]$	2.294(3)[h] 2.354(2)[i]	2.266(1)	3.342(1)	3.04(1)	92.0(15)	91.7(1)	81.7(1)		141	16
9 *cis*-$[\mathrm{Pt_2Cl_2(PPr^n{}_3)_2(\mu\text{-}SEt)_2}]$	2.274(7)[h] 2.371(7)[i]	2.262(5)	3.206(1)	2.99(1)	85.1 89.7	96.1(2)	80.2(3)		130	13(*b*)
10 *cis*-$[\mathrm{Pt_2(SCH_2Ph)_2(PMePh_2)_2(\mu\text{-}SCH_2Ph)_2}]$	2.322(4)[h] 2.380(4)[i]	2.248(4)	[g]	[g]	90.8(1)	94.2(2)	80.3(1)		138.8	13(*d*)
54a $[\mathrm{Ni_2(dppe)_2\{\mu\text{-}S(CH_2)_3NMe_2\}_2][BPh_4]_2}$	2.237(2)	2.188(2)	3.310(1)	3.009(2)	95.5(1)	95.4(1)	84.6(1)	85.8(1)	180	28(*a*)
54b $[\mathrm{Pd_2(dppe)_2\{\mu\text{-}S(CH_2)_3NMe_2\}_2]^{2+}}$	2.386(5)	2.263(5) 2.275(6)	3.504	[g]	94.4(3)	[g]	85.6(3)	84.7(2)	180	28(*b*)
54c $[\mathrm{Pt_2(dppe)_2\{\mu\text{-}S(CH_2)_3NMe_2\}_2]^{2+}}$	2.377(5)	2.242(5) 2.259(7)	3.556	[g]	96.7(3)	[g]	83.3(3)	85.2(2)	180	28(*b*)
55a $[\mathrm{Pd_2(dppe)_2(\mu\text{-}SC_5H_9NMe)_2][BPh_4]_2}$	2.427(2) 2.385(2)	2.271(2) 2.278(2)	3.497	[g]	93.1(1)	96.1(1) 95.0(1)	85.7(1) 88.2(1)	83.5(1) 84.2(1)	180	28(*b*)
55b $[\mathrm{Pt_2(dppe)_2(\mu\text{-}SC_5H_9NMe)_2][BPh_4]_2}$	2.393(2)	2.263(2)	3.550	3.210	95.7(1)	96.5(1)	84.3(1)	84.7(1)	180	28(*b*)
56 $[\mathrm{Pt_2(en)_e\{\mu\text{-}S(CH_2)_3NMe_2\}_2]Br_2}$	2.289(3)	2.111(8) 2.066(8)	[g]	[g]	96.9(1)	97.1(2)	83.1(1)	83.3(3)	180	28(*c*)
57 $[\mathrm{Pt_2(en)_2(\mu\text{-}SC_5H_9NMe)_2]Br_2\cdot 6H_2O}$	2.298(2)	2.075(6) 2.066(6)	[g]	[g]	97.3(1)	96.7(2)	82.7(1)	82.8(2)	180	28(*c*)
58 $[\mathrm{Pt_2(en)_2(\mu\text{-}SC_5H_9NHMe)_2]Br_4\cdot 2H_2O}$	2.301(2)	2.074(5) 2.071(5)	[g]	[g]	97.0(1)	96.4(1)	83.0(1)	82.2(2)	180	28(*c*)
59 $[\mathrm{Pt_2(bpy)_2(\mu\text{-}accys\text{-}}S)_2]$	2.308(5)	2.01(1)	[g]	[g]	[g]	[g]	[g]	[g]	180	31
60 *trans*-$[\mathrm{Pt_2Ph_2(PMe_2Ph)_2(\mu\text{-}SPh)_2}]$	2.386(4)[h] 2.371(4)[i]	2.232(4)	[g]	[g]	97.2(1)	98.5(1)	82.8(1)		180	46(*b*)
61 *trans*-$[\mathrm{Pt_2I_2(PPh_3)_2\{\mu\text{-}S(CH_2)_2C(Me){=}CH_2\}_2}]$	2.367(3)	2.267(3)	3.539(1)	[g]	[g]	178.0(1)[j]	[g]		180	46(*a*)
62 *trans*-$[\mathrm{Pd_2(SC_6F_5)_2(PPh_3)_2(\mu\text{-}SC_6F_5)_2}]$[k]	2.37	2.28	[g]	[g]	[g]	[g]	87.6		180	52(*a*)
	2.39	2.25	[g]	[g]	[g]	[g]	80.6		180	52(*b*)
63 *trans*-$[\mathrm{Pd_2Cl_2(PEt_3)_2(\mu\text{-}SPh)_2}]$	2.289(2) 2.382(2)	2.266(2)	3.463	[g]	95.7(1)	[g]	84.3(1)		180	53

[a] Mean values are cited for chemically equivalent bonds and angles from previously published structures. [b] S$_b$ denotes bridging sulfur atom. [c] L denotes terminal ligand; M–L bond distances are only cited if the L donor atom is nitrogen or phosphorus. [d] Refers to angle between S$_b$ and L donor atom *cis* to each other. [e] Angle is only cited for chelating or equal unidentate ligands L about a square planar M. [f] Dihedral angle between two S$_b$MS$_b$ planes. [g] Value not reported. [h] *cis* to phosphine. [i] *trans* to phosphine. [j] Only *trans* S$_b$–M–L is given. [k] Exists as two crystalline modifications.



54a: M = Ni, L_2 = dppe, R = $(CH_2)_3NMe_2$, n = 2
54b: M = Pd, L_2 = dppe, R = $(CH_2)_3NMe_2$, n = 2
54c: M = Pt, L_2 = dppe, R = $(CH_2)_3NMe_2$, n = 2
55a: M = Pd, L_2 = dppe, R = $C_5H_9NMe_2$, n = 2
55b: M = Pt, L_2 = dppe, R = $C_5H_9NMe_2$, n = 2
56: M = Pt, L_2 = en, R = $(CH_2)_3NMe_2$, n = 2
57: M = Pt, L_2 = en, R = $C_5H_9NMe_2$, n = 2
58: M = Pt, L_2 = en, R = C_5H_9NHMe, n = 4
59: M = Pt, L_2 = bpy, R = accys, n = 0



60: M = Pt, L = PMe_2Ph, L' = Ph, R = Ph
61: M = Pt, L = PPh_3, L' = I, R = $(CH_2)_2C(Me)=CH_2$
62: M = Pd, L = PPh_3, L' = SC_6F_5, R = C_6F_5
63: M = Pd, L = PEt_3, L' = Cl, R = Ph

determines the extent of hinging. Related work[48] on various binuclear d^8 transition metal complexes arrived at a similar conclusion. The observed hinging of the $\{M_2X_2\}$ core can be explained in terms of the attractive donor–acceptor interactions between the d_{z^2} and the p_z orbitals of the two metal atoms, modulated by the nature of the metal atom, the terminal ligands and the bridging atoms. The sulfide complexes appear to be more stable in the hinged form and their stability increases in the order $Ni^{II} < Pd^{II} < Pt^{II} < Rh^{I} < Ir^{I}$ for different metal atoms. Our experience with the heterometallic aggregates of **1b** suggests that quite generally, as the dihedral angle decreases, the heterometal–sulfur interactions strengthen at the expense of the Pt–S overlap.[26] In general, binding of a heterometal M to **1b** causes a weakening (lengthening) of the Pt–S bonds while co-ordination of additional ligands to M weakens the M–S bonds with a concomitant strengthening (shortening) of the Pt–S bonds. In particular, any ligand *trans* to an M–S bond will render it weakened more than the other M–S bond. This may be rationalised by considering a fundamental competition for interactions (*i.e.* M–L *vs.* M–S and M–S *vs.* Pt–S). Furthermore, *ab initio* calculations also indicate that M–S bonding is an important factor for M to accept additional ligands. This accounts for the differences in co-ordination behaviour between the isoelectronic species Tl^+ and Pb^{2+}.

5 Conclusion

The potential of using an $\{M_2S_2\}$ core in the development of multimetallic structures is appetising. We have formulated the key strategies in the ring contraction ($M_2S_2 \longrightarrow M_2S$), metallation ($M_2S_2 \longrightarrow M_3S_2 \longrightarrow M_4S_2$) and clusterification ($M_3S_2 \longrightarrow M_3S$) reactions. They form the basis of molecular design of polynuclear frameworks based on a stepwise introduction (or removal) of metal atoms to the $\{M_2S_2\}$ butterfly core with or without concomitant desulfurisation and/or metal–metal bond formation. The facile and controlled sulfide extrusion from $\{M_2S_2\}$ serves as a molecular model for (hydro)desulfurisation on precious metals. It also provides a fresh impetus for the insertion of other small molecules into the notoriously strong Pt–S bonds. The catalytic potential of these complexes has not been exploited but deserves more attention in the coming years. The conventional thinking is that sulfur, sulfides and other sulfur-containing substances pose a major threat to catalytic processes because of the poisoning effect of sulfur on almost all known catalysts. It would be a significant achievement if, on the basis of the work described, we can develop a catalyst which not only has a catalytically active M–S bond, but is also inherently immune to sulfur poisoning because of its sulfur-rich nature.

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