Fragmentation of Co-ordinated Carbon Disulphide and Dithiocarbene Ligands by Nucleophilic Attack at Carbon: The Crystal Structure of $[(Ph_3P)IPt(\mu\text{-}SMe)(\mu\text{-}CSMe)PtI(PPh_3)]\cdot Me_2CO$†

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Nucleophilic attack at the carbon atom of carbon disulphide in the complex $[Pt(\eta^2\text{-}CS_2)(dppe)]$ [dppe = 1,2-bis(diphenylphosphino)ethane] by the zero-valent platinum complex $[(Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ results in the formation of the dinuclear platinum thiocarbonyl complex $[(dppe)Pt(\mu\text{-}S)Pt(PPh_3)(CS)]$ (**2**). A similar attack at the carbon atom of the dithiocarbene ligand in either of the complexes $[PtI(PPh_3)_2\{C(SMe)_2\}]^+I^-$ (**3**) or $[PtI_2(PPh_3)\{C(SMe)_2\}]$ yields the complex $[(Ph_3P)IPt(\mu\text{-}SMe)(\mu\text{-}CSMe)PtI(PPh_3)]\cdot Me_2CO$, the crystal structure of which has been determined. Crystals of the complex are monoclinic, space group *C*2/*c*, with $Z = 8$, in a unit cell with lattice parameters $a = 27.218(2)$, $b = 11.814(2)$, $c = 27.407(2)$ Å, and $\beta = 99.636(6)°$. The structure has been refined to $R = 0.038$ ($R' = 0.035$) for 3 429 unique data. The complex consists of two distorted square-planar Pt fragments which are held together by bridging –SMe and –CSMe groups. Treatment of the carbene complex (**3**) with dppe yields the new carbene complex $[PtI(dppe)\text{-}\{C(SMe)_2\}]^+I^-$ which reacts similarly with $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ to yield $[(dppe)Pt(\mu\text{-}SMe)(\mu\text{-}CSMe)PtI(PPh_3)]^+I^-$. This latter complex is also the product of the reaction of the thiocarbonyl complex (**2**) with methyl iodide. The complexes have been characterized by elemental analysis, ^1H and $^{31}P\text{-}\{^1H\}$ n.m.r. and i.r. spectroscopy, and conductivity measurements.

Although thiocarbonyl complexes are known for many transition metals,[1] the only reports for the nickel triad are the complex $[Ni(CS)_4]$,[2] obtained by matrix isolation, and two independent reports [3,4] of the cation $[PtCl(CS)(PPh_3)_2]^+$. This latter complex, while exhibiting a strong thiocarbonyl absorption at 1 400 cm^{-1}, was never satisfactorily analysed and is very hydrolytically unstable.

Some years ago Baird and Wilkinson [5] reported that the complex $[Pt(\eta^2\text{-}COS)(PPh_3)_2]$ decomposes in refluxing chloroform to yield a bright yellow crystalline product later shown [6,7] by an *X*-ray structural determination to be the dinuclear platinum(I) complex $[(Ph_3P)_2Pt(\mu\text{-}S)Pt(PPh_3)(CO)]$. Our own studies and several recent publications by Stone and co-workers [8–10] indicate that this latter reaction probably occurs by nucleophilic attack of '$Pt(PPh_3)_2$' (formed *in situ* by dissociation of COS) at the carbon atom of the co-ordinated COS ligand in the complex $[Pt(\eta^2\text{-}COS)(PPh_3)_2]$. The fact that such dissociation readily occurs is shown by the conversion of $[Pt(\eta^2\text{-}COS)(PPh_3)_2]$ to $[Pt(PPh_3)_4]$ [11a] upon addition of phosphine in hexane suspension, or to $[Pt(\eta^2\text{-}CS_2)(PPh_3)_2]$ upon the addition of carbon disulphide.[11b] The product of this attack would be initially the dinuclear complex $[(Ph_3P)_2\text{-}Pt(\mu\text{-}COS)Pt(PPh_3)_2]$, a species which in solution could easily yield by loss of phosphine and C–S bond fission the observed product $[(Ph_3P)_2Pt(\mu\text{-}S)Pt(PPh_3)(CO)]$.

The complex $[Pt(\eta^2\text{-}CS_2)(PPh_3)_2]$ does not decompose in solution by a similar route; in fact we have found [12] that this complex dissociates in refluxing benzene by loss of a phosphine molecule rather than carbon disulphide to yield a polymeric metallodithiocarboxylato species [13] $[\{Pt(PPh_3)CS_2\}_n]$. It has been suggested [11b] that the difference in reactivities between the COS and CS_2 complexes is due to a greater stability of the co-ordinated C=S bond in the CS_2 complex. However if the above reaction does involve nucleophilic attack by a zerovalent platinum species then it seemed likely that if the complex $[Pt(\eta^2\text{-}CS_2)(PPh_3)_2]$ were to be treated with '$Pt(PPh_3)_2$,' introduced as the ethylene complex $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$, the dinuclear thiocarbonyl complex $[(Ph_3P)_2Pt(\mu\text{-}S)Pt(PPh_3)(CS)]$ might be formed by a similar route.

A preliminary report of part of this work has already been published [14] and a recent report [15] has also appeared describing the formation of $[(dppe)Pt(\mu\text{-}Se)Pt(PPh_3)(CS)]$ [dppe = 1,2-bis(diphenylphosphino)ethane] by an analogous attack of the ethylene complex on the complex $[Pt(\eta^2\text{-}CSSe)(dppe)]$.

Results and Discussion

The results of this investigation are summarized in the Scheme.

When a suspension of the complex $[Pt(\eta^2\text{-}CS_2)(PPh_3)_2]$ in acetone was treated with an equimolar amount of $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ a yellow microcrystalline solid was obtained. The product exhibited, in addition to the usual phosphine bands, a medium intensity band in the i.r. at 930 cm^{-1} assignable to $\nu(CS_2)$. The complex is extremely labile in solution and thus n.m.r. and molecular weight studies were precluded. However, elemental analysis, its solution behaviour, and the absorption at 930 cm^{-1} indicate that the complex is indeed that to be expected from nucleophilic attack of $Pt(PPh_3)_2$ at the carbon atom of the

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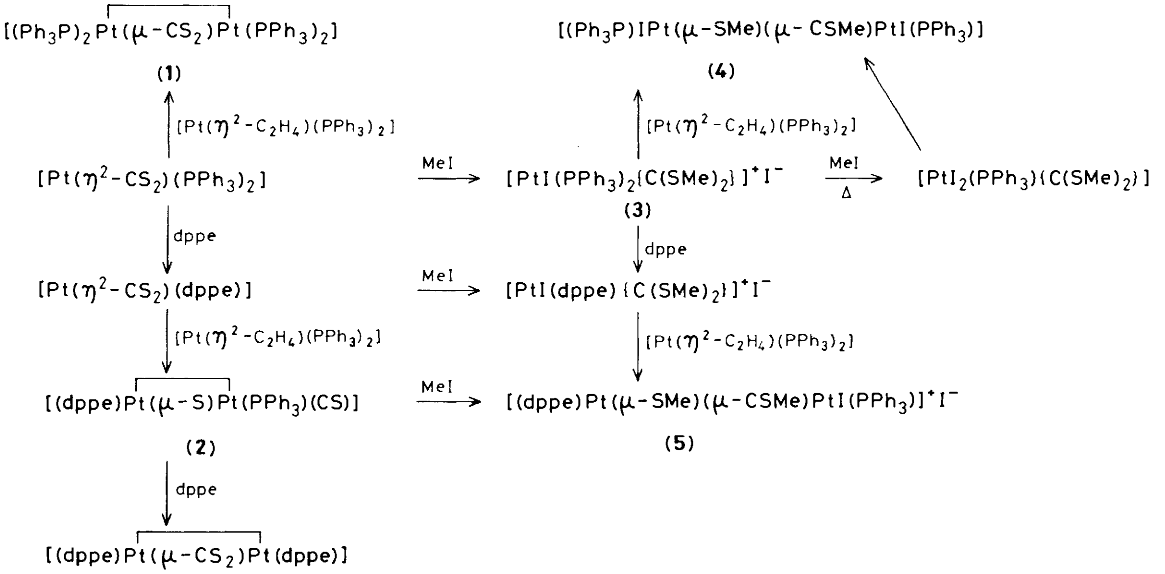
† μ-Methylsulphido-μ-methylthiomethanedi-ido-bis[iodo(triphenylphosphine)platinum]–acetone (1/1).

Supplementary data available (No. SUP 56349, 7 pp.): H-atom co-ordinates, thermal parameters, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Hydrogen-1 and $^{31}P-\{^{1}H\}$ n.m.r. spectra of the complexes at 25 °C[a]

Complex	$\delta(CH_3)$	$\lvert {}^3J(Pt-H)\rvert$	$\lvert {}^4J(Pt-H)\rvert$	$\lvert {}^4J(P-H)\rvert$	$\delta(^{31}P)$	$\lvert {}^1J(Pt-P)\rvert$	$\lvert {}^2J(Pt-P)\rvert$	$\lvert {}^2J(P-P)\rvert$	$\lvert {}^3J(P-P)\rvert$
$[Pt(\eta^2-CS_2)(PPh_3)_2]$					30.9[b]	4 856		18.4	
					19.5	2 815			
$[Pt(\eta^2-CS_2)(dppe)]$					45.8	2 552		34.3	
					39.9[b]	4 485			
$[(dppe)\overline{Pt(\mu-S)}Pt(PPh_3)(CS)]$ (**2**)					63.5	3 353	346.7		152.6
					52.7	3 308	91.6	0	26.7
					32.1	2 485	110.6		
$[PtI(PPh_3)_2\{C(SMe)_2\}]^+I^-$ (**3**)	3.23[c]		7.2[c]		11.0	2 494			
	2.00[c]		6.0[c]						
$[PtI(dppe)\{C(SMe)_2\}]^+I^-$	2.74		n.o.		40.6[d]	3 260		6.0	
	2.70		n.o.		37.1	2 248			
$[(Ph_3P)IPt(\mu-SMe)(\mu-CSMe)PtI(PPh_3)]$ (**4**)	3.44	44.5		5.4	5.4	3 766	29.0[e]		4.8[e]
	1.79		n.o.		5.1	3 659			
$[(dppe)Pt(\mu-SMe)(\mu-CSMe)PtI(PPh_3)]^+I^-$ (**5**)	2.51	42.3		5.3	44.8	2 274			
					35.9[b]	3 380	n.o.	0	
	1.91		n.o.		10.3[b]	3 757			

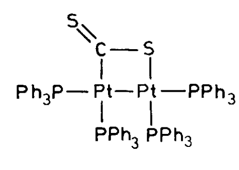
[a] δ In p.p.m., *J* in Hz; n.o. = not observed. [b] Resonance assigned to P atom *trans* to S on the basis of the $J(^{195}Pt-^{31}P)$ coupling constant. [c] Ref. 28. [d] Resonance assigned to P atom *trans* to I on the basis of the $J(^{195}Pt-^{31}P)$ coupling constant. [e] Assignment may be $\lvert {}^3J(Pt-P)\rvert$ and $\lvert {}^4J(P-P)\rvert$ due to absence of a Pt–Pt bond.



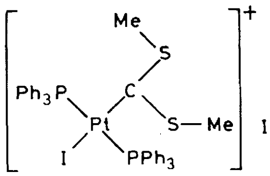
Scheme.

co-ordinated carbon disulphide, namely $[(Ph_3P)_2\overline{Pt(\mu-CS_2)}Pt(PPh_3)_2]$ (**1**).

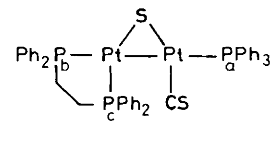
An *X*-ray structural determination[16] of $[Pt_2Cl_2(\mu-CS_2)(\mu-dppm)_2]$ [dppm = bis(diphenylphosphino)methane] shows the presence of a similar bridging CS_2 group between two platinum atoms with a non-co-ordinated *exo* sulphur atom. This complex also shows a medium intensity CS_2 absorption in its i.r. spectrum at 985 cm^{-1}, substantially lower than the values (1 100—1 175 cm^{-1}) normally associated with η^2-CS_2 complexes including those in which the *exo* sulphur atom bridges to another metal.[5,17] In addition a dinuclear platinum complex possessing a similar structure with bridging hexafluoroacetone, $[Pt_2(1,5-C_8H_{12})_2\{(CF_3)_2CO\}]$, has been reported.[18] In solution, complex (**1**) dissociates rapidly and although the i.r. spectrum of the resultant product mixture shows an absorption band at 1 305 cm^{-1} characteristic[19] of the expected terminal thiocarbonyl complex, it has not been possible to satisfactorily characterize this product mixture.



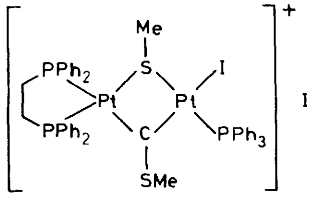
(**1**)



(**3**)



(**2**)



(**5**)

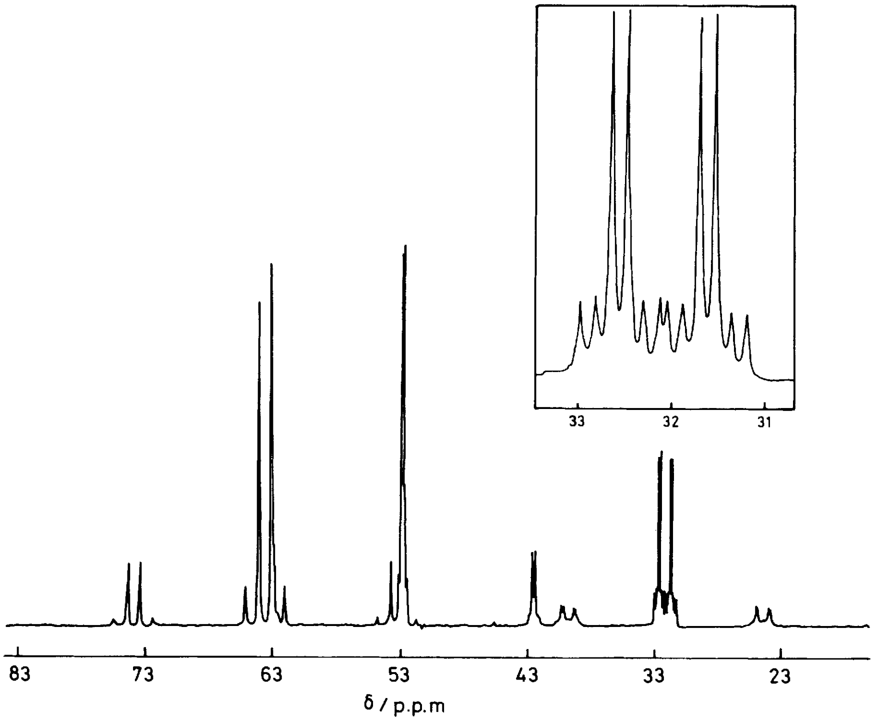


Figure 1. ^{31}P-{^{1}H} N.m.r. spectrum (162 MHz) of [(dppe)Pt(μ-S)Pt(PPh_3)(CS)] (**2**)

We have also prepared the previously unreported red complex [Pt(η^2-CS_2)(dppe)]. The i.r. spectrum of this complex contains bands at 1 141 and 650 cm^{-1} which are characteristic for η^2-CS_2[5,17] complexes and the ^{31}P-{^{1}H} n.m.r. spectrum (Table 1) shows a simple AB spin pattern, which is also consistent with such a structure. When a suspension of this complex was treated with an equimolar amount of [Pt(η^2-C_2H_4)(PPh_3)$_2$] a golden-yellow microcrystalline solid was produced. This product was identified as the novel sulphido-bridged Pt^I dinuclear thiocarbonyl complex [(dppe)Pt(μ-S)Pt(PPh_3)(CS)] (**2**). The complex exhibits a very strong i.r. band at 1 302 cm^{-1} assignable[19] to ν(C≡S) and has a molecular weight of 1 060 (calc. 1 127) measured by osmometry in chloroform solution. The complex is air stable but shows variable reactivity towards chlorinated solvents so that while solutions in chloroform darken after 2—3 h, the same effect only occurs in dichloromethane after several days. The ^{31}P-{^{1}H} n.m.r. spectrum (Figure 1) is consistent with the complex having the structure shown which is similar to that reported[7] for [(Ph_3P)$_2$Pt(μ-S)Pt(PPh_3)(CO)]. The latter complex was reported by Balch and co-workers[20] to occur in four isotopomeric forms resulting from the presence of naturally abundant ^{195}Pt. The spectrum, details of which are given in Table 1, contains three distinct phosphorus resonances [$\delta(P_a)$ 32.1, $\delta(P_c)$ 52.7, $\delta(P_b)$ 63.5 p.p.m.] which are chemically well enough separated from each other to give a first-order spectrum. Coupling is observed across the metal–metal bond between P_a and both P_b and P_c but no *cis* coupling between P_c and P_b is observed and this is consistent with other reports[21,22] of platinum complexes containing the dppe ligand. The assignment of the P_c and P_b resonances follows from their large downfield shift from the free ligand in a five-membered ring chelate[21–24] and the particularly large value of the P_b–P_a coupling constant.[20] The expected ^{195}Pt satellite resonances are all observed for the various isotopomers, including those for the isotopomer containing two ^{195}Pt atoms which is present in only 11.4% natural abundance and produces very weak lines which appear as satellites on the satellite resonances at *ca.* 74, 42.5, 40, and 24 p.p.m.

Nucleophilic attack by zero-valent platinum complexes has also been observed[8,9] to occur at the carbon atom of alkoxycarbene ligands, usually resulting in a bridging carbene ligand between two metals joined by a metal–metal bond. Similar results have been observed[25] with complexes containing carbyne ligands and it has even been possible[26] to interconvert the resultant bridging carbene and carbyne ligands by reactions with strong electrophiles and anionic nucleophiles respectively.

We have recently carried out[27] a single-crystal *X*-ray structure determination of the previously reported[28] dithiocarbene complex [PtI(PPh_3)$_2${C(SMe)$_2$}]$^+$I$^-$ (**3**) and shown it to possess *trans* phosphorus atoms. The single resonance observed in the ^{31}P-{^{1}H} n.m.r. spectrum of complex (**3**) (Table 1) is also consistent with such a structure. The presence of two methyl resonances in the ^{1}H n.m.r. spectrum has been previously assigned[28] to *syn* and *anti* methyl groups in the carbene ligand and this has been confirmed by the *X*-ray structure.[27] When complex (**3**) was reacted with an equimolar amount of [Pt(η^2-C_2H_4)(PPh_3)$_2$] a product was obtained, the i.r. spectrum of which exhibited only a very weak band at 950 cm^{-1} which could possibly be attributed to C–S vibrations. Since neither the i.r. nor the ^{1}H and ^{31}P-{^{1}H} n.m.r. spectra of this product were consistent with the expected bridging dithiocarbene complex a single-crystal *X*-ray structure determination was undertaken and this revealed the complex to be the dibridged diplatinum complex [(Ph_3P)IPt(μ-SMe)(μ-CSMe)PtI(PPh_3)] (**4**).

Crystals of complex (**4**) are built up from discrete dimeric Pt complexes, incorporating acetone in the crystal. The shortest contact between the molecules is 2.26 Å involving H(52) [bonded to C(52)] and H(52′) at (1 − *x*, *y*, 1.5 − *z*). Selected intramolecular distances are presented in Table 2. A perspective

Table 2. Selected bond distances (Å) and angles (°)

Pt(1)–I(1)	2.673(1)	Pt(2)–I(2)	2.656(1)
Pt(1)–P(1)	2.266(4)	Pt(2)–P(2)	2.273(4)
Pt(1)–S(1)	2.387(4)	Pt(2)–S(1)	2.385(4)
Pt(1)–C(2)	1.95(1)	Pt(2)–C(2)	1.97(1)
S(1)–C(1)	1.77(2)	S(2)–C(3)	1.78(1)
S(2)–C(2)	1.66(1)		
P(1)–C(11)	1.82(1)	P(2)–C(41)	1.80(1)
P(1)–C(21)	1.83(1)	P(2)–C(51)	1.81(1)
P(1)–C(31)	1.82(1)	P(2)–C(61)	1.83(1)
I(1)–Pt(1)–P(1)	90.3(1)	I(2)–Pt(2)–P(2)	92.5(1)
I(1)–Pt(1)–S(1)	94.8(1)	I(2)–Pt(2)–S(1)	93.7(1)
P(1)–Pt(1)–C(2)	103.2(4)	P(2)–Pt(2)–C(2)	101.4(4)
S(1)–Pt(1)–C(2)	72.3(4)	S(1)–Pt(2)–C(2)	72.0(4)
Pt(1)–S(1)–Pt(2)	77.7(1)	Pt(1)–C(2)–Pt(2)	99.5(6)
Pt(1)–S(1)–C(1)	112.4(6)	Pt(1)–C(2)–S(2)	122.5(8)
Pt(2)–S(1)–C(1)	112.5(7)	Pt(2)–C(2)–S(2)	133.9(9)
		C(2)–S(2)–C(3)	109.4(8)
C(11)–P(1)–Pt(1)	117.1(4)	C(41)–P(2)–Pt(2)	118.1(4)
C(21)–P(1)–Pt(1)	113.4(3)	C(51)–P(2)–Pt(2)	117.2(3)
C(31)–P(1)–Pt(1)	112.2(3)	C(61)–P(2)–Pt(2)	109.1(3)
C(11)–P(1)–C(21)	103.4(5)	C(41)–P(2)–C(51)	101.5(5)
C(11)–P(1)–C(31)	101.9(4)	C(41)–P(2)–C(61)	105.4(4)
C(21)–P(1)–C(31)	107.7(4)	C(51)–P(2)–C(61)	104.2(5)

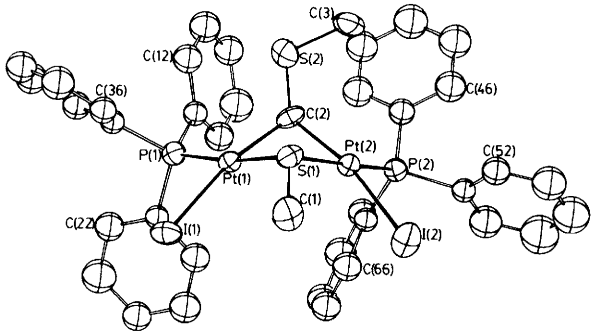


Figure 2. ORTEP Diagram of $[(Ph_3P)IPt(\mu\text{-}SMe)(\mu\text{-}CSMe)PtI(PPh_3)]\cdot Me_2CO$ (**4**)

view of the molecule together with the atom numbering scheme is given in Figure 2.

The complex consists of two distorted square-planar Pt fragments which are held together by bridging SMe and CSMe groups. The largest deviation from a weighted least-squares plane containing Pt(1) and its inner co-ordination sphere is 0.23(1) Å while a distance of 0.26(1) Å is observed in the same calculation for Pt(2). In both cases the atom involved was C(2) and the dihedral angle between the two planes is 69.1(1)°. The two bridging atoms C(2) and S(1) subtend angles of 72.3(4)° at Pt(1) and 72.0(4)° at Pt(2). The remaining angles at the Pt atoms are consistent with a square-planar geometry. The Pt–P distances are equivalent and normal,[29] as are the Pt–I values.[30] The Pt–S(1) bond lengths, 2.387(4) and 2.385(4) Å, are *ca.* 0.16 Å longer (16σ) than the values reported for the sulphido-bridged dimer $[Pt_2(\mu\text{-}S)(CO)(PPh_3)_3]$.[7] This is in accord with the methylation of S(1). The two Pt–C(2) distances, 1.95(1) and 1.97(1) Å, are indistinguishable and equivalent to the value of 1.997(9) Å observed for the Pt–C(bridging carbyne) distance in $[PtW(\mu\text{-}CC_6H_4Me\text{-}p)(CO)_2(PMe_2Ph)_2(\eta^5\text{-}C_5H_5)]$.[25] A value of 2.994(1) Å is calculated for the non-bonded Pt ··· Pt distance.

The angles which are subtended at the bridging atoms S(1) and C(2) are consistent with sp^3 and sp^2 hybridization respectively. This differing hybridization results in a slight tilting of the two square planes as opposed to a symmetric folding. The two C(sp^3)–S distances, C(1)–S(1) and C(3)–S(2), are statistically equivalent [1.77(2) and 1.78(1) Å] and longer than the C(sp^2)–S bond length, C(2)–S(2) [1.66(1) Å]. The C(2)–S(2) distance is comparable to the value reported[31] for the related distance in the complex $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_3(CSEt)][BF_4]$, 1.666(11) Å, and supports the suggestion of significant π-bonding in this C–S bond. A tetrahedral angle of 109.4(8)° is found for C(2)–S(2)–C(3).

All parameters associated with the PPh_3 ligands are normal.[29]

Although the final product from the reaction of complex (**3**) and $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ did not contain the expected bridging carbene ligand, we believe that formation of a bridging dithiocarbene ligand occurred initially followed by intramolecular cleavage of the carbene and oxidative addition of the S–CH_3 group to the metal–metal bond resulting in the formation of complex (**4**). While it would appear that this type of intramolecular conversion of a carbene ligand is unique, Stone and co-workers[32] have suggested the possibility of a closely related reaction. In his case, although the attack of the $p\text{-}MeC_6H_4S^-$ anion on a bridging carbyne ligand produced a stable bridging thiocarbene ligand in the case of $[PtRe(\mu\text{-}CC_6H_4Me\text{-}p)(CO)_2(PMe_2Ph)_2(\eta^5\text{-}C_5H_5)]^+$, a similar reaction with the manganese analogue yielded a product containing the bridging carbene ligand $\mu\text{-}C(PMe_2Ph)C_6H_4Me\text{-}p$, and a terminally bound $SC_6H_4Me\text{-}p$ group. It was suggested that the thiocarbene might have formed initially followed by exchange of the $SC_6H_4Me\text{-}p$ group with the terminal phosphine ligand.

The ^1H n.m.r. spectrum of complex (**4**) (Table 1) shows a single resonance at δ 1.79 p.p.m. for the methyl protons of the bridging CSMe group with no coupling being observed to ^{195}Pt. The expected 1:8:18:8:1 quintet of triplets for the bridging –SMe group (due to coupling to ^{195}Pt and two *trans* phosphorus atoms) is observed as a triplet of triplets (δ 3.44 p.p.m.). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum shows two closely spaced phosphorus resonances (δ 5.4 and 5.1 p.p.m.) which surprisingly, in spite of the relative phosphorus atom positions in the molecule, are weakly coupled to each other (4.8 Hz) and the more distant ^{195}Pt atoms (29 Hz). The large values of the coupling constants arising from the adjacent ^{195}Pt atoms are consistent with the observed *trans* phosphorus–sulphur configurations.

In view of the formation of the neutral complex (**4**) from the cationic carbene complex (**3**), which involves phosphine substitution by iodide, it is perhaps not surprising that complex (**4**) is also the product of the reaction between the ethylene complex and the previously reported[28] neutral carbene complex $[PtI_2(PPh_3)\{C(SMe)_2\}]$.

For comparative purposes we prepared (see Scheme) the new carbene complex $[PtI(dppe)\{C(SMe)_2\}]^+I^-$. This product can also be made, though only in low yield, by direct alkylation of $[Pt(\eta^2\text{-}CS_2)(dppe)]$ with methyl iodide but this reaction is complex and the results will be discussed elsewhere. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of $[PtI(dppe)\{C(SMe)_2\}]^+I^-$ shows a simple AB spin pattern with a small *cis* coupling of 6 Hz. The ^1H n.m.r. spectrum of this carbene complex, like that of complex (**3**), also shows two singlet methyl resonances (due to *syn* and *anti* configurations) but with very similar chemical shifts compared to those observed in the spectrum of complex (**3**) and with no coupling to ^{195}Pt being observed in this case. These resonances are superimposed on a broad multiplet (δ 1.8—3.3 p.p.m.) characteristic[21,33] of the methylene protons of the dppe ligand. The conductivity of $[PtI(dppe)\{C(SMe)_2\}]^+I^-$ is consistent with 1:1 electrolyte behaviour.

When the complex $[PtI(dppe)\{C(SMe)_2\}]^+I^-$ was reacted with equimolar amounts of $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ a similar reaction to that obtained with complex (**3**) occurred. The product has been identified as the cationic complex $[(dppe)Pt(\mu\text{-}SMe)(\mu\text{-}CSMe)PtI(PPh_3)]^+I^-$ (**5**). The product is thus equivalent to complex (**4**) obtained from reaction of the carbene complex (**3**) except that the presence of the chelate diphosphine ligand prevents substitution by the iodide ligand. The ^1H n.m.r. spectrum of complex (**5**) (Table 1) is very similar to that obtained for complex (**4**) with the CSMe resonance occurring as an uncoupled singlet at δ 1.91 p.p.m. and the SMe resonance as a triplet of triplets (δ 2.51 p.p.m.). These data are consistent with the structure shown with the iodide atom *trans* to the CSMe group, as was found in complex (**4**). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of complex (**5**) (Table 1) shows two non-coupled dppe resonances and the resonance for the PPh_3 ligand is observed at δ 10.3 p.p.m., the large value of the ^{195}Pt coupling constant being consistent with the PPh_3 ligand *trans* to the sulphur atom. Unlike complex (**4**), however, no coupling between ^{31}P atoms and the more distant ^{195}Pt or ^{31}P atoms is observable for complex (**5**). Complex (**5**), like complex (**4**), does not exhibit in the i.r. spectrum any absorptions, except for a very weak band at 950 cm^{-1}, which can be attributed to the bridging CSMe ligand. This is also the case with the very few other reports of complexes which contain this ligand.[10,31,34,35] The conductivity of complex (**5**) is consistent with 1 : 1 electrolyte behaviour.

When the thiocarbonyl complex (**2**) was treated with MeI the product obtained was identical to complex (**5**). Balch and co-workers[20] have reported that similar treatment of $[(Ph_3P)_2\overline{Pt(\mu\text{-}S)Pt}(PPh_3)(CO)]$ likewise results in alkylation of the bridging sulphur atom, but in the case of complex (**2**) alkylation of the thiocarbonyl ligand also occurs resulting in oxidation of the metal–metal bond and formation of the bridging CSMe group. As indicated in the Scheme, when the thiocarbonyl complex (**2**) was treated with dppe a highly insoluble lime-green product was formed which by analysis has the composition $Pt_2(dppe)_2CS_2$ and exhibits an identical absorption band in the i.r. (930 cm^{-1}) to that observed for complex (**1**), but no band characteristic of thiocarbonyl ligands. It thus appears possible that the fragmentation of the CS_2 ligand reported in this paper can be reversed under some conditions.

Experimental

All reactions were carried out under an atmosphere of nitrogen. I.r. spectra were determined as KBr discs using a Beckman IR-12 spectrophotometer. Proton and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra were obtained in $CDCl_3$ and CH_2Cl_2 respectively using Bruker WM-250 (operating at 250 and 101.25 MHz) or WH-400 (operating at 400 and 162 MHz) and Varian XL-200 (operating at 200 and 81 MHz) spectrophotometers. Phosphorus-31 chemical shifts were determined with reference to $P(OMe)_3$ but are reported with reference to 85% phosphoric acid; high-frequency shifts are positive. Molecular weights were determined in $CHCl_3$ using a Mechrolab 302 osmometer and conductivities were measured in $MeNO_2$ using a Beckman RC18 Bridge circuit. Microanalyses were performed by Analytische Laboratorien, West Germany. Melting points (uncorrected) were measured on a Reichert hot-stage microscope.

X-Ray Study of Complex (**4**).—Red crystals of $[Pt_2(\mu\text{-}SMe)(\mu\text{-}CSMe)I_2(PPh_3)_2]\cdot Me_2CO$ (**4**) were obtained by recrystallization from acetone. A photographic examination showed the crystals belonged to one of the monoclinic space groups *Cc* or *C*2/*c*. An examination of *X*-ray intensities following data collection strongly suggested a centrosymmetric structure and the chosen space group, *C*2/*c* (C_{2h}, no. 15),[36] was confirmed by a successful analysis.

Crystal data. $C_{42}H_{42}I_2OP_2Pt_2S_2$, M = 1 332.86, monoclinic, a = 27.218(2), b = 11.814(2), c = 27.407(2) Å, β = 99.636(6)°, U = 8 688.2 Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred high-angle reflections, λ =

Table 3. Atomic positional parameters ($\times 10^4$)[a]

Atom	*x*	*y*	*z*
Pt(1)	2 598(1)	4 020(1)	1 638(1)
Pt(2)	3 713(1)	3 989(1)	1 797(1)
I(1)	2 007(1)	2 272(1)	1 321(1)
I(2)	4 262(1)	2 196(1)	1 658(1)
S(1)	3 163(2)	2 929(4)	2 212(1)
S(2)	3 109(2)	6 062(4)	2 276(2)
P(1)	2 062(2)	5 222(3)	1 176(1)
P(2)	4 153(2)	5 138(3)	1 364(2)
C(1)	3 150(7)	1 477(14)	2 057(7)
C(2)	3 160(5)	4 990(11)	1 899(5)
C(3)	3 712(6)	6 474(14)	2 575(6)
C(11)	2 259(4)	6 690(8)	1 145(3)
C(12)	2 188(4)	7 443(8)	1 518(3)
C(13)	2 342(4)	8 567(8)	1 499(3)
C(14)	2 567(4)	8 937(8)	1 108(3)
C(15)	2 639(4)	8 184(8)	735(3)
C(16)	2 485(4)	7 060(8)	753(3)
C(21)	1 908(3)	4 804(9)	525(4)
C(22)	1 453(3)	5 066(9)	232(4)
C(23)	1 358(3)	4 727(9)	−262(4)
C(24)	1 719(3)	4 127(9)	−462(4)
C(25)	2 174(3)	3 864(9)	−168(4)
C(26)	2 268(3)	4 203(9)	326(4)
C(31)	1 478(4)	5 371(8)	1 414(3)
C(32)	1 134(4)	6 205(8)	1 230(3)
C(33)	705(4)	6 356(8)	1 438(3)
C(34)	620(4)	5 672(8)	1 830(3)
C(35)	965(4)	4 839(8)	2 014(3)
C(36)	1 394(4)	4 688(8)	1 806(3)
C(41)	4 203(3)	6 612(9)	1 530(4)
C(42)	3 784(3)	7 311(9)	1 437(4)
C(43)	3 827(3)	8 459(9)	1 556(4)
C(44)	4 287(3)	8 908(9)	1 767(4)
C(45)	4 706(3)	8 209(9)	1 860(4)
C(46)	4 664(3)	7 061(9)	1 741(4)
C(51)	4 798(4)	4 775(9)	1 361(3)
C(52)	5 101(4)	4 410(9)	1 793(3)
C(53)	5 608(4)	4 227(9)	1 798(3)
C(54)	5 813(4)	4 408(9)	1 372(3)
C(55)	5 510(4)	4 773(9)	940(3)
C(56)	5 003(4)	4 957(9)	934(3)
C(61)	3 866(4)	5 113(7)	710(4)
C(62)	3 831(4)	6 078(7)	414(4)
C(63)	3 628(4)	6 004(7)	−86(4)
C(64)	3 461(4)	4 964(7)	−290(4)
C(65)	3 496(4)	3 998(7)	6(4)
C(66)	3 699(4)	4 073(7)	507(4)
O	371(10)	3 385(27)	4 870(11)
C(71)	−324(17)	3 483(43)	4 305(11)
C(72)	−59(10)	3 162(37)	4 770(17)
C(73)	−279(15)	2 563(34)	5 123(16)

[a] Estimated standard deviations are given in parentheses, and correspond to the least significant digit(s). Positional parameters are given as fractional co-ordinates.

0.710 73 Å), $D_m = 2.03$ g cm^{-3}, $Z = 8$, $D_c = 2.04$ g cm^{-3}, $F(000) = 5\,148$. Crystal dimensions 0.006 × 0.020 × 0.010 cm; crystal faces {100}, {010}, {101}; μ(Mo-K_α) = 80.95 cm^{-1}.

Data collection and processing. CAD4 Diffractometer, $\theta/2\theta$ mode with scan width 0.80 + 0.35 tanθ, scan speed 1.0—11.0° min^{-1}, graphite-monochromated Mo-K_α radiation; 5 793 reflections measured ($1.0 \leqslant 2\theta \leqslant 45°$; $+h$, $+k$, $\pm l$), 3 429 unique (merging $R = 0.02$, data reduction SDP package*), empirical absorption corrected data[37] (transmission coefficients 0.655—1.00) with $I > 3\sigma(I)$; no decay observed.

Structure analysis and refinement. Patterson syntheses (Pt) followed by difference Fourier syntheses were employed using SHELX.[38] Full-matrix least-squares refinement was carried out. Rigid-group constraints were applied to the phenyl rings (D_{6h} symmetry and a C–C bond length of 1.395 Å). Hydrogen atoms were located in a difference Fourier synthesis and included in subsequent calculations with idealized positional co-ordinates (either sp^2 or sp^3 geometries and a C–H bond distance of 0.95 Å) but not refined. The refinement converged at $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.0379$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.0349$ with weights given by $w^{-1} = \sigma(F)^2 + 0.000\,096F^2$ (3 429 observations and 208 variables). In the final cycle no shift exceeded 0.09 of its standard deviation. A total difference Fourier synthesis calculated from the final structure factors contained no features of chemical significance with the highest peak, of electron density 0.86 e A^{-3}, at fractional co-ordinates (0.444, 0.441, 0.145). Final positional parameters for the non-hydrogen atoms are given in Table 3.

Preparation of the Complexes.—[Pt(η^2-CS_2)(PPh_3)$_2$],[5] [Pt(η^2-C_2H_4)(PPh_3)$_2$],[39] [PtI(PPh_3)$_2${C(SMe)$_2$}]$^+$I$^-$,[28] and [PtI$_2$(PPh_3){C(SMe)$_2$}][28] were prepared by literature methods.

[Pt(η^2-CS_2)(dppe)]. The complex [Pt(η^2-CS_2)(PPh_3)$_2$] (1.922 g, 2.41 mmol) was suspended in carbon disulphide (20 cm^3) and a solution of dppe (0.964 g, 2.41 mmol) in carbon disulphide (10 cm^3) added dropwise with stirring. The original solid dissolved yielding a red solution from which the product was immediately deposited as small red plates. These were filtered off and washed with carbon disulphide and light petroleum (b.p. 30—60 °C). Yield 1.46 g (90%), m.p. 190—200 °C (Found: C, 48.15; H, 3.55; S, 9.30. $C_{27}H_{24}P_2PtS_2$ requires C, 48.45; H, 3.60; S, 9.55%).

[(Ph_3P)$_2$$\overline{\text{Pt}(\mu\text{-CS}_2)\text{Pt}}$($PPh_3$)$_2$] (**1**). The complex [Pt(η^2-CS_2)(PPh_3)$_2$] (0.25 g, 0.314 mmol) was suspended in acetone (15 cm^3) and [Pt(η^2-C_2H_4)(PPh_3)$_2$] (0.235 g, 0.314 mmol) added. The suspension was stirred for 90 min, during which time the flask was protected from light. The product separated from solution as a microcrystalline yellow solid. This was filtered off in subdued light and washed well with acetone. Yield 0.38 g (80%), m.p. 125—127 °C (Found: C, 57.70; H, 4.05; S, 4.10. $C_{73}H_{60}P_4Pt_2S_2$ requires C, 57.85; H, 4.00; S, 4.25%).

[(dppe)$\overline{\text{Pt}(\mu\text{-S})\text{Pt}}$($PPh_3$)(CS)] (**2**). The complex [Pt(η^2-CS_2)(dppe)] (0.224 g, 0.334 mmol) was suspended in acetone (15 cm^3) and [Pt(η^2-C_2H_4)(PPh_3)$_2$] (0.25 g, 0.334 mmol) added. The mixture was stirred for 1 h during which time all solids dissolved to give a red solution from which the crude product separated as a microcrystalline yellow solid. This was filtered off and washed with acetone and then recrystallized from CH_2Cl_2–MeOH. Yield 0.245 g (65%), m.p. >350 °C (decomp.) (Found: C, 47.85; H, 3.55; S, 5.85. $C_{45}H_{39}P_3Pt_2S_2$ requires C, 47.95; H, 3.50; S, 5.70%).

[PtI(dppe){C(SMe)$_2$}]$^+$I$^-$. The complex [PtI(PPh_3)$_2${C(SMe)$_2$}]$^+$I$^-$·1.7CH_2Cl_2 (0.30 g, 0.245 mmol) was dissolved in CH_2Cl_2 (50 cm^3) and dppe (0.098 g, 0.246 mmol) added. After stirring for 30 min the solvent was removed under vacuum and the resultant yellow glass was extracted with acetone. Following filtration to remove a pale yellow solid (0.025 g) whose properties indicated it to be [PtI$_2$(dppe)], a clear yellow filtrate was obtained. The volume was reduced to 20 cm^3 and toluene (5 cm^3) was added. Upon the addition of hexane fine pale yellow crystals were precipitated. The crude product was recrystallized from acetone–toluene–hexane to yield pale yellow crystals. Yield 0.140 g (60%), m.p. 180—181 °C (Found: C, 36.85; H, 3.15; I, 25.20; S, 6.30. $C_{29}H_{30}I_2P_2PtS_2$ requires C, 36.55; H, 3.15; I, 26.60; S, 6.70%). Molar conductivity (10^{-3} mol dm^{-3} solution in $MeNO_2$) 92.2 Ω^{-1} cm^2 mol^{-1}.

[(Ph_3P)IPt(μ-SMe)(μ-CSMe)PtI(PPh_3)]·Me_2CO (**4**). (*a*) [PtI(PPh_3)$_2${C(SMe)$_2$}]$^+$I$^-$·1.7CH_2Cl_2 (0.240 g, 0.196 mmol) was dissolved in freeze-degassed CH_2Cl_2 (20 cm^3) and [Pt(η^2-C_2H_4)(PPh_3)$_2$] (0.150 g, 0.200 mmol) was added. A red solution was obtained which was stirred for 4 h. The solvent was then reduced to *ca.* 2 cm^3, placed on a silica gel column and eluted with CH_2Cl_2. A small orange fraction was eluted first and was discarded. A second larger red fraction was then collected and the solvent removed under vacuum. The product was recrystallized slowly from pure acetone as an orange-red crystalline solvate. Yield 0.120 g (46%), m.p. 237—239 °C (Found: C, 37.75; H, 3.25; I, 19.95; S, 4.70. $C_{42}H_{42}I_2OP_2Pt_2S_2$ requires C, 37.85; H, 3.15; I, 19.05; S, 4.80%).

(*b*) An identical product was obtained when the above reaction was carried out using the neutral carbene [PtI$_2$(PPh_3){C(SMe)$_2$}] as starting material. Yield 56%.

[(dppe)Pt(μ-SMe)(μ-CSMe)PtI(PPh_3)]$^+$I$^-$ (**5**). (*a*) [PtI(dppe){C(SMe)$_2$}]$^+$I$^-$ (0.173 g, 0.181 mmol) was dissolved in freeze-degassed CH_2Cl_2 (25 cm^3) and [Pt(η^2-C_2H_4)(PPh_3)$_2$] (0.135 g, 0.181 mmol) was added. A clear red solution formed quickly which was stirred for 4 h. The solvent was reduced to *ca.* 2 cm^3 and then placed on a silica gel column. The column was eluted with CH_2Cl_2 containing 15% acetone. A small amount of pale yellow material was eluted first as a narrow band and was discarded. A second much larger intense red band followed which was rather broad. The solvent was removed from this fraction under vacuum and the resulting solid was recrystallized from dichloromethane–ethanol–hexane as small orange-red plates. Yield 0.172 g (67%), m.p. 173—176 °C (Found: C, 39.65; H, 3.10; I, 16.05; S, 3.95. $C_{47}H_{45}I_2P_3Pt_2S_2$ requires C, 40.00; H, 3.20; I, 18.00; S, 4.55%). Molar conductivity (10^{-3} mol dm^{-3} solution in $MeNO_2$) 75.5 Ω^{-1} cm^2 mol^{-1}.

(*b*) [(dppe)$\overline{\text{Pt}(\mu\text{-S})\text{Pt}}$($PPh_3$)(CS)] (0.102 g) was reacted with methyl iodide (5 cm^3) for 10 min. The solution initially turned bright green and then red. Hexane (100 cm^3) was then added which precipitated a bright orange solid. This solid was filtered off, washed with hexane, dissolved in a minimum of CH_2Cl_2 and placed on a silica-gel column. The column was eluted with CH_2Cl_2 containing 10% acetone. A small amount of buff coloured material came off the column first and was not identified. This was followed by an orange-red fraction which was recrystallized from dichloromethane–hexane and obtained as a microcrystalline orange-red solid. Yield 0.104 g (81%), m.p. 173—176 °C.

[(dppe)$\overline{\text{Pt}(\mu\text{-CS}_2)\text{Pt}}$(dppe)]. The complex [(dppe)$\overline{\text{Pt}(\mu\text{-S})\text{Pt}}$($PPh_3$)(CS)] (0.10 g, 0.089 mmol) was suspended in acetone (25 cm^3) and dppe (0.036 g, 0.090 mmol) was added. The suspension was stirred for 1 h during which time the thiocarbonyl complex slowly dissolved and a lime-green solid was deposited. This was filtered off and washed with acetone. Yield 0.106 g (95%), m.p. 239 °C (Found: C, 50.35; H, 3.95; S, 5.15. $C_{53}H_{48}P_4Pt_2S_2$ requires C, 50.40; H, 3.85; S, 5.10%).

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* Enraf-Nonius Structure Determination Package running on a DEC PDP-11/23 computer.

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