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Syntheses and structural characteristics of [2-thiaalkyl]platinum complexes with phosphorus- and nitrogen-donor ligands†

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The preparation of a series of bis(2-thiaalkyl)platinum(II) complexes, *cis*-$\mathrm{Pt(CH_2SR)_2L^1{}_2}$ {R = Ph, $\mathrm{L^1 = PPh_3}$, $\mathrm{PMe_3}$, $\mathrm{PMe_2Ph}$, $\mathrm{PMePh_2}$ or $\mathrm{L^1{}_2}$ = dppe [1,2-bis(diphenylphosphino)ethane], dmpe [1,2-bis(dimethylphosphino)ethane], dcpe [1,2-bis(dicyclohexylphosphino)ethane], dppm [bis(diphenylphosphino)methane]; R = $\mathrm{C_6H_4Me}$-*p*, $\mathrm{L^1 = PPh_3}$, $\mathrm{PMe_3}$, $\mathrm{PMe_2Ph}$ or $\mathrm{L^1{}_2}$ = dppe, dmpe; R = Me, $\mathrm{L^1 = PPh_3}$, $\mathrm{PMe_3}$, $\mathrm{PMePh_2}$ or $\mathrm{L^1{}_2}$ = dppe} and their characterisation by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, are described. The relative *trans* influence of a range of heteromethyl ligands, $\mathrm{CH_2YR}_n$, is discussed [Y = S, Si, Ge, Sn and C; R = (variously) alkyl, aryl, alkenyl or alkynyl; n = (appropriately) 1 or 3]. Also reported are the formation and characteristics of the dinuclear platinum(II) species, $\mathrm{[Pt(CH_2SCH_3)(\mu\text{-}CH_2SCH_3)(PPh_3)]_2}$, containing bridging thiaalkyl ligands in a six-membered dimetallacycle. Thermolytic rearrangement of $\mathrm{Pt(CH_2SPh)_2(dppe)}$ leads to a metallacyclic product, $\overline{\mathrm{Pt(C_6H_4SC}}\mathrm{H_2)(dppe)}$. The syntheses and spectroscopic identification of asymmetric complexes *cis*-$\mathrm{Pt(CH_2SR)R'(PPh_3)_2}$ (R = Ph, R′ = Me, $\mathrm{C_6H_4Bu^t}$-*p*, $\mathrm{CH_2CMe_2Ph}$, $\mathrm{CH_2SiMe_2Ph}$; R = Me, R′ = $\mathrm{CH_2SiMe_3}$) are also reported, as are unsuccessful attempts to isolate related complexes *cis*-$\mathrm{Pt(CH_2SR)_2L_2}$ [$\mathrm{L_2}$ = polypyridyl N donor; L = $\mathrm{P(OMe)_3}$]. The molecular structures of *cis*-$\mathrm{Pt(CH_2SPh)_2(PPh_3)_2{\cdot}0.5CH_2Cl_2}$, $\mathrm{[Pt(CH_2SCH_3)(\mu\text{-}CH_2SCH_3)(PPh_3)]_2}$ and *cis*-$\mathrm{Pt(CH_2SPh)(CH_3)(PPh_3)_2}$ have been determined by X-ray diffractometry. Oxidative addition of $\mathrm{ClCH_2SPh}$ to appropriate dimethylplatinum(II) precursors has afforded two platinum(IV) derivatives, $\mathrm{PtCl(CH_2SPh)Me_2(dmpe)}$ and $\mathrm{PtCl(CH_2SPh)Me_2(bipy)}$ (bipy = 2,2′-bipyridyl), of differing stereochemistry.

The significance and potential of heteromethyl ligands, $\mathrm{CH_2YR}_n$ (Y = S, Si, Ge, Sn or C; R = alkyl, aryl, alkenyl or alkynyl; n = 1 or 3) in organometallic chemistry was recognised early by several workers, notably Wilkinson and Lappert.[2] The lack of readily transferable β substituents and the general reluctance of these fragments to form internal multiple bonds between carbon and the heteroatom, inhibited the β-hydrogen transfer route to σ-M−C scission. The result of this realization was rapid and expansive development in the area of isolable alkyltransition metals. Prominent among these were homoleptic derivatives featuring trimethylsilylmethyl ligands and their close relatives.[1] There were some brief excursions into heteroleptic complexes of platinum.[2] More recently, we have reported extensively upon the synthesis[3] and unusual reactivity[4] of a number of organoplatinum compounds which feature silicon (as well as germanium and tin[5] in the hydrocarbyl ligand. As an extension of our general interest in the reactivity of such heteroatom organometals, we embarked upon an investigation of alkylplatinum (as well as palladium and rhodium[6]) compounds containing a 2-sulfur atom. Organotransition metals with this type of ligand have received relatively little attention.[7] The reactivity of these compounds may differ from that of previous alkylplatinum(II) complexes, since the sulfur site offers a potentially versatile reaction centre. Previous studies of this type of ligand have featured the donor capacity of this sulfur atom and the possibility of intramolecular co-ordination in a fashion analogous to η^2-alkene compounds. Several documented attempts to prepare homoleptic 2-thiaalkyl metal derivatives of the first d block transition period have resulted in the formation of thiophenolate complexes *via* ($\mathrm{C^1}$ to $\mathrm{C^3}$) hydrocarbon elimination.[8] Other, closely related, compounds involving η^2 thioformaldehyde co-ordination have been more widely reported.[9] A review of salient aspects of these classes of compound has appeared.[10]

To date, the only homoleptic 2-thiaalkyl metal has been that reported by Miki *et al.*,[11] in which palladium is co-ordinated by μ-η^2-$\mathrm{CH_2SPh}$ groups in a tetrameric structure. We now report the reaction of $\mathrm{Mg(CH_2SMe)Cl}$ or $\mathrm{Li(CH_2SR){\cdot}tmen}$ (R = Ph or $\mathrm{C_6H_4Me}$; tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) with $\mathrm{PtCl_2(cod)}$ (cod = cycloocta-1,5-diene) to give similar platinum compounds. These undergo ligand metathesis by phosphorus donor species, $\mathrm{L^1}$ [$\mathrm{L^1 = PMe_3}$, $\mathrm{PPh_3}$, $\mathrm{PMe_2Ph}$, $\mathrm{PMePh_2}$; $\mathrm{L^1{}_2}$ = dppe {1,2-bis(diphenylphosphino)ethane}, dmpe {1,2-bis(dimethylphosphino)ethane} or dcpe {1,2-bis(dicyclohexylphosphino)ethane], affording an extensive series of dialkylbis(phosphine)-platinum(II) compounds, *cis*-$\mathrm{Pt(CH_2SR)_2L^1{}_2}$. Some of these derivatives are also accessible by reaction of $\mathrm{Li(CH_2SR){\cdot}tmen}$ with *cis*-$\mathrm{PtCl_2L^1{}_2}$. Brief reports of monoalkylplatinum complexes have also appeared previously.[12] We report alternative synthetic procedures as well as new spectroscopic data for a range of such species, *trans*-$\mathrm{PtCl(CH_2SR)(PPh_3)_2}$ (R = Ph or Me). Treatment of these with other transalkylating agents generates asymmetric dialkylplatinum complexes *cis*-$\mathrm{Pt(CH_2SPh)R'(PPh_3)_2}$ (R′ = Me or $\mathrm{CH_2SiMe_2Ph}$). Oxidative addition of $\mathrm{ClCH_2SPh}$ to *cis*-$\mathrm{PtMe_2L^2{}_2}$ has afforded

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† This paper is respectfully dedicated to the memory of Professor Sir Geoffrey Wilkinson, FRS (1921–1996), an inspiring colleague and friend. Geoff was among the first to recognise the significance of heteromethyl ligands, $\mathrm{CH_2YR}_n$, such as those featured here, and his own work in the area gave great impetus to the development of alkyltransition-metal chemistry.

two platinum(IV) derivatives, $PtCl(CH_2SPh)Me_2L^2_2$ [L^2_2 = dmpe or 2,2′-bipyridyl (bipy)].

Results and Discussion

Synthetic, structural and reactivity studies of *cis*-$Pt(CH_2SR)_2L^1_2$

(*a*) Synthesis. Methods of synthesis of bis(alkyl)platinum(II) complexes with phosphine (and other) ancillary ligands have been explored extensively in these laboratories, most recently as a result of our studies of 2-silaalkyl and related derivatives. A common approach has been to prepare the dialkyl(η-diene)platinum(II) derivative as a general precursor. The diene usually cycloocta-1,5-diene (cod) or bicyclo[2.2.1]hepta-2,5-diene (nbd), may then be displaced by a range of phosphorus- or nitrogen-donor ligands. In accord with this strategy, preparation of $Pt(CH_2SR)_2$(cod) was attempted by halide metathesis, reacting $Li(CH_2SPh)$·tmen or '$Mg(CH_2SCH_3)Cl$' (see below) with $PtCl_2$(cod). The ^1H NMR spectrum of the initial product in the former case indicated the absence of co-ordinated cycloocta-1,5-diene and broad, multiple signals in the aromatic and low-field alkyl regions of the spectrum. Treatment of this product with 2 equivalents of phosphine gave a symmetric product, according to its $^{31}P-\{^1H\}$ NMR spectrum which exhibits values of $^1J_{Pt-P}$ corresponding to *cis*-$Pt(CH_2SPh)_2(PR'_3)_2$ (see below). The product of alkylation with $Mg(CH_2SCH_3)Cl$ likewise, exhibits no ^1H NMR signals from co-ordinated diene. This compound, however, gradually decomposes at ambient temperature, depositing metallic platinum. In this case, however, *cis*-$Pt(CH_2SCH_3)_2L^1_2$ was obtained by immediate treatment of the reactive intermediate with 2 equivalents of phosphine. In practice, a one-pot synthesis was employed, giving the products in reasonable yields.

Most plausibly, the 2-sulfur atom co-ordinates in an intra- or inter-molecular fashion, displacing the diene ligand from platinum. It is not clear whether this occurs before or after formation of the Pt–C bond. An oligomeric compound, of the form $[Pt(CH_2SR)_2]_n$, results. The ligating sulfur may then be displaced by P donors to give monomeric phosphine complexes. With triphenylphosphine, however, a dimetallic, thiaalkyl-bridged species is the ultimate product. Its formation is unusual, since *cis*-$Pt(CH_2SCH_3)_2(PPh_3)_2$ is the apparent kinetic product, even in the presence of only 1 equivalent of phosphine. This phenomenon may, though, be limited by the solubility of $[Pt(CH_2SR)_2]_n$, leading to the situation where the more soluble phosphine is always in excess during addition. Monomeric *cis*-$Pt(CH_2SCH_3)_2(PPh_3)_2$ then aggregates more slowly, with loss of triphenylphosphine, yielding $[Pt(CH_2SCH_3)(\mu-CH_2SCH_3)(PPh_3)]_2$. We have begun to explore the mechanism of the transformation.

The preparative route to $Li(CH_2SPh)$·tmen was adapted successfully to the conversion of $CH_3S(C_6H_4Me$-*p*) to $Li[CH_2S(C_6H_4Me$-*p*)]·tmen. Reactions to give *cis*-$Pt[CH_2S(C_6H_4Me$-*p*)$]_2L^1_2$ resulted in lower yields, however. Attempts were also made to prepare $Li[CH_2S(C_6H_4F$-*p*)]·tmen. In this case, though, aromatic ring-lithiation occurs preferentially *ortho* to the fluoro group, giving $Li[C_6H_3F$-2-(SMe)-5]. The compound $Pt[C_6H_3F$-2-(SMe)-5$]_2$(dppe), characterised by NMR spectroscopy, has been prepared by its reaction with $PtCl_2$(dppe).

An alternative route to *cis*-$Pt(CH_2SR)_2L^1_2$, direct transalkylation on $PtCl_2L^1_2$ using organolithium or organomagnesium reagents, was investigated in some instances. Reaction of $Li(CH_2SCH_3)$·tmen[13] with $PtCl_2$(dppe) gave poor yields of the dialkyl product and a variety of by-products. While preparation of $Mg(CH_2SCH_3)Cl$ (see below) at concentrations ⩾0.5 M resulted in a very vigorous, exothermic reaction and apparent decomposition, concentrations of approximately 0.1 M were attainable. Transalkylations to give *cis*-$Pt(CH_2SCH_3)_2L^1_2$ proceeded in reasonable yields for most phosphines (see Experimental section). Some compounds were notably difficult to obtain, however. The compound $Pt(CH_2SCH_3)_2$(dmpe), for example, has only been identified by ^{31}P NMR spectroscopy. In addition, although *cis*-$Pt(CH_2SCH_3)_2(PMe_3)_2$ could not be obtained in satisfactory quantities by direct routes, it was attainable by ligand metathesis on *cis*-$Pt(CH_2SCH_3)_2(PPh_3)_2$. The phosphite derivative, *cis*-$Pt(CH_2SCH_3)_2\{P(OMe)_3\}_2$, was accessible by similar displacement of PPh_3 but could not be isolated in pure form (see below).

The nature of the organomagnesium reagent formed by reaction of $ClCH_2SCH_3$ with magnesium metal is of interest. The exothermic reaction proceeds after an induction period with production of a fine grey precipitate. At this stage, titration indicated a yield of MgC approaching 100%. Addition of 1,4-dioxane to the filtered solution resulted in no additional precipitation. A likely explanation is that the Schlenk equilibrium favours formation of a dialkylmagnesium derivative, $[Mg(CH_2SCH_3)_2]_n$ (with deposition of equimolar amounts of magnesium chloride). In the absence of rigorous characterisation, however, we have continued to refer to this organomagnesium precursor as '$Mg(CH_2SCH_3)Cl$'.

These dialkylbis(phosphine)platinum(II) complexes have varied solubility characteristics and usually were obtained as viscous oils prior to recrystallisation. Purification by this route proved extremely difficult in some cases. The identities of all of this series of compounds have been confirmed by conclusive ^1H, ^{13}C and ^{31}P NMR measurements, and by a molecular structure determination on one of them, *cis*-$Pt(CH_2SPh)_2(PPh_3)_2$ (see below). Satisfactory elemental analyses (see Experimental section) were obtained for all except *cis*-$Pt(CH_2SPh)_2(PMe_2Ph)_2$, $Pt[CH_2S(C_6H_4Me$-*p*)$]_2$(dmpe), $Pt[CH_2S(C_6H_4Me$-*p*)$]_2$(dppe), *cis*-$Pt[CH_2S(C_6H_4Me$-*p*)$]_2(PMe_3)_2$ and *cis*-$Pt(CH_2SCH_3)_2(PMe_3)_2$, which are characterised by their spectra alone.

Synthesis of dialkylplatinum(II) complexes of this type with chelating N-donor complexes is well developed. Typically, this has been achieved by displacement of the diene[3*a*,*c*,14] in precursors such as PtR_2(nbd) and PtR_2(cod) or by substitution of sulfur-donor ligands such as dimethyl sulfide and dimethyl sulfoxide (dmso).[3*a*,*c*,*e*,15]

Attempts were made to react the oligomer formed by the reaction of $PtCl_2$(cod) and $Li(CH_2SPh)$·tmen with 2,2′-bipyridyl (bipy) to form mononuclear N-donor complexes in the same way as for tertiary phosphines. Co-reaction of the precursors together in toluene at 50 °C resulted in no reaction. The mixture of oligomer and 2,2′-bipyridyl was subjected also to UV irradiation for several days without any indication of success.

Direct transalkylation of $PtBr_2$(bipy) with both $Li(CH_2SPh)$·tmen and $Mg(CH_2SPh)Cl$ was, additionally, explored. Dark red solutions, a characteristic colour for PtR_2(bipy), formed initially in both cases but were short-lived. In the first case, reaction with the Li reagent resulted in formation of a dark brown precipitate that was too insoluble to characterise. The reaction between $PtBr_2$(bipy) and $Mg(CH_2SPh)Cl$ gave a red solution but the colour faded as the solvent was removed *in vacuo*, leaving a pale solid. Treatment of this solid with a solution of triphenylphosphine and analysis of the product by ^{31}P NMR spectroscopy indicated a phosphine–platinum species with characteristics (δ 27.59, $^1J_{Pt-P}$ = 3099 Hz) consistent with *trans*-$PtBr(CH_2SCH_3)(PPh_3)_2$.

(*b*) Spectroscopic studies. ^1H *NMR*: cis-$Pt(CH_2SR)_2L^1_2$. The ^1H NMR spectroscopic data for the series of complexes, *cis*-$Pt(CH_2SR)_2L^1_2$, are presented in Table 1. The most characteristic feature in the ^1H NMR spectra of these alkylplatinum complexes is the resonance due to hydrogens of the ligating methylene group. These exhibit a distinctive splitting pattern due to spin–spin coupling ($^2J_{Pt-H}$) to 34% abundant ^{195}Pt as well as coupling to *cis* and *trans* ^{31}P ($^3J_{P-H}$). The former results in the characteristic impression of a 1 : 4 : 1 pattern of platinum satellites flanking the resonances not coupled to platinum. Each

Table 1 The ^{1}H NMR spectroscopic characteristics of bis(thiaalkyl)platinum(II) complexes with P-donor ligands[a]

	δ(^{1}H)[b]			
	Hydrocarbyl ligand			
Complex	Pt–CH_2	S–CH_3	Aromatic; PhCH_3-4	Ancillary ligand
cis-$Pt(CH_2SPh)_2(PPh_3)_2$	2.66 (**70.9**)	—	7.21 (dd, H^2, H^6), 6.98–7.05 (m,[c] H^3, H^5), 6.85 (m, H^4)	7.44 (m, H^2, H^6), 7.10 (m, H^3, H^5), 6.90–7.05 (m,[c] H^4)
$Pt(CH_2SPh)_2(dppe)$[d]	3.40 (**75.6**)	—	7.31 (d, H^2, H^6), 6.98–7.10 (m,[c] H^3, H^5), 6.78 (t, H^4)	7.66 (m,[e] H^2, H^6), 7.02 (m, H^3, H^5), 6.93 (m, H^4), 2.23 (m, P–CH_2)
$Pt(CH_2SPh)_2(dmpe)$	2.77 (**72.8**)	—	7.35 (dd, H^2, H^6), 7.22 (m, H^3, H^5), 7.00 (t, H^4)	1.62 (d, P–CH_3, **23.1**, J_{P-H} = 9.6), 1.67[f] (d, P–CH_2)
$Pt(CH_2SPh)_2(dcpe)$[d]	3.42 (**70.6**)	—	7.63 (dd, H^2, H^6), 7.08 (m, H^3, H^5), 6.86 (t, H^4)	2.0–2.4 (m,[e] P–CH_2), 1.11–1.67 (m,[e] P–CH, CH_2)
$Pt(CH_2SPh)_2(dppm)$[d]	3.11 (**75.4**)[g]	—	7.26 (dd, H^2, H^6), 7.17 (t, H^3, H^5), 6.96 (t, H^4)	7.69 (m, H^2, H^6), 7.38 (m, H^3, H^5), 7.11 (m,[c] H^4), 4.28 (t, P–CH_2–P, J_{P-H} = 9.4)
cis-$Pt(CH_2SPh)_2(PMe_3)_2$	2.64 (**69.3**)	—	7.32 (d,[e] H^2, H^6), 7.21 (t,[e] H^3, H^5), 7.00 (t,[e] H^4)	1.58 (m, P–CH_3, **21.1**, J_{P-H} = 8.6)
cis-$Pt(CH_2SPh)_2(PMe_2Ph)_2$	2.78 (**70.6**)	—	7.35 (m,[c] H^2, H^6), 7.21 (t, H^3, H^5), 7.00 (t, H^4)	7.49 (m, H^2, H^6), 7.35 (m,[c] H^3, H^5), 7.18[c] (H^4), 1.52 (d, PCH_3, **21.1**, J_{P-H} = 7.9)
cis-$Pt(CH_2SPh)_2(PMePh_2)_2$	2.55 (**70.3**)	—	7.20–7.32 (m,[c] H^2, H^6), 7.03–7.11 (m,[c] H^3, H^5), 6.90 (tt, H^4)	7.42 (td, H^2, H^6), 7.18–7.32 (m,[c] H^3, H^5), 7.03–7.11 (m,[c] H^4), 1.77 (m, P–CH_3, **21.8**)
cis-$Pt[CH_2S(C_6H_4Me$-*p*$)]_2(PPh_3)_2$	2.69 (**70.6**)	—	6.85 (s,[h] H^2, H^3, H^5, H^6), 2.20 (CH_3)	7.45 (t, H^2, H^6), 7.09 (m, H^3, H^4, H^6)
cis-$Pt[CH_2S(C_6H_4Me$-*p*$)]_2(dppe)$	2.89 (**75.4**)	—	7.06 (d, H^2, H^6), 6.92 (d, H^3, H^5), 2.22 (CH_3, J_{H-H} = 8.08)	7.68–7.75 (m, H^2, H^6), 7.39–7.42 (m, H^3, H^4, H^5), 2.20 (m,[c] P–CH_2)
$Pt[CH_2S(C_6H_4Me$-*p*$)]_2(dmpe)$	2.76 (**70.9**)	—	7.25 (d, H^2, H^6), 7.04 (d, H^3, H^5), 2.28 (CH_3, J_{H-H} = 7.75)	1.60 (P–CH_3, **22.8**, J_{P-H} = 9.56), 1.65[c] (P–CH_2)
cis-$Pt[CH_2S(C_6H_4Me$-*p*$)]_2(PMe_3)_2$	2.64 (**69.3**)	—	7.21 (d, H^2, H^6), 7.02 (d, H^3, H^5), 2.27 (CH_3, J_{H-H} = 7.92)	1.56 (P–CH_3, **21.1**, J_{P-H} = 7.92)
cis-$Pt[CH_2S(C_6H_4Me$-*p*$)]_2(PMe_2Ph)_2$	2.77 (**69.9**)	—	7.22 (d, H^2, H^6), 7.02 (d, H^3, H^5), 2.26 (CH_3, J_{H-H} = 7.75)	7.46–7.52 (m, H^2, H^6), 7.32–7.34 (m, H^3, H^4, H^6), 1.50 (d, P–CH_3, **21.1**, J_{P-H} = 7.92)
cis-$Pt(CH_2SMe)_2(PPh_3)_2$	2.34 (**70.0**)	1.66	—	7.37–7.46 (H^2, H^6), 7.10–7.27 (H^3, H^4, H^5)
$Pt(CH_2SMe)_2(dppe)$	2.60 (**73.6**)	1.95	—	7.41–7.44 (H^3, H^4, H^5), 7.69–7.75 (H^2, H^6), 2.15 (m, P–CH_2)
cis-$Pt(CH_2SMe)_2(PMe_2Ph)_2$[d]	2.93 (**70.3**)	2.17	—	7.55–7.65[e] (H^2, H^6), 7.05–7.15 (H^3, H^4, H^5), 1.25 (d, P–CH_3, J_{P-H} = 12.9)
cis-$Pt(CH_2SMe)_2(PMePh_2)_2$	2.25 (**69.3**)	1.82	—	7.38–7.45 (m, H^2, H^6), 7.21–7.34 (m, H^3, H^4, H^5), 1.73 (d, P–CH_3, **20.5**, J_{P-H} = 7.6)
cis-$Pt(CH_2SMe)_2(PMe_3)_2$	2.35 (**68.3**)	2.11	—	1.53 (d, P–CH_3, **20.8**, J_{P-H} = 7.6)
$[Pt(CH_2SCH_3)(\mu\text{-}CH_2SCH_3)(PPh_3)]_2$[i]	2.39, 3.06[j] ($^2J_{H-H}$ = 5.9)[k]	1.49[j] (**27.1**)	—	7.33–7.41 (m, H^3, H^4, H^5), 7.81–7.89 (m, H^2, H^6)
	1.85, 1.90[l] ($^2J_{H-H}$ = 5.1)	1.64[l]		

[a] Recorded in $CDCl_3$ at 270 MHz, except where noted; δ relative to $SiMe_4$. [b] J_{Pt-H}/Hz values in bold, other *J* values in Hz. [c] Obscured. [d] Recorded in C_6D_6. [e] Broad. [f] Resolved at 500 MHz. [g] ^{195}Pt satellites broad. [h] Isochronous. [i] At 233 K. [j] μ-CH_2SCH_3. [k] $^2J_{H-H} \approx {}^3J_{P-H}$. [l] Pendant CH_2SCH_3.

element of this pattern appears as an apparent quartet in most cases (though sometimes as a triplet) due to $^3J_{P-H}$. These characteristic, complex spin systems have been discussed in detail elsewhere.[16] The values of $^2J_{Pt-H}$ in these compounds range from 68.3 to 75.6 Hz with an average close to 70 Hz. This is slightly lower (by 5–11 Hz) than analogous, bis(silaneophyl)platinum(II) complexes [silaneophyl = phenyl(dimethyl)silylmethyl].[3b]

The substituent methyl group in *cis*-$Pt[CH_2S(C_6H_4Me$-*p*$)]_2L^1_2$ generates a single resonance in a narrow chemical shift range (δ 2.20–2.28) for differing ancillary ligands, suggesting minimal electronic effect at this distance. The methyl protons of the 2-thiapropyl complexes exhibit a wider range of chemical shifts (δ 1.66–2.17) and appear as singlets with no detectable $^4J_{Pt-H}$.

^{1}H *NMR*: $[Pt(CH_2SCH_3)(\mu\text{-}CH_2SCH_3)(PPh_3)]_2$. The dimetallic thiaalkyl-bridged compound, $[Pt(CH_2SCH_3)(\mu\text{-}CH_2SCH_3)(PPh_3)]_2$, also has ^{1}H NMR spectroscopic data displayed in Table 1. At ambient temperature, the methylene groups exhibit broad signals (δ 1.9–3.2). Cooling to 223 K results in resolution of fine structure; ^{195}Pt satellites emerge for some of the signals. [The resonances were too weak for the verification of signal attributions by two-dimensional correlation spectroscopy (COSY) experiments.] Assignments are required for the two types of hydrogen environments on the bridging thiaalkyl group as well as the diastereotopic protons of the methylene group in the terminal ligand. Two doublets are observed (δ 1.85 and 1.90) which might represent the mutually coupled diastereotopic protons of the pendant alkyl group ($^2J_{H-H}$ = 5.1 Hz). If this attribution was correct, the signals might be expected to exhibit second-order characteristics. Further downfield, binomial triplets with broad, featureless Pt satellites (δ 2.39 and 3.06) may be assigned, more safely, to the hydrogens of the thiaalkyl bridges. These are chemically distinct and mutually coupled. Their apparent triplet pattern may be ascribed to coupling with *trans* ^{31}P, where $^3J_{P-H} \approx {}^2J_{H-H}$ (5.9 Hz). The methyl groups generate a singlet and a 1:4:1 pattern, as a result of coupling to the sulfur-co-ordinated platinum ($^3J_{Pt-H}$ = 27.1 Hz). The dynamic process most plausibly responsible for the broadening, is inversion at co-ordinated sulfur. Such phenomena have been investigated in some detail,[17] notably by Abel *et al.*[17a] A mechanism involving π co-ordination of the lone-pair in a dπ–pπ transition state has been proposed to operate. There is no detachment of the sulfur atom and $^3J_{Pt-H}$ (associated with the methyl substituents of the bridge) would be retained throughout, consistent with our observations. As the sulfur alternates co-ordination *via* its donor pairs, rotation about the methylene carbon–sulfur bond exchanges the methylene hydrogen environments; those *syn* to methyl become *syn* to an unco-ordinated electron-pair (and *vice versa*).

The operation of such a process provides a more likely explanation for the appearance of the ^{1}H NMR spectrum at 223 K. If two ring conformers exist at low temperature, the two signals (δ 1.85 and 1.90), represent the pendant methylene protons in each conformer: one, where the bridging methyl groups are orientated to the same side of the ring (*syn* as in the solid state; see below) and a second in which they are directed to opposite sides of the ring (*anti*). This is more consistent with the first-order patterns for these two signals. The signal at δ 2.48 may be assigned to bridge methylene hydrogens of this second conformer. The remaining methylene signal, it must be concluded, is obscured. Clearly, there is no site-exchange between bridging and pendant thiaalkyl groups under these conditions. At higher temperatures (⩾308 K), the bridging methylene environments showed further broadening and shift-convergence but coalescence was not attained below operable conditions in $CDCl_3$.

^{31}P-{^1H} *NMR*. The ^{31}P-{^1H} NMR spectroscopic data for the complexes *cis*-$Pt(CH_2SR)_2L^1{}_2$ appear in Table 2. The magnitude of the coupling constant $^1J_{Pt-P}$ is perhaps one of the most useful pieces of information when establishing the identity and structural geometry of a complex of this type. The magnitude of this parameter is sensitive to (and indicative of) the nature of the ligand *trans* to phosphorus. The values of $^1J_{Pt-P}$ (1910–2100 Hz) in these complexes are typical of similar *cis*-dialkylbis(phosphine) compounds, where phosphorus is *trans* to a hydrocarbyl ligand. In this respect, these 2-thiaalkyl species are comparable to 2-silaalkyl complexes, with $^1J_{Pt-P}$ *ca.* 200–300 Hz larger than purely hydrocarbyl (*e.g.* neopentyl and neophyl) analogues (see below). The exception is $Pt(CH_2SR)_2$(dppm), which exhibits a notably small $^1J_{Pt-P}$ (1692 Hz). As has been noted, derivatives of this bidentate phosphine characteristically show unusually low values for $^1J_{Pt-P}$, ascribable to the angular strain inherent in the four-membered ring, which reduces the s character in the Pt−P bonds.[18]

Table 2 The ^{31}P NMR spectroscopic data for (2-thiaalkyl)platinum(II) complexes with P-donor ligands[a]

Complex	δ	$^1J_{Pt-P}$/Hz
trans-$PtCl(CH_2SPh)(PPh_3)_2$	27.24	3055
trans-$PtBr(CH_2SPh)(PPh_3)_2$	27.07	3025
trans-$PtI(CH_2SPh)(PPh_3)_2$	24.62	2991
trans-$PtCl(CH_2SCH_3)(PPh_3)_2$	28.34	3123
trans-$PtBr(CH_2SCH_3)(PPh_3)_2$	27.59	3099
cis-$Pt(CH_2SPh)_2(PPh_3)_2$	25.05	2113
cis-$Pt(CH_2SPh)_2(PMePh_2)_2$	4.71	2072
cis-$Pt(CH_2SPh)_2(PMe_2Ph)_2$	−12.87	2055
cis-$Pt(CH_2SPh)_2(PMe_3)_2$	−24.56	1994
$Pt(CH_2SPh)_2$(dppe)	43.97	2014
$Pt(CH_2SPh)_2$(dmpe)	24.77	1974
$Pt(CH_2SPh)_2$(dcpe)[b]	59.75	2041
$Pt(CH_2SPh)_2$(dppm)	−37.11	1692
cis-$Pt[CH_2S(C_6H_4Me\text{-}p)]_2(PPh_3)_2$	25.08	2102
cis-$Pt[CH_2S(C_6H_4Me\text{-}p)]_2(PMe_3)_2$	−24.62	1987
cis-$Pt[CH_2S(C_6H_4Me\text{-}p)]_2(PPhMe_2)_2$	−12.87	2045
$Pt[CH_2S(C_6H_4Me\text{-}p)]_2$(dppe)	43.78	2004
$Pt[CH_2S(C_6H_4Me\text{-}p)]_2$(dmpe)	24.68	1967
cis-$Pt(CH_2SCH_3)_2(PPh_3)_2$	25.49	2008
cis-$Pt(CH_2SCH_3)_2(PMePh_2)_2$	4.87	1994
cis-$Pt(CH_2SCH_3)_2(PMe_2Ph)_2$[b]	−13.18	1970
cis-$Pt(CH_2SCH_3)_2(PMe_3)_2$	−24.71	1912
$Pt(CH_2SCH_3)_2$(dppe)	43.62	1929
$Pt(CH_2SCH_3)_2$(dmpe)	23.87	1885
$[Pt(CH_2SCH_3)(\mu\text{-}CH_2SCH_3)(PPh_3)]_2$	24.34	2258

[a] Recorded in $CDCl_3$ unless otherwise noted; δ relative to 85% H_3PO_4–D_2O. [b] Recorded in C_6D_6.

A relative *trans* influence series, including thiaalkyl and related ligands, may be established by comparison of the coupling constants for alkyl complexes with the same phosphine. To maximise the scope of the comparison, the phosphines featured included dppe, PPh_3, $PMePh_2$, PEt_3 and PMe_3 (Table 3). *trans* Influence increases broadly in the order: $CH_2SPh < CH_2SC_6H_4Me < CH_2SiMePh_2$[19] $< CH_2SiMe_2C{\equiv}CBu^t$[20] $< CH_2SiMe_2Ph$[3b] $\leqslant CH_2SiMe_2CH{=}CH_2$[3f] $< CH_2SiMe_3$[3a] $\leqslant CH_2SMe < CH_2GeMe_3$[5] $< CH_2SnMe_3$[5] $(< CH_3) < CH_2CMe_2Ph$[20] $< CH_2CMe_3$.[21] The $^1J_{Pt-C}$ value varies in the opposite sense (see below). The compound $[Pt(CH_2SCH_3)(\mu\text{-}CH_2SCH_3)(PPh_3)]_2$ exhibits a larger $^1J_{Pt-P}$ (2258 Hz), suggesting that the thiaalkyl ligand exerts a weaker *trans* influence (*via* its ligating carbon) from a bridging position than from a terminal site. The extent of platinum 6s contribution to this bond, however, might be altered by S (rather than P) co-ordination *cis* to the phosphine.

^{13}C-{^1H} *NMR*. The ^{13}C-{^1H} NMR data for complexes *cis*-$Pt(CH_2SR)_2L^1{}_2$ are listed in Table 4. The platinum-bound methylene carbon atoms of the thiaalkyl ligands exhibit a predictable splitting pattern. For the aromatic-substituted thiaalkyl complexes, $^1J_{Pt-C}$ ranges from 577 to 640 Hz, with the exception of $Pt(CH_2SPh)_2$(dppm). Its larger value of $^1J_{Pt-C}$ (649 Hz) is in concert with the lower $^1J_{Pt-P}$ in this instance (see above). The bis(2-thiapropyl)platinum complexes, *cis*-$Pt(CH_2SCH_3)_2L^1{}_2$, have higher values for $^1J_{Pt-C}$ (598–651 Hz), parallel with their stronger *trans* influence.

Bent's theory of isovalent hydridisation[22] has been proposed as one explanation for variations in $^1J_{Pt-C}$ for related dialkylplatinum(II) compounds.[3–5] This argues that carbon atoms direct more 2s orbital character into bonds with more electropositive substituents. Thus, the presence of a more electronegative substituent on the co-ordinated methylene group should result in more carbon 2s orbital contribution to the metal–carbon bond. The magnitudes of $^1J_{Pt-C}$ in these complexes reflect this, with consistently larger values than comparable silaalkyl complexes with the same P donor,[3a,b,f] commensurate with the higher electronegativity of sulfur; the additional methyl substituents on silicon, presumably, accentuate this electronic effect. Representative comparisons are $Pt(CH_2SPh)$(dppe) ($^1J_{Pt-C} = 629$ Hz) with $Pt(CH_2SiMe_2Ph)$(dppe) ($^1J_{Pt-C} = 549$ Hz)[3b] and $Pt(CH_2SMe)$(dppe) ($^1J_{Pt-C} = 646$ Hz) with $Pt(CH_2SiMe_3)$(dppe) ($^1J_{Pt-C} = 551$ Hz).[3a]

Fewer $^1J_{Pt-C}$ values are available, on the other hand, for corresponding neopentyl and neophyl complexes. Those which have been reported generally do reflect larger $^1J_{Pt-C}$ for the purely hydrocarbyl ligands (concomitant also with their significantly greater *trans* influence). Among analogous P-donor derivatives, for example, $Pt(CH_2CMe_2Ph)_2$(dppe) has a $^1J_{Pt-C}$ value (717 Hz[23]), appreciably greater than corresponding complexes of any of the 2-thiaalkyl ligands reported here ($^1J_{Pt-C} = 623$–646 Hz).

Table 3 Collected values of $^1J_{Pt-P}$/Hz for *cis*-$PtR_2L^1{}_2$*

	R											
$L^1{}_2$	CH_2SPh	$CH_2SC_6H_4Me$	$CH_2SiMePh_2$	$CH_2SiMe_2CCBu^t$	CH_2SiMe_2Ph	$CH_2SiMe_2C_2H_3$	CH_2SiMe_3	CH_2SMe	CH_2GeMe_3	CH_2SnMe_3	CH_2CMe_2Ph	CH_2CMe_3
dppe	2014	2004	—	—	1954	1956	1938	1929	—	—	1584	—
$PMePh_2$	2072	—	2056	2051	2029	2020	1998	1994	1958	—	—	—
PPh_3	2113	2102	2060	2045	2034	2029	2005	2008	1968	1883	1668	—
PEt_3	—	—	—	—	2016	2014	1987	—	—	—	1678	1638
PMe_3	1994	1987	2023	1994	1987	1976	1945	1912	—	—	—	—

* Data from this work and from refs. cited in the text.

Table 4 The ^{13}C NMR spectroscopic data for bis(2-thiaalkyl)platinum(II) complexes withn P-donor ligands[a]

	δ(^{13}C)[b]			
	Hydrocarbyl ligand			
Complex	Pt−CH$_2$	S−CH$_3$	Aromatic; PhCH$_3$-4	Ancillary ligand
cis-Pt(CH$_2$SPh)$_2$(PPh$_3$)$_2$	21.06 [**634.8**, $J_{\mathrm{C-P}\ (trans)} = 96.5$, $J_{\mathrm{C-P}\ (cis)} = 7.6$]	—	145.34 (C^1, **118.4**), 127.46 (C^2, C^6), 125.27 (C^3, C^5), 122.48 (C^4)	131.62 (C^1, **19.5**, $J_{\mathrm{C-P}} = 50.0$), 134.45 (C^2, C^6, **14.7**), 127.55 (C^3, C^5), 129.54 (C^4)
Pt(CH$_2$SPh)$_2$(dppe)	17.45 [**628.9**, $J_{\mathrm{C-P}\ (trans)} = 98.6$, $J_{\mathrm{C-P}\ (cis)} = 5.2$]	—	146.85 (C^1, **107.5**), 127.81 (C^2, C^6), 125.64 (C^3, C^5), 122.70 (C^4)	131.00 (C^1, **24.9**, $J_{\mathrm{P-C}} = 45.4$), 133.38 (C^2, C^6, **17.9**, $J_{\mathrm{P-C}} = 11.1$), 128.54 (C^3, C^5, $J_{\mathrm{C-P}} = 9.9$), 130.63 (C^4), 28.87 (dd, C^7, C^8)
Pt(CH$_2$SPh)$_2$(dmpe)	14.72 [**585.4**, $J_{\mathrm{C-P}\ (trans)} = 100.7$, $J_{\mathrm{C-P}\ (cis)} = 6.1$]	—	146.80 (C^1, **103.1**), 128.07 (C^2, C^6), 124.69 (C^3, C^5), 122.79 (C^4)	28.84 (P−CH$_2$, $^1J_{\mathrm{C-P}} = 34.2$, $^2J_{\mathrm{C-P}} = 13.4$), 12.38 (P−CH$_3$, **34.0**, $J_{\mathrm{C-P}} = 28.1$)
Pt(CH$_2$SPh)$_2$(dcpe)	13.90 [**584.1**, $J_{\mathrm{C-P}\ (trans)} = 96.4$, $J_{\mathrm{C-P}\ (cis)}$][c]	—	147.32 (C^1, **107.4**), 127.87 (C^2, C^6), 124.96 (C^3, C^5), 122.36 (C^4)	28.66 (C^1, $J_{\mathrm{P-C}} = 30.5$), 34.51 (C^2, C^6, $J_{\mathrm{P-C}} = 25.6$), 25.48–27.18 (C^3, C^4, C^5), 23.63 (P−CH$_2$)
Pt(CH$_2$SPh)$_2$(dppm)[d]	15.73 [**648.9**, $J_{\mathrm{C-P}\ (trans)} = 107.5$, $J_{\mathrm{C-P}\ (cis)} = 7.4$]	—	146.58 (C^1, C^1, **55.1**),[e] 127.80 (C^2, C^6), 124.98 (C^3, C^5), 122.68 (C^4)	132.89 (C^2, C^6), 128.43 (C^3, C^5), 130.55 (C^4), 46.54 (t, C^7, $J_{\mathrm{P-C}} = 26.9$)
cis-Pt(CH$_2$SPh)$_2$(PMe$_3$)$_2$	17.54 [**577.4**, $J_{\mathrm{C-P}\ (trans)} = 102$, $J_{\mathrm{C-P}\ (cis)} = 9.2$]	—	145.79 (C^1, **109.9**), 128.12 (C^2, C^6), 124.66 (C^3, C^5), 122.90 (C^4)	15.72 (P−CH$_3$)
cis-Pt(CH$_2$SPh)$_2$(PMe$_2$Ph)$_2$	18.64 [**592.1**, $J_{\mathrm{C-P}\ (trans)} = 101.4$, $J_{\mathrm{C-P}\ (cis)} = 9.7$]	—	146.49 (C^1, **112.3**), 128.88 (C^2, C^6), 125.52 (C^3, C^5), 123.63 (C^4)	137.07 (C^1, $J_{\mathrm{C-P}} = 46.4$), 131.82 (C^2, C^6), 129.02 (C^3, C^5), 130.62 (C^4), 14.13 (PCH$_3$)
cis-Pt(CH$_2$SPh)$_2$(PMePh$_2$)$_2$	19.88 [**612.8**, $J_{\mathrm{C-P}\ (trans)} = 98.9$, $J_{\mathrm{C-P}\ (cis)} = 8.6$]	—	145.52 (C^1, **114.7**), 127.89[c] (C^2, C^6), 124.94 (C^3, C^5), 122.61 (C^4)	133.71 (C$_1$, $J_{\mathrm{C-P}} = 48.8$), 132.58 (C^2, C^6), 127.88[c] C^3, C^5), 129.65 (C^4), 12.73 (P−CH$_3$)
cis-Pt[CH$_2$S(C$_6$H$_4$Me-*p*)]$_2$-(PPh$_3$)$_2$	22.18 [**639.6**, $J_{\mathrm{C-P}\ (trans)} = 97.7$, $J_{\mathrm{C-P}\ (cis)} = 7.3$]	—	141.67 (C^1, **114.8**), 132.11 (C^4), 20.70 (CH$_3$), 128.38 (C^2, C^6), 125.84 (C^3, C^5)	131.79 (C^1, **18.4**, $J_{\mathrm{P-C}} = 48.8$), 134.49 (C^2, C^6, **14.6**), 127.51 (C^3, C^5), 129.49 (C^4)
cis-Pt[CH$_2$S(C$_6$H$_4$Me-*p*)]$_2$-(PMe$_3$)$_2$	18.31 [**581.8**, $J_{\mathrm{C-P}\ (trans)} = 101.8$, $J_{\mathrm{C-P}\ (cis)} = 9.0$]	—	142.31 (C^1, **107.2**), 132.59 (C^4), 20.83 (CH$_3$), 129.02 (C^2, C^6), 125.08 (C^3, C^5)	15.89 (P−CH$_3$, **25.0**, $J_{\mathrm{P-C}} = 32.1$)
cis-Pt[CH$_2$S(C$_6$H$_4$Me-*p*)]$_2$-(PMe$_2$Ph)$_2$	18.51 [**593.3**, $J_{\mathrm{C-P}\ (trans)} = 101.3$, $J_{\mathrm{C-P}\ (cis)} = 8.5$]	—	143.09 (C^1, **112.3**), 132.44 (C^4), 20.74 (CH$_3$), 128.90 (C^2, C^6), 125.02 (C^3, C^5)	136.48 (C^1, $J_{\mathrm{P-C}} = 46.4$), 131.05 (C^2, C^6), 128.21 (C^3, C^5), 129.76 (C^4)
Pt[CH$_2$S(C$_6$H$_4$Me-*p*)]$_2$-(dppe)	17.85 [**623.2**, $J_{\mathrm{C-P}\ (trans)} = 97.7$, $J_{\mathrm{C-P}\ (cis)} = 4.9$]	—	143.05 (C^1, **107.5**), 132.15 (C^4), 20.74 (CH$_3$), 128.39 (C^2, C^6), 125.48 (C^3, C^5)	130.84 (C^1, **24.4**, $J_{\mathrm{P-C}} = 41.5$), 133.25 (C^2, C^6, **17.0**), 128.56 (C^3, C^5), 130.53 (C^4)
Pt[CH$_2$S(C$_6$H$_4$Me-*p*)]$_2$-(dmpe)	15.19 [**583.6**, $J_{\mathrm{C-P}\ (trans)} = 100.1$, $J_{\mathrm{C-P}\ (cis)} = 4.9$]	—	143.18 (C^1, **103.8**), 132.33 (C^4), 20.78 (CH$_3$), 128.90 (C^2, C^3), 124.84 (C^3, C^5)	12.38 (P−CH$_3$, **34.0**, $J_{\mathrm{P-C}} = 28.1$), 28.81 (P−CH$_2$, $^1J_{\mathrm{P-C}} = 34.2$, $^2J_{\mathrm{P-C}} = 14.7$)
cis-Pt(CH$_2$SMe)$_2$(PPh$_3$)$_2$	26.19 [**651.1**, $J_{\mathrm{C-P}\ (trans)} = 97.7$, $J_{\mathrm{C-P}\ (cis)} = 7.3$]	22.14 [**122.1**, $J_{\mathrm{C-P}\ (trans)} = 4.9$]	—	132.19 (C^1, **17.1**, $J_{\mathrm{C-P}} = 47.6$), 134.56 (C^2, C^6), 127.39 (C^3, C^5), 129.36 (C^4)
Pt(CH$_2$SMe)$_2$(dppe)	23.04 [**645.8**, $J_{\mathrm{C-P}\ (trans)} = 100.1$]	23.65 [**109.9**, $J_{\mathrm{C-P}\ (trans)} = 9.8$, $J_{\mathrm{C-P}\ (cis)} = 6.1$]	—	131.27 (C^1, **25.0**, $J_{\mathrm{C-P}} = 44.0$), 133.28 (C^2, C^6, **8.0**, $J_{\mathrm{C-P}} = 12.2$), 128.34 (C^3, C^5, $J_{\mathrm{C-P}} = 9.8$), 130.39 (C^4), 28.62 (dd, P−CH$_2$)
cis-Pt(CH$_2$SMe)$_2$-(PMePh$_2$)$_2$	26.03 [**629.9**, $J_{\mathrm{C-P}\ (trans)} = 100.1$, $J_{\mathrm{C-P}\ (cis)} = 8.6$]	22.66 [**123.3**, $J_{\mathrm{C-P}\ (trans)} = 4.9$]	—	134.37 (C^1, $J_{\mathrm{C-P}} = 47.6$), 132.65 (C^2, C^6), 127.71 (C^3, C^5), 129.45 (C^4), 12.82 (d, P−CH$_2$)
cis-Pt(CH$_2$SMe)$_2$(PMe$_3$)$_2$	24.14 [**598.2**, $J_{\mathrm{C-P}\ (trans)} = 103.8$, $J_{\mathrm{C-P}\ (cis)} = 8.6$]	23.24 [**118.5**, $J_{\mathrm{C-P}\ (trans)} = 4.8$]	—	15.83 (P−CH$_3$, $J_{\mathrm{C-P}} = 31.8$)
[Pt(CH$_2$SMe)(μ-CH$_2$SMe)-(PPh$_3$)]$_2$	22.85 [μ-CH$_2$, **671**, $J_{\mathrm{C-P}\ (trans)} = 102$], 14.75 [CH$_2$, **719**, $J_{\mathrm{C-P}\ (cis)} = 3.7$]	26.23 [**124**, $J_{\mathrm{C-P}\ (trans)} = 8.6$], 22.09 (**140**)	—	130.95 (C^1, $J_{\mathrm{C-P}} = 45.1$), 134.66 (C^{2,6}, $J_{\mathrm{C-P}} = 11.0$), 127.78 (C^{3,5}, $J_{\mathrm{C-P}} = 9.8$), 129.74 (C^4)

[a] Recorded in CDCl$_3$, except where noted; δ relative to SiMe$_4$. [b] $J_{\mathrm{Pt-C}}$ values in bold, other J values in Hz. [c] Not resolved. [d] Recorded in C$_6$D$_6$. [e] Obscured.

Irrespective of speculation as to the electronic (or steric) origin of the variations in $^1J_{\mathrm{Pt-C}}$, however, is the more fundamental question of whether this parameter (and, by corollary, $^1J_{\mathrm{Pt-P}}$) is a reliable indicator of metal–ligand bond strength. Indeed, the attribution of relative *trans* influence (see above), based on $^1J_{\mathrm{Pt-P}}$, embodies this very assumption. We have been able, recently, to provide evidence in support of this view. Thermochemical measurement of relative Pt−C bond enthalpies for *trans*-PtCl(CH$_2$CMe$_3$)(PMe$_3$)$_2$ ($^1J_{\mathrm{Pt-C}} = 749$ Hz) and *trans*-PtCl(CH$_2$SiMe$_3$)(PMe$_3$)$_2$ ($^1J_{\mathrm{Pt-C}} = 651$ Hz) reveal that the Pt−CH$_2$CMe$_3$ bond is stronger, by 14 ± 6 kJ mol^{-1}, than Pt−CH$_2$SiMe$_3$.[24] We assume that the variations in $^1J_{\mathrm{Pt-C}}$, discussed here, are a similar reflection of Pt−C bond strength.

Substantial $^3J_{\mathrm{Pt-C}}$ values (of the order of 100 Hz) are also

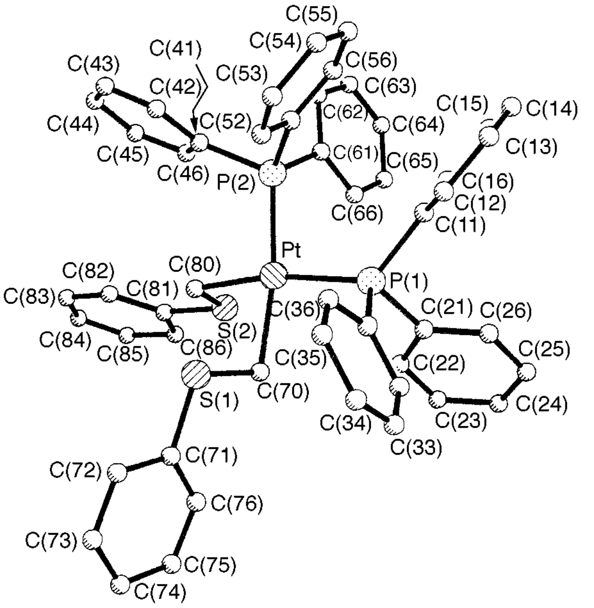


Fig. 1 Molecular structure of *cis*-$Pt(CH_2SPh)_2(PPh_3)_2$

Table 5 Selected bond lengths (Å) and angles (°) for *cis*-$Pt(CH_2SPh)_2(PPh_3)_2\cdot 0.5CH_2Cl_2$

Pt–P(1)	2.318(2)	Pt–P(2)	2.300(1)
Pt–C(70)	2.112(4)	Pt–C(80)	2.084(7)
S(1)–C(70)	1.791(5)	S(1)–C(71)	1.761(6)
S(2)–C(80)	1.794(6)	S(2)–C(81)	1.770(8)
P(1)–Pt–P(2)	99.8(1)	P(1)–Pt–C(70)	87.3(2)
P(2)–Pt–C(80)	90.3(1)	C(70)–Pt–C(80)	83.2(2)
Pt–C(70)–S(1)	105.5(3)	Pt–C(80)–S(2)	104.0(3)
C(70)–S(1)–C(71)	105.6(3)	C(80)–S(2)–C(81)	105.7(4)

measurable from the spectrum. The quaternary C^1 carbon of the aryl-substituted thiaalkyl ligands (though of low intensity, with attendant ^{195}Pt satellites) can be identified unequivocally as the lowest-field resonance in the ^{13}C spectra of these compounds. The $^3J_{Pt-C}$ value ranges from 103 to 118 Hz apart from the expectedly low value (55 Hz) for $Pt(CH_2SPh)_2(dppm)$. The methyl carbon of the 2-thiapropyl complexes also exhibits a large $^3J_{Pt-C}$ in the range 110–123 Hz, slightly larger than the aryl-substituted coupling on average. Long range coupling to ^{31}P *trans* to the alkyl group is also measurable in these cases ($^4J_{P-C} \approx 5$–10 Hz).

Infrared and mass spectrometry. Infrared data for each of these complexes appear in the Experimental section. Bands in the region 1575–1590 cm^{-1} and at 1430–1475 cm^{-1} are typical aromatic C–C deformations. A characteristically sharp X-sensitive band for phenylphosphine complexes occurs at 1090–1100 cm^{-1}. Aromatic out of plane C–H bending modes are also observable for most of the complexes as strong bands at 690–700 and 730–750 cm^{-1}. Unambiguous assignment of platinum–carbon stretching modes in this type of complex (540–600 cm^{-1}) is not possible.

The major ion detected in all of the mass spectra produced for the complexes *cis*-$Pt(CH_2SR)_2L^1{}_2$ corresponded to the $[Pt(CH_2SR)L^1{}_2]^+$ fragment. A molecular ion was detectable at very low intensity in almost every case.

(c) X-Ray diffraction studies. *Crystal and molecular structure of* cis-$Pt(CH_2SPh)_2(PPh_3)\cdot 0.5CH_2Cl_2$. The molecular structure of *cis*-$Pt(CH_2SPh)_2(PPh_3)_2\cdot 0.5CH_2Cl_2$ is depicted in Fig. 1.[25] The complex exhibits approximate square-planar geometry with some distortion. From the bond angle data (Table 5) it appears that the mutually *cis* triphenylphosphine ligands cause the P(1)–Pt–P(2) bond angle to open significantly to 99.8(1)° due to the large steric requirements of this phosphine. The angle between the alkyl groups in the platinum co-ordination sphere is consequently reduced, C(70)–Pt–C(80) 83.2(2)°, while the angles between each phosphine and alkyl ligand are close to right angles, P(1)–Pt–C(70) 87.3(2) and P(2)–Pt–C(80) 90.3(1)°.

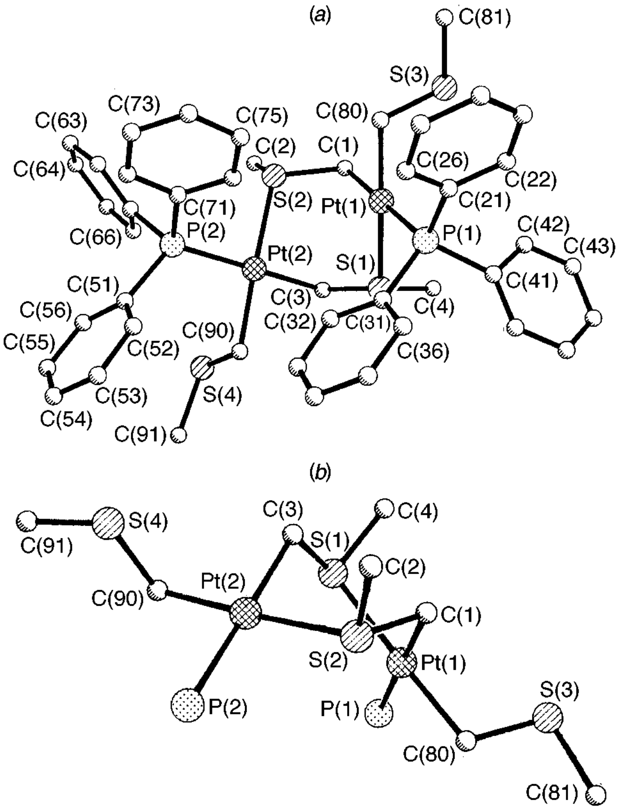


Fig. 2 (*a*) Molecular structure and (*b*) ring conformation in $[Pt(CH_2SCH_3)(\mu\text{-}CH_2SCH_3)(PPh_3)]_2$

Table 6 Selected bond lengths (Å) and angles (°) for $[Pt(CH_2SCH_3)(\mu\text{-}CH_2SCH_3)(PPh_3)]_2$

Pt(1)–P(1)	2.293(2)	Pt(1)–S(1)	2.379(2)
Pt(1)–C(1)	2.082(7)	Pt(1)–C(80)	2.068(8)
Pt(2)–P(2)	2.288(2)	Pt(2)–S(2)	2.374(2)
Pt(2)–C(3)	2.073(8)	Pt(2)–C(90)	2.068(8)
C(1)–S(2)	1.788(7)	S(2)–C(2)	1.806(9)
C(3)–S(1)	1.792(8)	S(1)–C(4)	1.809(10)
C(80)–S(3)	1.778(8)	S(3)–C(81)	1.789(13)
C(90)–S(4)	1.806(8)	S(4)–C(91)	1.793(11)
P(1)–Pt(1)–S(1)	91.1(1)	P(1)–Pt(1)–C(80)	92.7(2)
S(1)–Pt(1)–C(1)	89.9(2)	C(1)–Pt(1)–C(80)	86.2(3)
P(2)–Pt(2)–S(2)	89.6(1)	P(2)–Pt(2)–C(90)	93.1(2)
S(2)–Pt(2)–C(3)	90.6(2)	C(3)–Pt(2)–C(90)	86.7(3)
Pt(1)–C(1)–S(2)	106.6(4)	Pt(1)–S(1)–C(3)	108.3(3)
Pt(2)–C(3)–S(1)	108.3(4)	Pt(2)–S(2)–C(1)	108.6(2)

Selected bond lengths are also presented (Table 5) and are fairly typical, with the Pt–C bonds 2.112(4) and 2.084(7) Å respectively (mean value 2.098 Å). The Pt–C bond lengths *trans* to triphenylphosphine in a symmetric metallacyclic alkyl complex, $[Pt(CH_2)_4(PPh_3)_2]$, were measured[26] at 2.12(2) and 2.06(2) Å (mean value 2.09 Å). The Pt–P bonds in the latter complex, 2.285(6) and 2.279(5) Å are shorter than those in the current case (mean 2.309 Å).

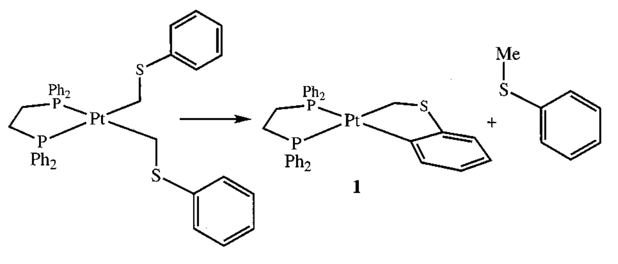
Crystal and molecular structure of $[Pt(CH_2SCH_3)(\mu\text{-}CH_2SCH_3)(PPh_3)]_2$. The molecular structure of $[Pt(CH_2SCH_3)(\mu\text{-}CH_2SCH_3)(PPh_3)]_2$ is depicted in Fig. 2. The bond angle data in Table 6 indicate that both platinum atoms have approximately square-planar geometry. The internal bond angles formed by the ligands in the ring, S(1)–Pt(1)–C(1) 89.9(2) and S(2)–Pt(2)–C(3) 90.6(2)° are very close to right angles. The steric bulk of the triphenylphosphine again has some effect on the angle between the pendant alkyl ligand and the bridging alkyl ligand with some closing of the angle, C(1)–Pt(1)–C(80) 86.2(3) and C(3)–Pt(2)–C(90) 86.7(3)° respectively. This allows more space for the phosphine itself and consequently the angles between the pendant alkyl ligands and the phosphine ligands are a little greater than 90°, P(1)–Pt(1)–C(80) 92.7(2) and P(2)–Pt(2)–C(90) 93.1(2)°. The more rigid ligand groups with bridging sulfur atoms form approximate right angles with the triphenylphosphine ligands, P(1)–Pt(1)–S(1) 91.1(1) and P(2)–Pt(2)–S(2) 89.6(1)°.

The ring formed by the bridging thiaalkyl ligands takes up an interesting conformation which best corresponds to a 'twist–boat' conformation. This is illustrated in Fig. 2(*b*). The conformation is determined by the constraints of near right angles at the platinum centres and near tetrahedral angles at the carbon and sulfur atoms of the ring. The planes containing the platinum atoms are tilted such that the phosphine groups point in opposite directions away from the ring but both point downwards [with reference to the view presented in Fig. 2(*b*)]. This means that the methyl groups from each of the bridging methyl sulfide ligands both point up but at divergent angles. The steric bulk of the phosphine substituents prevents the methyl groups from orientating on the opposite faces of the ring. The steric constraints imposed by the triphenylphosphine may well be such that the conformation in the solid state is also the lowest energy configuration in solution. Evidence from ^{1}H NMR spectroscopy indicates a sulfur-inversion process in progress at around room temperature (see above). Examination of a space-filling model (using Harvard CPK® atomic models) allows the low energy solid-state configuration and a higher energy conformation to be visualised. The more strained configuration has the ring methyl groups pointing in opposite directions. Stepwise exchange between these two configurations is proposed to account for the broadening of the methylene proton signals in the NMR spectrum at ambient temperature.

The Pt–S bond lengths in this complex, 2.379(2) and 2.374(2) Å, compare closely to structural data for thioether ligands co-ordinated to platinum, for example, in *cis*-$PtPh_2(SMe_2)_2$ [2.370(2) and 2.389(2) Å, mean 2.380 Å][27] and in the mixed sulfur–phosphorus donor complex, [PtCl(Me){PhP(CH_2CH_2)$_2$S}] [2.374(2) Å[28]]. The Pt–C bond *trans* to sulfur in this complex, 2.084(7) Å, appears marginally larger, but not significantly so, than those exhibited in the pendant alkyl groups [2.068(8) Å] *trans* to the sulfur bridges in our complex. The values of the ring Pt–C bonds [2.073(8) and 2.082(7) Å] are slightly longer. This might be indicative of a degree of strain in the ring, although the effect of the higher *trans* influence (relative to SR_2) of the triphenylphosphine ligand may also be responsible for the difference.

(***d***) **Reactivity studies.** *Reaction of* cis-$Pt(CH_2SCH_3)_2(PPh_3)_2$ *with* $P(OMe)_3$. Treatment of *cis*-$Pt(CH_2SCH_3)_2(PPh_3)_2$ with an excess of $P(OMe)_3$ results in substitution of the phosphine by phosphite. Isolation of these complexes free of triphenylphosphine and the excess trimethylphosphite has proved impractical so far. Both *cis*-$Pt(CH_2SCH_3)_2(PPh_3)[P(OMe)_3]$ and *cis*-$Pt(CH_2SCH_3)_2[P(OMe)_3]_2$ can be observed, however, by ^{31}P-{^{1}H}, ^{13}C-{^{1}H} and ^{1}H NMR spectroscopy (see Experimental section). Dialkylbis(phosphite)platinum complexes are rare, although [$PtMe_2L^3{}_2$] [$L^3 = P(OMe)_3$ or $P(OEt)_3$] have been reported.[29]

Phosphite complexes of platinum generally have $^1J_{\mathrm{Pt-P}}$ magnitudes larger than corresponding phosphine complexes, exemplified by the bis(phosphite) complex, *cis*-$Pt(CH_2SMe)_2[P(OMe)_3]_2$, (δ 129.51, $^1J_{\mathrm{Pt-P}} = 3306$ Hz). The ratio of $^1J_{\mathrm{M-P}}$ between phosphite complexes and otherwise similar phosphine complexes (at least for Pt$^{\mathrm{II}}$, Rh$^{\mathrm{I}}$ and Rh$^{\mathrm{III}}$) has been found[30] to fall generally in the range 1.5–1.8 : 1. The ratio of $^1J_{\mathrm{Pt-P}}$ for this complex and *cis*-$Pt(CH_2SMe)_2(PMe_3)_2$, falls within this range (1.73 : 1).



Scheme 1 Thermolytic rearrangement of $Pt(CH_2SPh)_2(dppe)$

In the mixed complex, *cis*-$Pt(CH_2SMe)_2(PPh_3)[P(OMe)_3]$, the phosphite resonance has ^{31}P-{^{1}H} characteristics, δ 126.31, $^1J_{\mathrm{Pt-P}} = 3408$ Hz. The co-ordinated triphenylphosphine (δ 26.00, $^1J_{\mathrm{Pt-P}} = 1957$ Hz) exhibits a significantly reduced coupling to the metal [relative to *cis*-$Pt(CH_2SCH_3)_2(PPh_3)_2$; $^1J_{\mathrm{Pt-P}} = 2038$ Hz]. The magnitude of mutual ^{31}P–^{31}P coupling ($^2J_{\mathrm{P-P}} = 22.1$ Hz) is typical for *cis* stereochemistry. The magnitude of $^2J_{\mathrm{Pt-H}}$ is slightly smaller for the methylene protons *trans* to phosphite than for the methylene protons *trans* to most examples of phosphine. Comparison of *cis*-$Pt(CH_2SMe)_2(PMe_3)_2$ with *cis*-$Pt(CH_2SMe)_2[P(OMe)_3]_2$, however, gives almost the same value for $^2J_{\mathrm{Pt-H}}$, 68.3 and 68.0 Hz, respectively, with the signal resonating at slightly lower field for the phosphite complex (δ 2.38 and 2.59 respectively). This seems to indicate broad similarity of the relative *trans* influence for corresponding phosphites and phosphines. The lack of measurable $^3J_{\mathrm{P-H}}$ for the methylene protons *trans* to phosphite is a significant difference. This signal for the bis(phosphite) complex appears as an unresolved triplet.

From ^{13}C-{^{1}H} NMR spectroscopic data for *cis*-$Pt(CH_2SMe)_2[P(OMe)_3]_2$, (δ 23.51, $^1J_{\mathrm{Pt-C}} = 598$ Hz), coupling to phosphorus is stronger than that for the corresponding phosphine complexes, in accord with the earlier discussion (*trans* $^2J_{\mathrm{P-C}} = 147$ and *cis* $^2J_{\mathrm{P-C}} = 16.1$ Hz). The mixed complex, *cis*-$Pt(CH_2SMe)_2(PPh_3)[P(OMe)_3]$, has ^{13}C NMR characteristics (δ 29.35, $^1J_{\mathrm{Pt-C}} = 607$, *trans* $^2J_{\mathrm{P-C}} = 143$, *cis* $^2J_{\mathrm{P-C}} = 7.2$ Hz), attributable to the ligand *trans* to the phosphite, on the basis of its large *trans* coupling to ^{31}P and smaller coupling to ^{195}Pt. The other methylene carbon, *trans* to PPh_3, is assigned as the signal at δ 19.59 ($^1J_{\mathrm{Pt-C}} = 628$, *trans* $^2J_{\mathrm{P-C}} = 94.6$, *cis* $^2J_{\mathrm{P-C}} = 10.8$ Hz) which shows enhanced coupling to the metal centre, a smaller *trans* coupling to ^{31}P (consistent with *trans* PPh_3) and the slightly larger *cis* coupling to ^{31}P.

Thermolytic rearrangements. Generally, the series of bis(thiaalkyl)platinum complexes are unreactive thermally, at least in the absence of a halide source (such as a chlorocarbon solvent). Thermolysis of $Pt(CH_2SPh)_2(dmpe)$ in $CDCl_3$ resulted in facile formation of $PtCl(CH_2SPh)(dmpe)$. Such is the propensity for formation of $PtCl(CH_2SR)L^1{}_2$, that thermolysis must be undertaken in media which are rigorously free of chlorocarbons. The frequent presence of dichloromethane in solid samples as solvent of crystallisation is an additional problem.

The thiaalkyl complex $Pt(CH_2SPh)_2(dppe)$ was found to rearrange slowly to one product (>90%) at 145 °C. If the reaction temperature is raised above this level, a more complex distribution of products is obtained. From ^{31}P NMR spectroscopy two phosphorus environments are evident in equal proportions, (δ 50.94, $^1J_{\mathrm{Pt-P}} = 2079$ Hz, δ 48.06, $^1J_{\mathrm{Pt-P}} = 1740$ Hz) suggesting an asymmetric product. The other spectroscopic parameters for this rearrangement product (see Experimental section) are all consistent with the 3-platina-1-thiaindan, $\overline{Pt(C_6H_4S}CH_2)(dppe)$ **1** (Scheme 1). Volatile products from the thermolysis were analysed by gas chromatography mass spectrometry (GCMS) and thioanisole was identified as the only major component. This

Table 7 The ^1H NMR spectroscopic data for *cis*-$Pt(CH_2SR)R'(PPh_3)_2$[a]

		δ(^{1}H)			
		Hydrocarbyl ligand			
R	R′	Pt−CH_2	Pt−R^1	Aromatic	Ancillary ligand
Ph	Me	2.25 [**71.2**, $J_{C-P\,(trans)}$ = 11.1, $J_{C-P\,(cis)}$ = 6.1]	0.70 [Pt−CH_3, **66.0**, $J_{C-P\,(trans)}$ = 7.4]	7.21 (dd, H^2, H^6), 7.04 (m, H^3, H^5), 6.87 (m,[c] H^4)	7.52 (m, H^2, H^6), 7.31 (m, H^{2}, $H^{6'}$), 7.05–7.15 (m,[c] H^3, $H^{3'}$, H^5, $H^{5'}$), 6.86–6.90 (m,[c] H^4, $H^{4'}$)
Ph	CH_2SiMe_2Ph	2.40 [**70.8**, $J_{C-P\,(trans)}$ = 11.2, $J_{C-P\,(cis)}$ = 6.3]	1.00 [Pt−CH_2, **79.5**, $J_{C-P\,(trans)}$ = 12.0, $J_{C-P\,(cis)}$ = 8.4], 0.10 [$Si(CH_3)_2$]	7.20–7.25[c] (H^2, H^6), 7.0–7.1[c] (H^3, H^5), 6.83 (m, H^4) 7.56 (m, $H^{2'}$, $H^{6'}$), 7.08–7.12[c] ($H^{3'}$, $H^{4'}$, $H^{5'}$)	7.47 (m, H^2, H^6), 7.20–30[c] ($H^{2'}$, $H^{6'}$), 7.05–7.15[c] (H^3, $H^{3'}$, H^5, H^5), 6.80–7.00[c] (H^4, $H^{4'}$)
Ph	CH_2CMe_2Ph[d]	2.54,[e] [$J_{C-P\,(trans)}$ = 12.3, $J_{C-P\,(cis)}$ = 6.2]	2.42 [Pt−CH_2,[e] $J_{C-P\,(trans)}$ = 12.8, $J_{C-P\,(cis)}$ = 6.2], 1.38 [$C(CH_3)_2$]	7.5[c] (H^2, H^6), 6.8–7.1[c] (H^3, H^5), 6.5–6.8[c] (H^4) 7.3–7.8[c] ($H^{2'}$, $H^{6'}$), 7.0–7.2[c] ($H^{3'}$, $H^{4'}$, $H^{5'}$)	7.3–7.8[c] (H^2, H^6, $H^{2'}$, $H^{6'}$), 6.9–7.2[c] (H^3, $H^{3'}$, H^4, H^4, H^5, H^5)
Ph	$C_6H_4Bu^t$-4[f]	2.96 [**52.2**, $J_{C-P\,(trans)}$ = 12.0, $J_{C-P\,(cis)}$ = 5.9]	1.56 [$C(CH_3)_3$]	*c*	*c*
Me	CH_2SiMe_3	2.63 [**69.7**, $J_{C-P\,(trans)}$ = 11.7, $J_{C-P\,(cis)}$ = 6.1]	[Pt−CH_2Si],[g] 0.29 [$Si(CH_3)_3$]	—	7.45–7.6 (m, H^2, H^6), 7.7–7.8 (m, $H^{2'}$, $H^{6'}$), 6.85–7.05 (m, H^3, $H^{3'}$, H^4, H^4, H^5, H^5)

[a] Recorded in $CDCl_3$; δ relative to $SiMe_4$. [b] J_{Pt-H} values in bold, other *J* values in Hz. [c] Obscured due to overlapping ligand resonances. [d] Recorded in [$^2H_8$]toluene. [e] $^1J_{Pt-H}$ not resolved. [f] Recorded in C_6D_6. [g] Signal obscured by impurity.

Table 8 The ^{31}P NMR spectroscopic data for *cis*-$Pt(CH_2SR)R'(PPh_3)_2$[a]

R	R′	Assignment	δ (^{31}P)	$^1J_{Pt-P}$/Hz	$^2J_{P-P}$/Hz
Ph	Me[b]	*trans*-CH_2SR	26.32	2113	10.2
		trans-R′	28.94	1931	
Ph	$C_6H_4Bu^t$-4	*trans*-CH_2SR	22.77	2157	11.9
		trans-R′	24.31	1682	
Ph	CH_2CMe_2Ph	*trans*-CH_2SR	29.89	1951	6.8
		trans-R′	29.46	1821	
Ph	CH_2SiMe_2Ph	*trans*-CH_2SR	24.91	2089	11.9
		trans-R′	26.66	2087	
Me	CH_2SiMe_3	*trans*-CH_2SR	25.04	1990	10.2
		trans-R′	27.07	2070	

[a] Recorded in C_6D_6 unless otherwise indicted; δ relative to 85% H_3PO_4–D_2O. [b] Recorded in $CDCl_3$.

behaviour is analogous to that of neophylplatinum(II) derivatives[20] and to that of silaneophylplatinum(II) complexes with monodentate N-donor ancillary ligands.[4b] It is in contrast, however, with the reactivity of corresponding silaneophylplatinum(II) species with P-donor ligands.[4b]

Synthesis and structural characteristics of *cis*-$Pt(CH_2SPh)R'(PPh_3)_2$

The monoalkyl derivative, *trans*-$PtCl(CH_2SR)(PPh_3)_2$, may be obtained readily by oxidative addition of $ClCH_2SR$ to $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$, in yields similar to those reported previously for analogous syntheses of this species from $Pt(PPh_3)_3$.[12] A number of asymmetric complexes, *cis*-$Pt(CH_2SR)R'(PPh_3)_2$ have been prepared by reaction of *trans*-$PtCl(CH_2SR)(PPh_3)_2$ with either MgClR′ or LiR′. Among these, *cis*-$Pt(CH_2SPh)(CH_3)(PPh_3)_2$ and *cis*-$Pt(CH_2SPh)(CH_2SiMe_2Ph)(PPh_3)_2$ have been characterised fully. Proton, ^{31}P-{^{1}H} and ^{13}C-{^{1}H} NMR spectroscopic data appear in Tables 7, 8 and 9. As for symmetric bis(2-thiaalkyl)platinum(II) complexes, the asymmetric dialkyl metal derivatives favour *cis* geometry.

Assignment of the signals for the ^{31}P-{^{1}H} NMR spectra of the asymmetric complexes has been made primarily on the grounds of relative *trans* influence of the differing alkyl groups. For each compound the resonance with larger $^1J_{Pt-P}$ has been assigned as *trans* to the alkyl ligand with weaker *trans* influence, in each case the thiaalkyl ligand. In the complex, *cis*-$Pt(CH_2SPh)(CH_2SiMe_2Ph)(PPh_3)_2$, both values of $^1J_{Pt-P}$ are very similar. Comparison of the data for the symmetric compounds *cis*-$PtR_2(PR'_3)_2$ shows that where R = CH_2SPh values of $^1J_{Pt-P}$ are consistently larger than in the corresponding complexes with R = CH_2SiMe_2Ph. By this measure, the CH_2SPh group exerts a weaker *trans* influence than the silaneophyl group and the ^{31}P NMR spectrum is assigned accordingly.

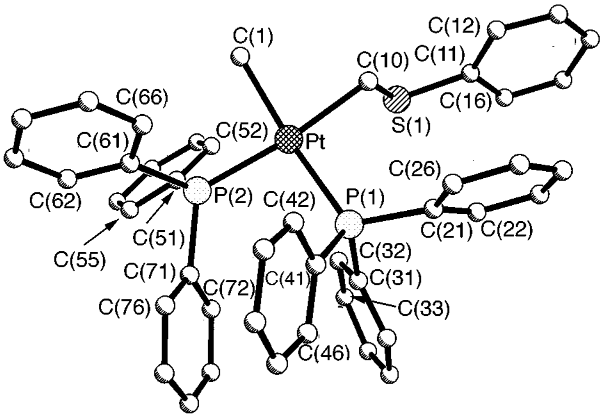


Fig. 3 Molecular structure of *cis*-$Pt(CH_2SPh)(CH_3)(PPh_3)_2$

A notable feature of the ^{13}C NMR spectroscopic data exhibited by the two complexes recorded is the close similarity of the coupling constants, $^1J_{Pt-C}$ (652 Hz) and $^3J_{Pt-C}$ (125 Hz), in the thiaalkyl portion of the spectrum for both compounds. The position of the thiaalkyl methylene carbon and the thiaalkyl *ipso*-carbon resonances are slightly upfield in the complex where R′ = silaneophyl from their chemical shifts in the compound R′ = methyl (δ 19.2 and 145.7 respectively compared with δ 23.1 and 146.1).

The molecular structure of *cis*-$Pt(CH_2SPh)(CH_3)(PPh_3)_2$, determined by X-ray diffraction, is depicted in Fig. 3. The platinum atom exhibits approximately square-planar geometry. Some degree of distortion is evident, though slightly less than for *cis*-$Pt(CH_2SPh)_2(PPh_3)_2$ (see above), from the bond angle data (Table 10) with the P(1)−Pt−P(2) bond angle opened to 98.2(1)°. The alkyl groups exhibit an angle C(1)−Pt−C(10) of 84.7(3)° indicating a smaller steric requirement of the methyl group compared with CH_2SPh in *cis*-$Pt(CH_2SPh)_2(PPh_3)_2$. The angles between the phosphine and alkyl ligands are close to

Table 9 The ^{13}C NMR spectroscopic data for *cis*-$Pt(CH_2SR)R'(PPh_3)_2$ [a]

		$\delta(^{13}C)$ [b]			
		Hydrocarbyl ligand			
R	R′	Pt−CH_2SR	Pt−R′	Aromatic	Ancillary ligand
Ph	Me	23.10 [**651.8**, $J_{C-P\,(trans)}$ = 98.9, $J_{C-P\,(cis)}$ = 4.9]	7.78 [Pt−CH_3, **582.2**, $J_{C-P\,(trans)}$ = 94.0, $J_{C-P\,(cis)}$ = 6.1]	146.14 (C^1, **124.5**), 127.32 (C^2, C^6), 124.96 (C^3, C^5), 122.23 (C^4)	132.23, 133.11 (C^1, $C^{1'}$), 134.41, 134.70 ($C^{2,2'}$, $C^{6,6'}$), 127.44 ($C^{3,3'}$, $C^{5,5'}$), 129.33 (C^4, $C^{4'}$)
Ph	CH_2SiMe_2Ph	19.21 [**651.8**, $J_{C-P\,(trans)}$ = 100.7, $J_{C-P\,(cis)}$ = 5.5]	7.73 [Pt−CH_2, **542.0**, $J_{C-P\,(trans)}$ = 89.1, $J_{C-P\,(cis)}$ [c]]	145.69 (C^1, **124.5**), 126.85 (C^2, C^6), 125.29 (C^3, C^5), 122.37 (C^4)	132.89, 132.26 (C^1, $C^{1'}$), 134.25, 134.57 ($C^{2,2'}$, $C^{6,6'}$), 127.41 ($C^{3,3'}$, $C^{5,5'}$), 129.24 (C^4, $C^{4'}$)
			2.72 [$Si(CH_3)_2$, **26.8**]	145.48 ($C^{1'}$, **17.2**), 134.07 ($C^{2'}$, $C^{6'}$), 127.57 ($C^{3'}$, $C^{5'}$), 128.23 ($C^{4'}$)	

[a] Recorded in $CDCl_3$; δ relative to $SiMe_4$. [b] J_{Pt-C} values in bold, other J values in Hz. [c] Not resolved.

Table 10 Selected bond lengths (Å) and angles (°) for *cis*-$Pt(CH_2SPh)(CH_3)(PPh_3)_2$

Pt−P(1)	2.311(2)	Pt−P(2)	2.308(2)
Pt−C(1)	2.107(8)	Pt−C(10)	2.098(8)
S(1)−C(10)	1.786(8)	S(1)−C(11)	1.759(9)
P(1)−Pt−P(2)	98.2(1)	C(1)−Pt−C(10)	84.7(3)
P(2)−Pt−C(1)	87.3(3)	P(1)−Pt−C(10)	90.5(2)
Pt−C(10)−S(1)	103.5(3)	C(10)−S(1)−C(11)	105.4(4)

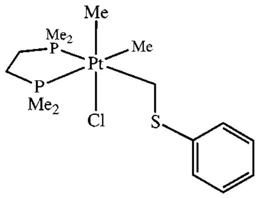


Fig. 4 Oxidative adduct of $ClCH_2SPh$ and $PtMe_2(dmpe)$

right angles, P(2)−Pt−C(1) 87.3(3) and P(1)−Pt−C(10) 90.5(2)°. Bond lengths (Table 10) are broadly similar to those for the symmetric bis(2-thiaalkyl) complex (see above). The metal–carbon distances are respectively Pt−C(1) 2.107(8) and Pt−C(10) 2.098(8) Å. The platinum–phosphorus bonds measure 2.311(2) and 2.308(2) and, again, are very similar to the symmetric example.

Synthetic and spectroscopic studies of (2-thiaalkyl)platinum(IV) complexes

Platinum(IV) complexes containing a 2-thiaalkyl ligand can be prepared by oxidative addition of the thiaalkyl halide to a platinum(II) centre. (Chloromethyl) phenyl sulfide has been found to react with platinum(II) substrates to give platinum(IV) products.

(*a*) $PtCl(CH_2SPh)Me_2(dmpe)$. Addition of $ClCH_2SPh$ to $PtMe_2(dmpe)$ results in the formation of $PtCl(CH_2SPh)Me_2(dmpe)$. The ^{31}P NMR spectrum shows two signals of equal intensity (δ 6.76, $^1J_{Pt-P}$ = 1424 Hz and δ 2.17, $^1J_{Pt-P}$ = 1255 Hz) indicating the formation of an asymmetric complex. From the magnitudes of $^1J_{Pt-P}$, the phosphine environments can be assigned *trans* to CH_2SPh and *trans* to CH_3 respectively. This indicates *cis* addition of the alkyl halide with the remaining methyl group and chloride mutually *trans* (Fig. 4).

The asymmetry of this structure generates characteristic features in the ^1H NMR spectrum. The methylene hydrogens of the thiaalkyl ligand are diastereotopic and display appreciably different chemical shifts (δ 3.43 and 2.42). They appear as multiplets, as a result of mutual coupling and coupling to both ^{31}P nuclei. The lower field signal approximates to a triplet of doublets with ^{195}Pt satellites and eight lines are visible for the higher field signal also with distinguishable satellites. Naturally, two different methyl groups are also observed (δ 0.87, $^1J_{Pt-H}$ = 53.8 Hz and δ = 0.71, $^1J_{Pt-H}$ = 71.9 Hz) which are assigned as CH_3 *trans* to phosphorus and CH_3 *trans* to chloride respectively. These signals emerge as approximate triplets due to coupling to ^{31}P, with the latter exhibiting a slightly smaller *cis* coupling ($^3J_{P-H}$ = 6.6 Hz) than that exhibited by the methyl group *trans* to phosphine ($^3J_{P-H}$ = 7.3 Hz). The hydrogens of the dmpe ligand also give rise to complex multiplets, a result of four chemically inequivalent methyl groups and the hydrogen environments on the dmpe backbone.

The ^{13}C-{^1H} NMR spectrum confirms the structure of this platinum(IV) complex. Both methyl groups are defined (δ 2.29, $^1J_{Pt-C}$ = 481.8 Hz and δ −5.28, $^1J_{Pt-C}$ = 627.4 Hz). In the former case, coupling to *trans* ^{31}P ($^2J_{P-C}$ = 119.6 Hz) generates a doublet, split further by a smaller $^2J_{P-C}$ (3.6 Hz). The signal at δ −5.28 shows coupling to only one ^{31}P (*cis* $^2J_{P-C}$ = 2.5 Hz). The larger coupling to ^{195}Pt for this ligating ^{13}C is consistent with a position *trans* to the chloride ligand, with its inherently lower *trans* influence. The methylene carbon of the thiaalkyl ligand generates a doublet at lower field (δ 16.64, $^2J_{P-C}$ = 136.7 Hz, $^1J_{Pt-C}$ = 544.4 Hz) due to coupling to *trans* ^{31}P but with no apparent coupling to *cis* ^{31}P. Most of the aromatic carbons of the S−Ph group are in the expected shift range (see Experimental section); $^3J_{Pt-C}$ for the quaternary *ipso*-carbon could not be distinguished.

The *fac* arrangement of the alkyl ligands in this platinum(IV) complex is explicable on the thermodynamic basis of relative *trans* influence of ligands. The P-donor components are constrained to mutually *cis* positions. The outcome with CH_3 *trans* to Cl places the ligand with the highest *trans* influence opposite that with weakest *trans* influence of the four. The remaining methyl group and the thiaalkyl group are then placed *trans* to the phosphine ligands, which have more moderate *trans* influence.

(*b*) $PtCl(CH_2SPh)Me_2(bipy)$. A platinum(II) precursor containing a bidentate N-donor ligand, $PtMe_2(bipy)$, also affords a platinum(IV) product, $PtCl(CH_2SPh)Me_2(bipy)$, upon oxidative addition. By contrast, attempts to prepare platinum(II) complexes with these (thiaalkyl) ligands, supported by N-donor ancillary ligands, have been unsuccessful (see above). Oxidative addition of (chloromethyl) phenyl sulfide to $PtMe_2(bipy)$ resulted in precipitation of a red-brown solid. This was recrystallised from dichloromethane and methanol to give orange needles; ^1H NMR data appear in the Experimental section.

The methylene protons of the CH_2SPh group are visible as a singlet (δ 2.86) with platinum satellites ($^2J_{Pt-H}$ = 64.7 Hz). A single methyl group environment is also observed (δ 1.43, $^2J_{Pt-H}$ = 69.0 Hz), indicating that the ultimate platinum(IV)

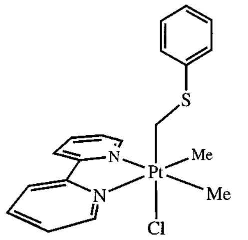


Fig. 5 Oxidative adduct of $ClCH_2SPh$ and $PtMe_2(bipy)$

product must be that of *trans* addition (Fig. 5). This structure contains an approximate mirror plane (assuming free rotation about the Pt−CH_2SPh bond) and so the methylene protons are not diastereotopic as is the case for the chelating phosphorus-donor complex discussed above, where the structure is that resulting from *cis* addition. The methylene hydrogens are chemically equivalent, as are the methyl environments which remain *trans* to nitrogen, therefore singlets are observed for each in the ^1H NMR spectrum. It is not clear why the preferred geometry for the platinum(IV) adduct involves *trans* addition for the N-donor complex but *cis* addition for the P-donor complex. The explanation seems more likely to be thermodynamic (*e.g.* fine *trans* influence balance) than kinetic in origin.

Conclusion

(*a*) A wide range of 2-thiaalkyl complexes of platinum(II), with P-donor ancillary ligands, is accessible by transalkylation and oxidative addition routes. (*b*) Mono(2-thiapropyl)platinum(IV) derivatives are attainable by oxidative addition. (*c*) From comparisons of NMR coupling constants, $^1J_{Pt-P}$, a series of relative *trans* influence emerges: $CH_2SPh < CH_2SC_6H_4Me < CH_2SiMePh_2 < CH_2SiMe_2C{\equiv}CBu^t < CH_2SiMe_2Ph \leqslant CH_2SiMe_2CH{=}CH_2 < CH_2SiMe_3 \leqslant CH_2SMe < CH_2GeMe_3 < CH_2SnMe_3$ ($< CH_3$) $< CH_2CMe_2Ph < CH_2CMe_3$; $^1J_{Pt-C}$ (and, presumably, Pt−C bond strength) varies, broadly, in the opposite sense. (*d*) The mononuclear platinum(II) derivative, *cis*-$Pt(CH_2SCH_3)_2(PPh_3)_2$, rearranges readily to afford a dinuclear platinum(II) species, $[Pt(CH_2SCH_3)(\mu\text{-}CH_2SCH_3)(PPh_3)]_2$, containing bridging thiaalkyl ligands in a six-membered dimetallacycle. (*e*) Rather than S−C scission routes, thermolytic rearrangement of *cis*-$Pt(CH_2SPh)_2$(dppe) proceeds by aromatic C−H activation and H transfer, to generate the metallacyclic derivative, $Pt(C_6H_4SCH_2)_2$(dppe), with release of 1 equivalent of thioanisole (Scheme 1).

Experimental

General and instrumental

Elemental analyses were by Imperial College Microanalytical Laboratories or by the Analytical Division, BP Research, Sunbury-on-Thames; NMR spectra were recorded on a JEOL GSX 270 spectrometer (^1H, 270.17 MHz, ^{13}C, 67.94 MHz, ^{31}P, 109.37 MHz). Infrared data from 4% dispersions in KBr were collected using a Perkin-Elmer 683 instrument; mass spectra were obtained on a VG AutospecQ instrument, using fast atom bombardment (FAB) as ionising technique.

All reactions were carried out under an inert atmosphere (oxygen-free nitrogen or argon) using standard anaerobic manipulation techniques.[31] Solvents were distilled under nitrogen prior to use from sodium (toluene and benzene), sodium–benzophenone [diethyl ether, hexane and tetrahydrofuran (thf)] and calcium hydride (dichloromethane). The solvent $CDCl_3$ was used as supplied from Aldrich Chemical Company, $[^2H_8]$toluene and C_6D_6 were also supplied by Aldrich but were distilled from sodium and stored under argon in grease-free vessels prior to use. Potassium tetrachloroplatinate(II) was purchased from Johnson Matthey Chemicals, 2,2′-bipyridyl (bipy) and triphenylphosphine were supplied by Aldrich Chemical Company and were recrystallised from ethanol prior to use. Bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe) and 1,2-bis(dicyclohexylphosphino)ethane (dcpe) were supplied by Strem Chemicals and were recrystallised (from ethanol) and stored under argon. 1,2-Bis(dimethylphosphino)ethane (dmpe), dimethyl(phenyl)phosphine and methyl(diphenyl)phospine, also from Strem Chemicals, were distilled at reduced pressure and stored under argon. Methyl phenyl sulfide (thioanisole), methyl (*p*-tolyl) sulfide and (chloromethyl) methyl sulfide were all obtained from Aldrich Chemical Company and were distilled carefully under reduced pressure and stored under argon immediately prior to use. Cycloocta-1,5-diene (cod) was also from Aldrich Chemical Company and was used as supplied. Dichloro(cycloocta-1,5-diene)platinum(II),[32] (ethene)bis(triphenylphosphine)platinum,[33] dimethyl[1,2-bis(dimethylphosphino)ethane]platinum(II)[34] and dimethyl(2,2′-bipyridyl)platinum(II)[35] were prepared according to published procedures.

Synthesis

Preparation of *trans*-$PtCl(CH_2SPh)(PPh_3)_2$. (Ethene)bis(triphenylphosphine)platinum(0) (0.90 g, 1.2 mmol) was dissolved in dry degassed toluene (35 cm^3). The solution was cooled to 0–10 °C in an ice–water bath and a solution of (chloromethyl) phenyl sulfide in toluene (8.0 cm^3, 0.15 M) was added dropwise to the reaction. The solution was allowed to reach ambient temperature and stirred for a further 18 h. The solvent and other volatile materials were removed *in vacuo* leaving a reasonably pure product. Yield 1.02 g (97%). IR: 3050w, 1585w, 1480s, 1430vs, 1310w, 1185w, 1160w, 1095vs, 1025mw, 740s, 690vs, 550m, 520vs and 320mw.

Preparation of *trans*-$PtCl(CH_2SCH_3)(PPh_3)_2$. (Ethene)bis(triphenylphosphine)platinum(0) (0.50 g, 0.67 mmol) was dissolved in dry degassed thf (20 cm^3). The solution was cooled to 0–10 °C and (chloromethyl) methyl sulfide (2.8 cm^3, 0.24 M) in thf was added dropwise. The mixture was stirred for 24 h and then the solvent removed *in vacuo*. Yield 0.50 g (92%).

Preparation of *cis*-$Pt(CH_2SPh)_2(PPh_3)_2$. (*i*) *Preparation of* $[Pt(CH_2SPh)_2]_n$ in situ. Thioanisole (0.25 g, 2.0 mmol) and tmen (0.233 g, 2.0 mmol) were dissolved in dry degassed thf (30 cm^3) and *n*-butyllithium (1.25 cm^3, 1.6 M) was added at −78 °C. After 3–4 h stirring at ambient temperature the mixture was re-cooled to −78 °C and solid $PtCl_2$(cod) (0.25 g, 0.67 mmol) was quickly added. The solid dissolved rapidly to give an orange solution which was stirred for a further 1 h at ambient temperature.

(*ii*) *Formation of* cis-$Pt(CH_2SPh)_2(PPh_3)_2$. The solution resulting from the above procedure was transferred to a solution of triphenylphosphine (0.35 g, 1.33 mmol) in 10% (v/v) acetone–thf (25 cm^3) at −78 °C. The solution was stirred for 18 h and then re-cooled once again to −78 °C when saturated aqueous ammonium chloride (20 cm^3) was added. The organic layer was separated and dried over magnesium sulfate, filtered and the solvent removed *in vacuo* to give a light green oily product. This was recrystallised from dichloromethane–methanol (1 : 1), to give a white, crystalline solid product. Yield 0.48 g (74%) [Found (calc.) for $Pt(CH_2SPh)_2(PPh_3)_2{\cdot}CH_2Cl_2$: C, 58.2 (58.3); H, 4.4 (4.4)%]. IR: 3049w, 2927w, 2906w, 1585m, 1569m, 1476s, 1449sh, 1433vs, 1384vs, 1262m, 1181w, 1156w, 1098m, 1076m, 1024m, 998w, 882ws, 802w, 737s, 691vs, 618m, 538m, 524s, 514s, 495m, 470mw and 423mw.

Preparation of *cis*-$Pt(CH_2SPh)_2(PMe_3)_2$. A solution of $[Pt(CH_2SPh)_2]_n$ prepared *in situ* [as in part (*i*) above] was transferred to a solution of trimethylphosphine (1.34 cm^3, 1.0 M) in 10% (v/v) acetone–thf (25 cm^3) at −78 °C. After stirring for 18 h at ambient temperature the solution was re-cooled to −78 °C and saturated aqueous ammonium chloride solution (20 cm^3)

was added. The organic layer was collected, dried over $MgSO_4$, filtered and the solvent removed *in vacuo* to give an off-white solid. Recrystallisation from thf–hexane gave pure white product. Yield 0.26 g (65%) [Found (calc.) for $Pt(CH_2SPh)_2(PMe_3)_2$: C, 40.6 (40.5); H, 5.4 (5.4)%]. IR: 3064w, 2966w, 2932w, 1581s, 1567s, 1475s, 1416s, 1385s, 1309w, 1303w, 1284m, 1262s, 1075s, 1024s, 994s, 848m, 803s, 743s, 733s, 690s and 471s.

Prepared according to the same method were: *cis*-$Pt(CH_2SPh)_2(PMe_2Ph)_2$. White crystalline solid from methanol–hexane. Yield 0.30 g (63%). IR: 3053w, 2908w, 1574m, 1475m, 1435ms, 1385mw, 1310w, 1264w, 1106m, 1075m, 1024m, 943ms, 906s, 840m, 734s, 693s, 617m, 486m, 472m, 428m and 370m.

cis-$Pt(CH_2SPh)_2(PMePh_2)_2$. White crystalline solid from dichloromethane–methanol. Yield 0.38 g (67%) [Found (calc.) for $Pt(CH_2SPh)_2(PMe_2Ph)_2$: C, 49.5 (50.0); H, 5.1 (5.1)%]. IR: 3048w, 2964w, 2904w, 1569m, 1484ms, 1434s, 1385m, 1286w, 1262m, 1178w, 1094s, 1076m, 1024s, 881s, 804m, 738s, 690vs, 617mw, 577mw, 522m, 507s, 490m, 478m, 449m and 416m.

$Pt(CH_2SPh)_2(dppe)$. White crystalline solid from dichloromethane–methanol. Yield 1.38 g (77%) [Found (calc.) for $Pt(CH_2SPh)_2(dppe)\cdot 0.5CH_2Cl_2$: C, 54.5 (55.1); H, 4.4 (4.5)%]. IR: 3051w, 2914w, 2876vw, 1583m, 1566m, 1475ms, 1434s, 1418m, 1385m, 1307w, 1266m, 1104ms, 1075m, 1021m, 998mw, 874w, 818m, 736s, 690vs, 648m, 524vs, 490m and 445m.

$Pt(CH_2SPh)_2(dmpe)$. White solid from dichloromethane–methanol. Yield 0.41 g (65%) [Found (calc.) for $Pt(CH_2SPh)_2(dmpe)$: C, 40.8 (40.6); H, 5.0 (5.1)%]. IR: 3065w, 2905mw, 2868m, 1583m, 1568m, 1476s, 1435m, 1417m, 1385m, 1285mw, 1154w, 1130w, 1075m, 1024mw, 940s, 896m, 841w, 804w, 739s, 720m, 693s, 657mw, 619w, 473m and 454w.

$Pt(CH_2SPh)_2(dcpe)$. White crystalline solid from thf–hexane. Yield 0.29 g (50%) [Found (calc.) for $Pt(CH_2SPh)_2(dcpe)$: C, 55.3 (55.6); H, 7.2 (7.2)%]. IR: 2923s, 2850ms, 1475ms, 1445m, 1416m, 1384ms, 1271w, 1179w, 1112w, 1074mw, 1024w, 736s, 691s, 663m, 535m and 473m.

Preparation of *cis*-$Pt[CH_2S(C_6H_4Me\text{-}p)]_2(PPh_3)_2$. Methyl (*p*-tolyl) sulfide (0.25 g, 1.8 mmol) and tmen (0.21 g, 1.8 mmol) were dissolved in dry degassed thf (30 cm^3) and $LiBu^n$ (1.1 cm^3, 1.6 M) was added at −78 °C. The solution was stirred at room temperature for 18 h and then re-cooled to −78 °C for the addition of solid $PtCl_2(PPh_3)_2$ (0.357 g, 0.45 mmol). The mixture was allowed to warm to ambient temperature giving an olive green solution after stirring for 24 h. The solution was again cooled to −78 °C and saturated aqueous ammonium chloride solution (20 cm^3) was added. The organic layer was separated, dried over $MgSO_4$, filtered and the solvent removed *in vacuo* to give the crude product as a pale green oil. This was recrystallised from dichloromethane–methanol. Yield 0.28 g (63%) {Found (calc.) for $Pt[CH_2S(C_6H_4Me\text{-}p)]_2(PPh_3)_2$: C, 58.9 (62.8); H, 5.0 (4.9)%}. IR: 3048vw, 2965w, 2921w, 1579s, 1489m, 1433s, 1385vs, 1238w, 1262m, 1181w, 1095ms, 1028m, 881w, 806m, 739mw, 693m, 649mw, 619m, 523m, 511m, 497m and 437w.

Prepared according to the same method were: $Pt[CH_2S(C_6H_4Me\text{-}p)]_2(dmpe)$. White crystalline solid from dichloromethane–methanol. Yield 0.12 g (39%). IR: 3063m, 3027mw, 2908s, 2877s, 2785m, 1902mw, 1799w, 1598s, 1558m, 1489vs, 1425s, 1417s, 1405s, 1395s, 1385s, 1303m, 1283s, 1263m, 1239m, 1212m, 1183m, 1119ms, 1091ms, 1058s, 1014m, 974m, 936vs, 889s, 834m, 810vs, 745s, 719s, 655s, 623s, 583m, 490s, 450ms and 398ms.

$Pt[CH_2S(C_6H_4Me\text{-}p)]_2(dppe)$. Methyl (*p*-tolyl) sulfide (0.277 g, 2.0 mmol) and tmen (0.233 g, 2.0 mmol) were dissolved in dry degassed thf (40 cm^3) and $LiBu^n$ (1.25 cm^3, 1.6 M) was added at −78 °C. After 1.5 h at room temperature the solution was re-cooled to −78 °C and solid $PtCl_2(cod)$ (0.25 g, 0.67 mmol) was added. After a further 1.5 h the mixture was transferred at −78 °C to a solution of dppe (0.266 g, 0.67 mmol) in 10% (v/v) acetone–thf (30 cm^3). This solution was stirred for 8 h at ambient temperature and then cooled to −78 °C for the addition of saturated aqueous NH_4Cl solution (20 cm^3). The organic layer was separated, dried over $MgSO_4$, filtered, and the solvent removed *in vacuo* to give a crude oily product. Recrystallisation from acetone–ethanol gave off-white crystals. Yield 0.35 g (61%). IR: 3051w, 2962m, 2922m, 1573m, 1488m, 1435s, 1413m, 1385m, 1307w, 1262m, 1180mw, 1100s, 1026ms, 878w, 804s, 746m, 692s, 624m, 531s, 486s and 402m.

Prepared according to the same method were: *cis*-$Pt[CH_2S(C_6H_4Me\text{-}p)]_2(PMe_3)_2$. White crystalline solid from dichloromethane–methanol. Yield 0.226 g (54%). IR: 3089w, 2950w, 2891w, 1597m, 1560m, 1489s, 1418ms, 1385m, 1301w, 1286w, 1264w, 1119w, 1092w, 1065w, 1015w, 948s, 935s, 859s, 843w, 801s, 727m, 671m, 623m, 586m, 517m, 488s and 399w.

cis-$Pt[CH_2S(C_6H_4Me\text{-}p)]_2(PMe_2Ph)_2$. White crystalline solid from dichloromethane–methanol. Yield 0.258 g (52%) {Found (calc.) for $Pt[CH_2S(C_6H_4Me\text{-}p)]_2(PMe_2Ph)_2$: C, 49.6 (51.53); H, 5.4 (5.41)%}. IR: 3072mw, 2968m, 2916ms, 2854m, 1598m, 1573m, 1489s, 1434s, 1415m, 1385s, 1311w, 1293w, 1279mw, 1262m, 1103s, 1077m, 1014mw, 948m (sh), 942m, 912(sh), 906vs, 866w, 838mw, 808m, 799s, 746m, 707m, 696m, 682m, 624mw, 489m, 438m and 427m.

Preparation of (2-thiapropyl)magnesium chloride. Magnesium granules (6.0 g, 0.25 mol) were placed in a three-necked flask (500 cm^3) fitted with a pressure-equalising dropping funnel and reflux condenser and the apparatus was thoroughly flame-dried. The magnesium was then activated by the addition of 1,2-dibromoethane (0.2 cm^3) in dry degassed thf (30 cm^3). A solution of (chloromethyl) methyl sulfide (2.0 cm^3, 24 mmol) in dry degassed thf (220 cm^3) was added dropwise to the stirred suspension. After stirring for 18 h the mixture was filtered carefully and the effective concentration estimated by titration of a hydrolysed aliquot with aqueous HCl (0.1 M). Yield *ca.* 100% (0.1 M).

Preparation of *cis*-$Pt(CH_2SCH_3)_2(PPh_3)_2$. The compound $PtCl_2(cod)$ (0.75 g, 2.0 mmol) was placed in a flame-dried flask fitted with a graduated pressure-equalising dropping funnel. The solid was suspended in dry degassed thf (25 cm^3) and stirred at −78 °C, $Mg(CH_2SCH_3)Cl$ (42 cm^3, 0.1 M, 4.2 mmol) was transferred to the dropping funnel and added dropwise. The mixture quickly became homogeneous giving a yellow solution. After stirring at room temperature for 10 h the solution was transferred to a solution of triphenylphosphine (1.10 g, 4.2 mmol) in 10% (v/v) acetone–thf (30 cm^3) at −78 °C. The mixture was stirred for 18 h at room temperature before being re-cooled to −78 °C for the addition of saturated aqueous ammonium chloride solution (20 cm^3). The organic layer was collected, dried over $MgSO_4$, filtered and the solvent removed *in vacuo* giving the crude product as a light brown oil. This was recrystallised from dichloromethane–methanol to give a white crystalline solid. Yield 1.15 g (68%) [Found (calc.) for $Pt(CH_2SMe)_2(PPh_3)_2$: C, 51.6 (57.0); H, 5.0 (4.8)%] IR: 3051w, 2963mw, 2892mw, 2861w, 1586w, 1574w, 1478m, 1432s, 1385m, 1301w, 1262s, 1182w, 1093vs, 1026s, 944w, 880w, 802s, 755m, 738m, 692vs, 618mw, 534m, 514s, 495s, 419w and 396w.

Prepared according to the same method were: $Pt(CH_2SCH_3)_2(dppe)$. White crystalline solid from dichloromethane–methanol. Yield 0.27 g (57%) [Found (calc.) for $Pt(CH_2SMe)_2(dppe)$: C, 50.2 (50.3); H, 4.8 (4.8)%]. IR: 3055w, 2965w, 2898m, 2872m, 1598w, 1573w, 1483m, 1434vs, 1417m, 1385m, 1305m, 1264w, 1180w, 1159w, 1103s, 1026mw, 999w, 941w, 888mw, 830m, 748s, 694s, 657vs, 600m, 529vs, 495m, 424mw and 393mw.

cis-$Pt(CH_2SCH_3)_2(PMePh_2)_2$. Off-white microcrystalline solid from benzene–hexane. Yield 0.21 g (44%) [Found (calc.) for $Pt(CH_2SMe_2)_2(PMePh_2)_2$: C, 49.0 (50.2); H, 5.0 (5.1)%]. IR: 3070w, 3046w, 2972w, 2896mw, 1484mw, 1434s, 1385m, 1310w, 1291w, 1122w, 1098m, 1071w, 1027w, 999w, 948w, 898m, 882s, 739m (sh), 733s, 693vs, 618w, 582w, 568w, 522s, 512s, 478ms, 439m and 418m.

cis-Pt(CH$_2$SCH$_3$)$_2$(PMe$_3$)$_2$. The compound Pt(CH$_2$SMe)$_2$(PPh$_3$)$_2$ (0.30 g, 0.36 mmol) was dissolved in dry degassed thf (25 cm^3) and trimethylphosphine (0.9 cm^3, 1.0 M) in thf was added. The mixture was stirred for 24 h and then concentrated *in vacuo* to about one quarter volume and hexane (4 cm^3) added. After cooling at −20 °C for 24 h the white crystalline product was filtered off. Yield 0.20 g (64%). IR: 2965m, 2903m, 1479mw, 1431s, 1385s, 1355mw, 1302w, 1279m, 1263m, 1093ms, 1024m, 977m, 958s, 851w, 803mw, 745m, 697s, 678m, 620mw, 534s, 512m, 497m and 461mw.

[Pt(CH$_2$SCH$_3$)(μ-CH$_2$SCH$_3$)(PPh$_3$)]$_2$. The compound Pt(CH$_2$SMe)$_2$(PPh$_3$)$_2$ (0.20 g, 0.24 mmol) was dissolved in dry degassed dichloromethane (15 cm^3) and stirred at room temperature for 8 d. The solvent was removed *in vacuo* and the solid recrystallised from dichloromethane–methanol to give the white crystalline product. Yield 0.11 g (79%) {Found (calc.) for [Pt(CH$_2$SCH$_3$)(μ-CH$_2$SCH$_3$)(PPh$_3$)]$_2$: C, 43.2 (43.1); H, 4.8 (4.8)%}. IR: 3051w, 2963m, 2900w, 2867w, 1479w, 1432m, 1417mw, 1385w, 1303w, 1262vs, 1095vs, 1024vs, 951w, 863w, 802vs, 755w, 738m, 691s, 619w, 575w, 531s, 510m, 495m and 395m.

Reaction of *cis*-Pt(CH$_2$SCH$_3$)$_2$(PPh$_3$)$_2$ with P(OMe)$_3$. The compound Pt(CH$_2$SMe)$_2$(PPh$_3$)$_2$ (0.30 g, 0.36 mmol) was dissolved in dry degassed thf (20 cm^3). After the addition of P(OMe)$_3$ (0.15 g, excess) the mixture was stirred for 24 h at ambient temperature. The solvent was removed *in vacuo* and the residue washed with hexane (2 × 5 cm^3). Analysis of the crude material by NMR spectroscopy showed a mixture of products A and B, assigned as *cis*-Pt(CH$_2$SMe)$_2$(PPh$_3$)[P(OMe)$_3$] and *cis*-Pt(CH$_2$SMe)$_2$[P(OMe)$_3$]$_2$. NMR (25 °C, CDCl$_3$); ^{1}H (270.17 MHz); A: δ 2.75 ($^2J_{\mathrm{Pt-H}}$, 71.3 Hz, Pt−CH$_2$−S *trans* to PPh$_3$, 2 H), 2.11 [$^2J_{\mathrm{Pt-H}}$, 67.4 Hz, Pt−CH$_2$−S *trans* to P(OMe)$_3$, 2 H], 2.19 (SCH$_3$ *trans* to PPh$_3$, 3 H), 1.63 [SCH$_3$ *trans* to P(OMe)$_3$, 3 H], 3.37 [P(OCH$_3$)$_3$, 9 H]; B: δ 2.59 ($^2J_{\mathrm{Pt-H}}$, 68.0 Hz, Pt−CH$_2$−S, 4 H), 2.16 (SCH$_3$, 6 H), 3.68 [P(OCH$_3$)$_3$, 18 H]; ^{13}C (selected, 67.94 MHz), A: δ 19.59 ($^1J_{\mathrm{Pt-C}}$, 628 Hz, Pt−CH$_2$−S *trans* to PPh$_3$), 29.35 [$^1J_{\mathrm{Pt-C}}$, 607 Hz, Pt−CH$_2$−S *trans* to P(OMe)$_3$]; B: δ 23.51 ($^1J_{\mathrm{Pt-C}}$, 598 Hz, Pt−CH$_2$−S); ^{31}P (109.37 MHz), A: δ 26.00 ($^1J_{\mathrm{Pt-P}}$, 1957 Hz, PPh$_3$), 126.31 [$^1J_{\mathrm{Pt-P}}$, 3408 Hz, P(OMe)$_3$], B: δ 129.51 [$^1J_{\mathrm{Pt-P}}$, 3306 Hz, P(OMe)$_3$].

***cis*-Pt(CH$_2$SPh)(CH$_3$)(PPh$_3$)$_2$.** The compound PtCl(CH$_2$SPh)(PPh$_3$)$_2$ (0.91 g, 0.46 mmol) was placed in a flame-dried flask and dissolved in dry degassed thf (35 cm^3) and stirred at −78 °C. Methyllithium (1.0 cm^3, 1.6 M) in diethyl ether was added dropwise after dilution in further thf (15 cm^3) and the mixture was allowed to warm up to −20 °C. After stirring at this temperature for ≈48 h the mixture was re-cooled to −78 °C and saturated aqueous NH$_4$Cl (15 cm^3) was added. The organic layer was separated and dried over MgSO$_4$, filtered and the solvent removed *in vacuo* to give the product. Recrystallised from dichloromethane–methanol. Yield 0.74 g (84%). IR: 3072m, 3049m, 2939m, 2891m, 2802w, 1579mw, 1475m, 1432s, 1384mw, 1309w, 1263w, 1180w, 1090ms, 997w, 802w, 735m, 692vs, 521s, 494s and 417w.

***cis*-Pt(CH$_2$SPh)(CH$_2$SiMe$_2$Ph)(PPh$_3$)$_2$.** To a flame-dried three-necked flask was added PtCl(CH$_2$SPh)(PPh$_3$)$_2$ (0.20 g, 0.23 mmol). The solid was suspended in dry, degassed diethyl ether (15 cm^3) and stirred at −78 °C, Mg(CH$_2$SiMe$_2$Ph)Cl (0.71 cm^3, 0.48 M) was added dropwise after dilution in diethyl ether (10 cm^3). The mixture was allowed to warm to ambient temperature and stirred for *ca.* 12 h. The reaction was quenched with 10% (v/v) acetone–diethyl ether (20 cm^3) and the solvents evaporated *in vacuo.* The residue was extracted in toluene (3 × 10 cm^3) and concentrated to *ca.* one quarter volume before addition of hexane (8 cm^3). The mixture was stored at −20 °C and a white crystalline solid precipitated. Yield 0.16 g (69%). IR: 3045w, 2954w, 2886w, 2850w, 1577m, 1475m, 1434s, 1384m, 1259w, 1236w, 1184w, 1151w, 1089m, 1022m, 950w, 831w, 811m, 746m, 736m, 725m, 694vs, 626w, 538m, 520m, 511m, 491m, 470w and 418w.

PtCl(CH$_2$SPh)Me$_2$(dmpe). The compound PtMe$_2$(dmpe) (0.15 g, 0.4 mmol) was dissolved in dry degassed thf (25 cm^3) and stirred at 0–5 °C. (Chloromethyl) phenyl sulfide (0.8 mmol, 2 equivalents) was added dropwise and the mixture was stirred at room temperature for *ca.* 12 h. The solvent was removed *in vacuo* to give the crude product. The off-white solid was recrystallised from diethyl ether. Yield 0.12 g (56%). NMR (25 °C, CDCl$_3$); ^{1}H (270.17 MHz); δ 0.72 ($^2J_{\mathrm{Pt-H}}$, 71.9 Hz, Pt−CH$_3$, 3 H), 0.86 ($^2J_{\mathrm{Pt-H}}$, 53.8 Hz, Pt−CH$_3$, 3 H), 1.35 (P−CH$_3$, 3 H), 1.50 (P−CH$_3$, 3 H), 1.68 (P−CH$_3$, 3 H), 1.86 (P−CH$_3$, 3 H), 1.55–2.20 (P−CH$_2$, 4 H), 2.42 ($^2J_{\mathrm{Pt-H}}$, 46.6 Hz, Pt−CH$_2$−S, 1 H), 3.43 ($^2J_{\mathrm{Pt-H}}$, 80.2 Hz, Pt−CH$_2$−S, 1 H), 7.01 (aromatic *p*-H, 1 H), 7.22 (aromatic *m*-H, 2 H), 7.31–7.34 (aromatic, *o*-H, 2 H); ^{13}C (67.94 MHz); δ −5.28 ($^1J_{\mathrm{Pt-C}}$, 627 Hz, Pt−CH$_3$, *trans* to Cl), 2.29 ($^1J_{\mathrm{Pt-C}}$, 482 Hz, Pt−CH$_3$, *trans* to P), 6.42 (P−CH$_3$), 7.81 (P−CH$_3$), 8.88 (P−CH$_3$), 10.15 (P−CH$_3$), 16.64 ($^1J_{\mathrm{Pt-C}}$, 544 Hz, Pt−CH$_2$−S), 27.30 (P−CH$_2$), 27.76 (P−CH$_2$), 123.50 (aromatic C^4), 125.37 (aromatic C^{3,5}), 128.21 (aromatic C^{2,6}), 145.53 (aromatic C^1); ^{31}P (109.37 MHz): δ 2.17 ($^1J_{\mathrm{Pt-P}}$, 1255 Hz, P *trans* to CH$_3$), 6.76 ($^1J_{\mathrm{Pt-P}}$, 1424 Hz, P *trans* to CH$_2$SPh).

PtCl(CH$_2$SPh)Me$_2$(bipy). The compound PtMe$_2$(bipy) (0.20 g, 0.52 mmol) was dissolved in dichloromethane (25 cm^3) and stirred at 0–5 °C. (Chloromethyl) phenyl sulfide (*ca.* 1.0 mmol, 2 equivalents) was added and the mixture was stirred at room temperature for *ca.* 12 h during which time the solution visibly paled from orange to yellow. The solvent was removed *in vacuo* to give the crude product. Recrystallisation from dichloromethane–methanol (1:1) gave the pure product. Yield 89%. NMR (25 °C, CD$_2$Cl$_2$); ^{1}H (270.17 MHz): δ 1.43 ($^2J_{\mathrm{Pt-H}}$, 69.0 Hz, Pt−CH$_3$, 6 H), 2.86 ($^2J_{\mathrm{Pt-H}}$, 64.7 Hz, Pt−CH$_2$−S, 2 H), 6.92–7.50 (aromatic H of SPh), 7.62, 8.00, 8.84 (H of bipy).

Thermolysis

The sample of Pt(CH$_2$SPh)$_2$(dppe)·0.5CH$_2$Cl$_2$ was repeatedly dissolved in toluene and evaporated to dryness. After five cycles the sample was dissolved/suspended in distilled, degassed [^{2}H$_8$]toluene in a Teflon-capped anaerobic NMR tube (J. Young Scientific Glassware, Acton). The sample was then further deoxygenated by five freeze–pump–thaw cycles before heating in a silicone-oil bath. The sample underwent slow conversion to a single product (>90%) at 145 °C over a period of several weeks, monitored by ^{31}P NMR spectroscopy. All spectroscopic parameters are consistent with $\overline{\mathrm{Pt(C_6H_4SC}}\mathrm{H_2)}$(dppe). NMR (25 °C, [^{2}H$_8$]toluene); ^{1}H (270.17 MHz): δ 1.96 (P−CH$_2$, 4 H), 3.95 ($^2J_{\mathrm{Pt-H}}$, 66 Hz, Pt−CH$_2$, 2 H), 6.9–8.0 (aromatic H, 24 H); ^{13}C (67.94 MHz): δ 26.55 (Pt−CH$_2$), 29.31 (P−CH$_2$), 30.81 (P−CH$_2$), 119.36 (SPh, C^4), 120.90 (SPh, C^6), 122.90 (SPh, C^5), 135.94 (SPh, C^3), 143.77 (SPh, C^1), 165.92 (SPh, C^2), 130.4–132.5 (aromatic C of phosphine), 130.6–134.7 (aromatic C of phosphine); ^{31}P (109.37 MHz): δ 50.94 ($J_{\mathrm{Pt-P}}$, 2079 Hz, P *trans* to CH$_2$S), 48.06 ($J_{\mathrm{Pt-P}}$, 1740 Hz, P *trans* to aromatic).

Crystallography

(*a*) *cis*-Pt(CH$_2$SPh)$_2$(PPh$_3$)$_2$·0.5CH$_2$Cl$_2$. *Crystal data.* C$_{50.5}$H$_{45}$ClP$_2$PtS$_2$, $M = 1008.6$, triclinic, space group $P\bar{1}$, $a = 12.177(3)$, $b = 13.887(3)$, $c = 15.123(4)$ Å, $\alpha = 90.31(2)$, $\beta = 94.79(2)$, $\gamma = 113.43(2)°$, $U = 2336$ Å^3 (by least-squares refinement of diffractometer angles for 33 automatically centred reflections in the range $16 < 2\theta < 27°$, $\lambda = 0.710\,73$ Å), $Z = 2$, $F(000) = 1010$, $D_c = 1.43$ g cm^{-3}, μ(Mo-Kα) = 3.27 mm^{-1}. Colourless block 0.56 × 0.48 × 0.44 mm.

The ω–2θ technique was used to measure 8678 reflections (8255 unique) in the range $5 < 2\theta < 50°$ on a Nicolet R3mV diffractometer equipped with graphite-monochromated Mo-Kα radiation. Three standard reflections monitored every 97 scans showed no significant change in intensity throughout the data collection. Data were corrected for Lorentz and polarisation effects and for absorption based on additional azimuthal scan data. Omission of intensities $I < 3\sigma(I)$ gave 7236 observed data which were employed in the analysis. The structure was solved by direct methods and developed using alternating cycles of least-squares refinement and Fourier-difference synthesis. All non-hydrogen atoms were refined anisotropically and hydrogens were placed at idealised positions (C−H 0.96 Å) and assigned a common isotropic thermal parameter ($U = 0.08$ Å^2). In the latter cycles of refinement the presence of lattice dichloromethane was recognised. This was successfully refined with an occupancy of 50%. The final cycles of least-squares refinement included 523 parameters and did not shift any parameter by more than 0.02 times its standard deviation. The final residuals were $R = 0.0337$ and $R' = 0.0370$ [weighting scheme $w^{-1} = \sigma^2(F) + 0.001F^2$].

(*b*) $[Pt(CH_2SCH_3)(\mu\text{-}CH_2SCH_3)(PPh_3)]_2$. *Crystal data.* $C_{40}H_{50}P_2Pt_2S_4$, $M = 1159.3$, monoclinic, space group $P2_1/n$, $a = 11.223(2)$, $b = 21.642(6)$, $c = 18.666(5)$ Å, $\beta = 92.07(2)°$, $U = 4531$ Å^3 (by least-squares refinement of diffractometer angles for 30 automatically centred reflections in the range $10 < 2\theta < 28°$, $\lambda = 0.710\,73$ Å), $Z = 4$, $F(000) = 2256$, $D_c = 1.70$ g cm^{-3}, μ(Mo-Kα) = 6.51 mm^{-1}. Colourless block 0.48 × 0.40 × 0.40 mm.

A total of 8646 reflections (7928 unique) were collected and corrected as described above. Omission of intensities $I < 3\sigma(I)$ gave 5928 observed data which were employed in the analysis. The structure was solved and refined as described above. The final cycles of least-squares refinement included 469 parameters and did not shift any parameter by more than 0.01 times its standard deviation. The final residuals were $R = 0.0339$ and $R' = 0.0341$ [weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,234F^2$].

(*c*) *cis*-$Pt(CH_2SPh)(CH_3)(PPh_3)_2$. *Crystal data.* $C_{44}H_{40}P_2PtS_2$, $M = 857.9$, monoclinic, space group $P2_1/a$, $a = 19.044(7)$, $b = 20.886(9)$, $c = 10.913(5)$ Å, $\beta = 121.33(3)°$, $U = 3708$ Å^3 (by least-squares refinement of diffractometer angles for 28 automatically centred reflections in the range $13 < 2\theta < 25°$, $\lambda = 0.710\,73$ Å), $Z = 4$, $F(000) = 1712$, $D_c = 1.54$ g cm^{-3}, μ(Mo-Kα) = 3.99 mm^{-1}. Colourless block 0.44 × 0.34 × 0.28 mm.

A total of 6839 relfections (6442 unique) were collected and corrected as described above. Omission of intensities $I < 3\sigma(I)$ gave 4536 observed data which were employed in the analysis. The structure was solved by Patterson methods and refined as described above. The final cycles of least-squares refinement included 433 parameters and did not shift any parameter by more than 0.01 times its standard deviation. The final residuals were $R = 0.0354$ and $R' = 0.0338$ [weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,12F^2$].

All calculations were carried out using the SHELXTL PLUS program package[25] on a MicroVax II computer.

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