Reactions of Cyclopalladated Compounds. Part 21.[1] Various Examples of Sulphur-assisted Intramolecular Palladation of Aryl and Alkyl Groups

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The cyclopalladation reactions of several sulphur-containing ligands have been investigated. The thioethers benzyl methyl sulphide, methyl naphthyl sulphide, 2,6-dimethylphenyl methyl sulphide, and neopentyl phenyl sulphide have been metallated by palladium acetate in acetic acid at either aryl or alkyl carbon atoms to afford, after reaction with lithium chloride in acetone, dimeric chloride-bridged cyclopalladated complexes in moderate (22%) to good (81%) yields. In these products each metal is part of a five-membered ring. The same reaction with 2-biphenyl methyl sulphide afforded a dimeric complex containing a six-membered cyclopalladated ring through palladation of the *ortho* position of the biphenyl group. 4,4′-Dimethoxythiobenzophenone and *N*,*N*,*N*′,*N*′-tetramethylthiourea have been palladated by using a ligand-exchange reaction with $[\{Pd(C_6H_4CH_2NMe_2\text{-}2)Cl\}_2]$ in the presence of stoicheiometric amounts of trifluoroacetic acid. This afforded good yields of dimeric palladocyclic complexes through the metallation of a carbon *ortho* to the thioketone, or of a methyl group of the thiourea respectively. With 1,3-bis(methylthiomethyl)benzene this latter reaction, by metallation of the 2 position of the aryl ring, afforded excellent yields of a monomeric compound in which both sulphur atoms are co-ordinated to the palladium centre.

The metallation of organic substrates by transition-metal complexes where the formation of the metal–carbon bond is assisted by a two-electron donor atom is very well documented.[2] It is noteworthy that this intramolecular activation of a carbon–hydrogen bond has often been encountered for nitrogen-containing ligands, the metal being, in most cases palladium(II). The cyclopalladated compounds thus obtained have been shown to be important starting materials for organic syntheses, and it is possible to observe either the selective functionalization of the metallated carbon atom[2i] or the formation of heterocyclic compounds through reactions involving both the palladated carbon atom and the co-ordinated nitrogen atom of the ligand.[2i,3] In this respect we have recently found that these organometallic compounds can be activated by using their iodide or cationic derivatives, so that reactions with internal alkynes afford several new syntheses of heterocyclic compounds, the nitrogen atom being part of six- to eight-membered rings.[3b–d]

We anticipated that these procedures for obtaining heterocycles would be of great potential interest if they could be extended to the synthesis of sulphur-containing molecules. However, since the number of cyclopalladated complexes in which a sulphur atom is part of the metallocyclic unit is relatively limited compared to their nitrogen counterparts,[2d,4] a prerequisite for the achievement of our goal was to increase the availability of such compounds.

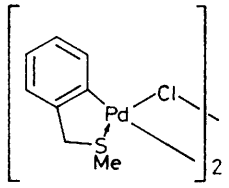
The major aim of this work was to ascertain whether or not there is a thermodynamic reason for the non-palladation of sulphur-containing ligands (abbreviated hereafter as S ligands) and to see whether this difficulty could be overcome by using the new metallating agents reported recently. In this paper we describe several unprecedented metallation reactions of a number of S ligands by palladium(II) that lead to a variety of new cyclopalladated compounds.

Results and Discussion

Synthesis of Sulphur-containing Cyclopalladated Complexes by Metallation of Aryl Groups.—It has been reported by several authors that benzyl methyl sulphide cannot be metallated by palladium(II) compounds.[5,6] However, it was shown that this ligand can be easily metallated by manganese(I) when using $[MnR(CO_5)]$ (R = Me or CH_2Ph) as the starting material.[6] The reason for the non-palladation in the previous attempts is likely to be due to the fact that chloride-containing palladium complexes $\{Li_2PdCl_4$ or $[Pd(PhCN)_2Cl_2]\}$ were used.[5,6] We have now found that treating $PhCH_2SMe$ with palladium acetate in acetic acid at reflux temperature affords good yields[3b] of the desired chloride-bridged cyclopalladated complex $[\{Pd(C_6H_4CH_2SMe\text{-}2)(\mu\text{-}Cl)\}_2]$, (**1**), after treatment with LiCl. Thus, the presence at the sulphur atom of bulky groups such as phenyl, t-butyl, or isobutyl is by no means necessary to achieve palladation of the benzyl unit of these thioethers.[4k]

The direct palladation of a ligand by palladium acetate can also be successfully employed for metallating the second peri position of the naphthyl group in methyl 1-naphthyl sulphide. The compound $[\{Pd(C_{10}H_6SMe\text{-}8)(\mu\text{-}Cl)\}_2]$, (**2**), was thus synthesized in good yields. When this method was applied to the palladation of one *ortho* carbon atom of 2-biphenyl methyl sulphide it led almost quantitatively to the formation of the chloride-bridged dimeric complex $[\{Pd[C_6H_4(C_6H_4SMe\text{-}o)\text{-}2](\mu\text{-}Cl)\}_2]$, (**3**), with the palladium being part of a six-membered ring. This type of compound, in which the metallocyclic unit contains six atoms, is still rare for nitrogen-containing ligands[7] and to our knowledge no such example for S ligands has ever been described in the literature, if one excludes the compounds obtained by Holton *et al.*[4l] who palladated methylthiomethyl derivatives of *O*,*N*-dimethylnorbelladine [belladine = 4-(*p*-hydroxyphenylethylaminomethyl)pyrocatechol)]. The metallation of the aryl ring in these ligands is assisted both by a nitrogen and a sulphur atom, this giving rise to five- and six-membered cyclopalladated rings respectively.[4l]

It is known that 4,4′-dimethoxythiobenzophenone can be palladated by Na_2PdCl_4 to afford compound (**4**) but in only 45% yield.[4a] The yield of compound (**4**) can be markedly



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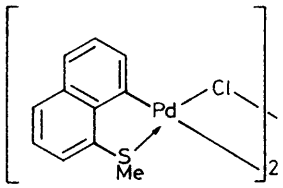

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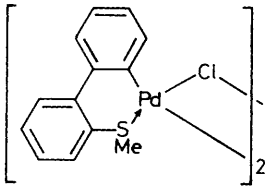
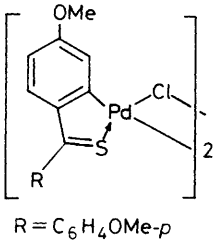


(3)

improved by using a recently described method[8] which consists in a ligand-exchange reaction between $[\{Pd(C_6H_4CH_2NMe_2\text{-}2)(\mu\text{-}Cl)\}_2]$ and the ligand that has to be metallated. Use of this new palladation method, *i.e.* the exchange of a ligand between 4,4′-dimethoxythiobenzophenone and $[\{Pd(C_6H_4CH_2NMe_2\text{-}2)(\mu\text{-}Cl)\}_2]$ in the presence of 1 equivalent of trifluoroacetic acid per palladium atom led to the formation of (**4**) in greater than 85% yield.

The direct palladation at the 2 position of the 1,3-bis(methylthiomethyl)benzene occurred almost quantitatively with this method, affording the monomeric bicyclic compound (**5**) in which both sulphur atoms are linked to the palladium



R = C_6H_4OMe-*p*

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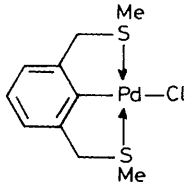
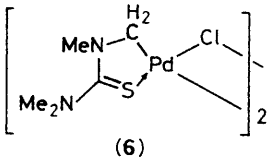


(5)

centre. It is noteworthy that the reaction of 1,3-bis(methylthiomethyl)benzene with palladium acetate in acetic acid followed by metathesis of the acetato group by LiCl afforded compound (**5**) in less than 10% yield.

Synthesis of Sulphur-containing Cyclopalladated Complexes by Metallation of Alkyl Groups.—It has been shown in many instances that the metallation of methyl groups of various nitrogen- or phosphorus-containing ligands can readily be achieved.[2] The situation is very different from S ligands for which only two examples of metallation of methyl groups have been reported so far; it was shown that *N*,*N*-dimethylthiobenzamide can be palladated at one of the methyl groups,[4g] whereas *N*,*N*,*N*′,*N*′-tetramethylthiourea also undergoes a similar reaction but with Pt^{II}.[9] Since these reactions led to the first successful metallations of *N*-methyl groups, it was therefore very tempting to check whether the latter reaction with tetramethylthiourea could also be performed with Pd^{II}.

We found that upon treatment of a red solution of $[\{Pd(C_6H_4CH_2NMe_2\text{-}2)Cl\}_2]$–$CF_3CO_2H$ in toluene with tetramethylthiourea at room temperature an orange-yellow precipitate was formed. Since the ^1H n.m.r. spectrum of this product displays only one singlet at 3.25, it is most likely to be a palladium complex containing the urea ligand co-ordinated to the metal *via* its sulphur atom only. Heating a suspension of the latter product in toluene at reflux for *ca.* 2 h afforded almost quantitatively the pale yellow, dimeric cyclopalladated complex (**6**).

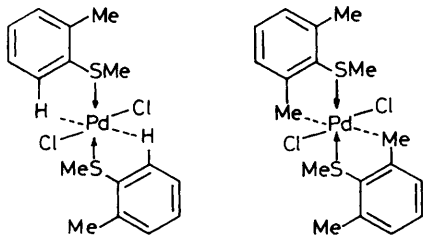


(6)

The ^1H n.m.r. spectrum of (**6**) in CD_2Cl_2 at 200 MHz is temperature dependent. Thus at low temperatures (below −30 °C) the methylene protons appear as an AB spin system centred at 4.0 p.p.m. The signals of these protons broaden at higher temperature and coalesce at *ca.* 5 °C. This behaviour can be explained by inversion of the configuration of the endocyclic nitrogen atom in (**6**), leading to equivalent methylenic environments at temperatures above 5 °C.[10]

Attempts to palladate the methyl group *ortho* to the SMe unit of methyl 2-tolyl sulphide led only to the stable bis adduct $[Pd(MeC_6H_4SMe\text{-}2)_2Cl_2]$, (**7**) whatever the starting palladium complex. The reaction between 2,6-dimethylphenyl methyl sulphide and lithium tetrachloropalladate in methanol afforded the stable bis adduct (**8**), whereas with palladium acetate [following a procedure similar to that used for the synthesis of (**1**)] the cyclopalladated dimer (**9**) was obtained in good yields. The structure of this latter compound is based on its ^1H n.m.r. spectrum in which the palladated CH_2 group appears as an AB pattern because of the chirality of the sulphur atom. Thus the two latter S ligands, methyl 2-tolyl sulphide, and 2,6-dimethylphenyl methyl sulphide, display different behaviour in the palladation reaction of the tolyl methyl unit. This difference can be understood by examining the ^1H n.m.r. spectra of the adducts (**7**) and (**8**). The spectrum of compound (**8**) in CD_2Cl_2 at 200 MHz is temperature dependent. At room temperature it shows a singlet at 2.81 for the two methyl groups *ortho* to the SMe unit. However, at −97 °C this signal is split into two singlets at 3.08 and 2.47. The signal at lower field can be assigned to a methyl group in an axial position with respect to the metal co-ordination plane interacting with the palladium centre. Indeed, it has been shown that when a proton interacts with a palladium atom in its axial position it should experience a significant down-field shift.[11,12] In the ^1H n.m.r. spectrum of compound (**7**) at room temperature the signal for the aromatic proton *ortho* to the SMe unit is found at 7.86, *i.e.* it is shifted significantly down-field compared to the other aromatic protons. Therefore, in this compound the conformation of the co-ordinated ligand is such that interaction of the methyl *ortho* to the SMe unit with the palladium centre cannot occur, this role being played by an aromatic proton, whereas in (**8**) this metal–methyl interaction is always possible. This different behaviour might well explain why the metallation of the latter ligand takes place whereas that of the former, S ligand, does not.

This result is in agreement with that observed earlier for the closely related dimethyl(2-tolyl)amine. In this case too we isolated an adduct $[\{Pd(MeC_6H_4NMe_2\text{-}2)Cl_2\}_2]$ in which the ligand is bonded to the palladium centre *via* its NMe_2 unit only and for which the ^1H n.m.r. spectrum showed a clear downfield shift of the methyl *ortho* to the NMe_2 group.[13b] Here again, the configuration of the co-ordinated ligand is imposed by steric hindrance around the NMe_2 group so that the methyl unit must be interacting with the palladium centre. This ligand was



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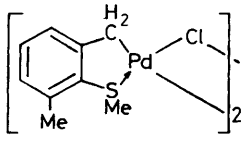
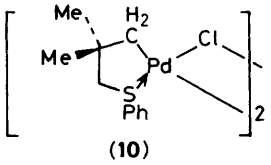


(9)

shown to be easily palladated at the methyl tolyl group by palladium acetate and the compound $[Pd_3(CH_2C_6H_4NMe_2\text{-}2)_2(O_2CMe)_4]$ was obtained in high yields.[13] It is well established, however, that this 'non-bonding' interaction of C–H groups with palladium(II) centres evidenced in complexes (**7**), (**8**), and $[\{Pd(MeC_6H_4NMe_2\text{-}2)Cl_2\}_2]$ is not the true intermediate stage in the C–H bond activation process. Recently Deeming *et al.*[11] reported that this latter reaction can only occur when the C–H bond is activated by Pd^{II} within the co-ordination plane of the metal. Nevertheless, our results show that if a C–H · · · Pd interaction in an axial position of the metal co-ordination plane does not exist, the metallation of this C–H group cannot occur. This clearly means that if the methyl group of a ligand is not forced into the co-ordination sphere of the palladium centre it is unlikely that the metallation reaction of such a group will be observed.

It is known that one methyl group of dimethyl(neopentyl)-amine can be metallated by palladium acetate to afford trimetallic species.[14] More recently it was reported that the reaction between neopentyl t-butyl sulphide and palladium acetate in benzene afforded a trimetallic complex $[Pd_3(Bu^tSCH_2Bu^t)_2Ph_2(O_2CMe)_4]$ arising from the metallation of the solvent (benzene), and that no cyclopalladated complexes were detected.[15] In contrast we found that treatment of the related neopentyl phenyl sulphide ligand with palladium acetate in acetic acid, followed by reaction with LiCl in acetone, led to the cyclopalladated complex (**10**) in moderate but reasonable yields (22%). This marked difference is obviously due, not only to the different solvent used in these reactions (benzene *vs.* acetic acid), but also to the different substituents present on the sulphur atom (t-butyl *vs.* phenyl).



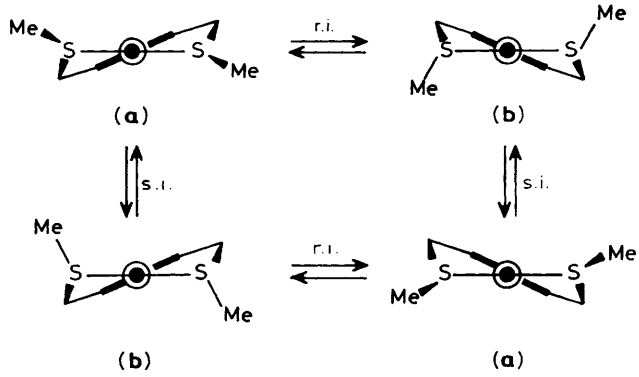
(10)

Behaviour of Cyclopalladated Thioether Compounds in Solution.—The ^1H n.m.r. spectra of the cyclopalladated compounds (**1**)—(**3**), (**5**), (**9**), and (**10**), taken at various temperatures, show that these compounds are fluxional in solution. Indeed, that of compound (**3**) at room temperature shows broad signals for all the protons of the molecule whereas the methylene groups of compound (**5**) appear as two broad signals under the same conditions. Compound (**10**) shows two singlets at 2.84 and 2.39 p.p.m. for the CH_2 units and the two methyl groups give rise to one singlet only at 1.11 p.p.m. These latter features are obviously in contradiction to the existence of a pyramidal sulphur atom which, when co-ordinated to the palladium centre, must be chiral.

The fluxionality of the molecules studied in this paper can be assigned to the existence of two independent phenomena: (*i*) the pyramidal inversion of the sulphur unit[16] and/or (*ii*) the inversion of the ring puckering of the palladocycles which has been shown to occur in many related five-[17] or six-membered[7d,e,18] metallated rings (see the Scheme).

The low-temperature spectra of compounds (**3**) and (**10**) show a significant broadening of the signals, but we could not reach the slow-exchange limit for these two species. In the ^1H n.m.r. spectrum of compound (**1a**) at room temperature the prochiral methylene groups appear as a single AB pattern whereas a singlet is observed for the methyl group. This feature militates in favour of a symmetrical compound, *i.e.* the sulphur atoms should be *trans* to each other with respect to the Pd_2Cl_2 bridge. This molecule is, however, also fluxional since at temperatures below −40 °C the resonance of the SMe group separates into two singlets, and below −80 °C the AB pattern of the methylene protons becomes more complicated. Unfortunately our investigations on this fluxionality were limited due to extensive precipitation of the complex at lower temperature, resulting in poorly resolved spectra.

Compound (**5**), however, was more amenable to a variable-temperature study. The coalescence of the methylene signals and those of the methyl groups occurred at *ca.* 45 and −5 °C respectively. Below −30 °C the CH_2 units appeared as two well resolved AB patterns. This points to the presence of two isomers present in a 4:5 ratio. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum at −40 °C confirmed this hypothesis since it revealed the presence of only two species with non-equivalent populations. Moreover, the aromatic carbon atoms appeared as eight singlets and therefore we conclude that each isomer has a C_2 symmetry axis which contains the palladium and the chlorine atoms as well as the C(1) and C(4) carbon atoms of the aryl ring. Thus the two isomers [(**a**) and (**b**)] present in solution should be of the type described in the Scheme. It is reasonable to assume,



Scheme. Newman projection of the two isomers (**a**) and (**b**) of compound (**5**), showing the two ways through which they can interconvert: r.i. = ring inversion; s.i. = sulphur inversion

on steric grounds, that the most abundant isomer is (**b**), which has the methyl groups in the axial position with respect to the palladium co-ordination plane. This was indeed the structure found in the solid state for a related compound in which the methyl groups were replaced by t-butyl moieties.[4h] It is clear that either inversion of the configurations at the sulphur atoms, or ring puckering, can explain the fluxionality of the molecule.

At this stage of our investigations we are unable to make a definitive statement about which of these processes is operative.

Experimental

Unless otherwise specified the reactions were routinely carried out using Schlenk techniques under an atmosphere of pure dry nitrogen and using dry oxygen-free solvents. Infrared spectra were recorded as KBr pellets in the region 4 000—400 cm^{-1} on a Perkin-Elmer 398 spectrophotometer, ^1H and ^{13}C-$\{^1H\}$ n.m.r. spectra at 200.13 and 100.26 MHz using a Bruker SY200 and a AM400 instrument, respectively. Proton and carbon chemical shifts are positive downfield relative to external $SiMe_4$. Elemental analyses were carried out by the Service Central de Microanalyses du CNRS (France). Analytical data and ^1H n.m.r. data for compounds (**1**)—(**10**) are given in Tables 1 and 2, respectively.

Syntheses.—The complex $[\{Pd(C_6H_4CH_2NMe_2\text{-}2)(\mu\text{-}Cl)\}_2]$ was prepared according to a previously described method.[19] All other reagents were obtained from commercial sources and were used as received without further purification.

Syntheses of the S Ligands.—The S ligands were prepared using slight modifications of the literature method.[20] Two typical examples are given below.

2,6-*Dimethylphenyl methyl sulphide*. To a stirred solution of 2-bromo-1,3-dimethylbenzene (8.2 cm^3, 60 mmol) in hexane (80 cm^3) and diethyl ether (2 cm^3), n-butyl lithium (40 cm^3, 1.6 mol dm^{-3} in hexane) was added dropwise. The mixture was heated at reflux temperature for 2 h and then stirred at room temperature for 15 h. The white precipitate thus obtained was filtered off, washed with hexane (3 × 20 cm^3), and dried *in vacuo* (4.0 g, 60%). This lithium compound was dissolved in tetrahydrofuran (thf) (60 cm^3) and sulphur (1.2 g, 40 mmol) in thf (40 cm^3) was added dropwise. The reaction mixture was stirred at room temperature for 2 h, methyl iodide (8.5 g, 60 mmol) was added, and the orange-red solution was stirred at room temperature for 15 h. The solvent was then removed under reduced pressure at 20 °C, and water (50 cm^3) was added. The organic product was extracted with hexane (4 × 60 cm^3) and dried over $MgSO_4$. Removal of the solvent under reduced pressure afforded a light yellow liquid which was used without further purification (2.74 g, 45%). ^1H N.m.r.: $\delta_H(CDCl_3)$ 7.04 (m, 3 H, aromatic), 2.52 (s, 3 H, SMe), and 2.22 (s, 6 H, 2 Me).

1,3-*Bis(methylthiomethyl)benzene*. A mixture of a 1,3-bis-(bromomethyl)benzene (7.9 g, 30 mmol) and sodium methanethiolate (4.48 g, 64 mmol) in toluene (40 cm^3) was heated at reflux temperature for 6 h. The white suspension thus obtained was filtered through a Celite column (4 cm) to afford a colourless solution. Removal of the solvent under reduced pressure afforded the thioether as white crystals which were used without purification (5.84 g, 98%). ^1H N.m.r.: $\delta_H(CDCl_3)$ 7.21 (m, 4 H, aromatic), 3.63 (s, 4 H, 2 CH_2SMe), and 1.98 (s, 6 H, 2 SMe).

$[\{Pd(C_6H_4CH_2SMe\text{-}2)(\mu\text{-}Cl)\}_2]$, (**1**). To a solution of palladium acetate (0.67 g, 3 mmol) in acetic acid (50 cm^3) was added benzyl methyl sulphide (0.52 g, 3.5 mmol). The reaction mixture was stirred at 90 °C for 0.5 h and then evaporated to dryness. The brown residue was washed with pentane (3 × 20 cm^3), suspended in acetone (45 cm^3), and lithium chloride (0.5 g, 12 mmol) was added. The suspension was stirred at room temperature for 0.15 h and evaporated to dryness. The resulting solid was dissolved in dichloromethane (350 cm^3) and filtered through an alumina column (7 cm). The column was washed with dichloromethane–methanol (50:1, 500 cm^3) to afford a yellow-orange solution. These solutions were combined and concentrated to *ca.* 10 cm^3, then pentane (70 cm^3) was added to afford a yellow powder which was collected by filtration, washed with pentane (3 × 25 cm^3), and dried *in vacuo* (0.54 g, 72%).

$[\{Pd(C_{10}H_6SMe\text{-}8)(\mu\text{-}Cl)\}_2]$, (**2**). This compound was prepared by the same method as for (**1**). Quantities used were: palladium acetate (1.12 g, 5 mmol), methyl 1-naphthyl sulphide (0.96 g, 5.5 mmol), acetic acid (40 cm^3). Yield: 0.94 g, 60%.

$[\{Pd[C_6H_4(C_6H_4SMe\text{-}o)\text{-}2](\mu\text{-}Cl)\}_2]$, (**3**). To a solution of palladium acetate (2.25 g, 10 mmol) in acetic acid (75 cm^3) was added 2-biphenyl methyl sulphide (2.2 g, 11 mmol). The reaction mixture was heated at *ca.* 80 °C for 0.5 h and evaporated to dryness under reduced pressure. The residue was washed with pentane (3 × 20 cm^3) and then suspended in acetone (25 cm^3). Lithium chloride (0.85 g, 20 mmol) was added and the suspension was stirred for 0.3 h at room temperature. The solvent was removed *in vacuo* and the brown residue extracted with dichloromethane (450 cm^3). The extracts were filtered through an alumina column (6 cm) to afford a yellow solution which was concentrated to *ca.* 10 cm^3. Addition of hexane (70 cm^3) afforded a white solid which was collected by filtration, washed with hexane (3 × 25 cm^3), and dried *in vacuo* (2.76 g, 81%).

$[\{Pd[C_6H_3(OMe\text{-}5)C(C_6H_4OMe\text{-}4')=S\text{-}2](\mu\text{-}Cl)\}_2]$, (**4**). To a mixture of $[\{Pd(C_6H_4CH_2NMe_2\text{-}2)(\mu\text{-}Cl)\}_2]$ (1.1 g, 2 mmol) and trifluoroacetic acid (0.35 cm^3) in toluene (70 cm^3) was added 4,4′-dimethoxythiobenzophenone (1.15 g, 4.5 mmol). The reaction mixture was heated at reflux for 2 h, and allowed to cool to room temperature. The red cyclopalladated complex (**4**) was collected by filtration, washed with toluene (3 × 10 cm^3), diethyl ether (3 × 25 cm^3), and dried *in vacuo* (1.46 g, 92%).

$[Pd\{C_6H_3(CH_2SMe)_2\text{-}2,6\}Cl]$, (**5**). A yellow solution of $[\{Pd(C_6H_4CH_2NMe_2\text{-}2)Cl\}_2]$ (1.66 g, 3 mmol), 1,3-bis(methylthiomethyl)benzene (1.3 g, 6.5 mmol), and acetic acid (1 cm^3) in benzene (40 cm^3) was heated at reflux temperature for 2.5 h, during which time the solution became first red, then yellow. The solvent was removed *in vacuo* and the remaining oil was washed with pentane (4 × 25 cm^3) (to remove the acetic acid). The residue thus obtained was dissolved in a minimum volume of dichloromethane (5 cm^3). Pentane (50 cm^3) was added to precipitate a light yellow solid which was collected by filtration, washed with pentane (3 × 30 cm^3), and dried *in vacuo* (1.97 g, 97%). ^{13}C-$\{^1H\}$ N.m.r. (CD_2Cl_2, −40 °C): isomer (**a**) δ 158.9 [C(1)], 148.3 [C(2) and C(2′)], 123.9 [C(4)], 121.9 [C(3) and C(3′)], 48.2 (CH_2), and 22.0 (Me); isomer (**b**) 158.8 [C(1)], 147.8 [C(2) and C(2′)], 124.0 [C(4)], 121.7 [C(3) and C(3′)], 47.7 (CH_2), and 22.2 p.p.m. (Me).

$[\{Pd\{CH_2NMeC(NMe_2)=S\}(\mu\text{-}Cl)\}_2]$, (**6**). This pale yellow compound was prepared by the same method as described for compound (**4**). Quantities used were: $[\{Pd(C_6H_4CH_2NMe_2\text{-}2)(\mu\text{-}Cl)\}_2]$ (1.1 g, 2 mmol), trifluoroacetic acid (0.35 cm^3), toluene (60 cm^3), and *N*,*N*,*N*′,*N*′-tetramethylthiourea (0.8 g, 6 mmol). Yield: 0.89 g, 82%.

$[Pd\{MeS(C_6H_4Me\text{-}2)\}_2Cl_2]$, (**7**). To a solution of $[Pd(PhCN)_2Cl_2]$ (0.38 g, 1 mmol) in methanol (20 cm^3) was added methyl *o*-tolyl sulphide (0.28 g, 2 mmol) and the mixture was stirred for 0.5 h. The yellow complex (**7**) was filtered off, washed with methanol (3 × 10 cm^3), hexane (3 × 20 cm^3), and dried *in vacuo* (0.4 g, 90%).

$[Pd(MeSC_6H_3Me_2\text{-}2,6)_2Cl_2]$, (**8**). To a solution of Li_2PdCl_4 (1.27 g, 2 mmol) in methanol (30 cm^3) was added 2,6-dimethylphenyl methyl sulphide (0.32 g, 2.1 mmol) and the mixture was stirred for 1 h. The red solution thus obtained was then concentrated to *ca.* 5 cm^3 under reduced pressure. Water (50 cm^3) was added to afford complex (**8**) which was filtered off, washed with water (3 × 20 cm^3), diethyl ether (3 × 20 cm^3), and dried *in vacuo* (0.29 g, 90%).

Table 1. Yields, colours, and microanalytical data for compounds (**1**)—(**10**)

Compound	Yield (%)	Colour	Molecular formula	Analyses (%) C	H
(**1**)	72	Yellow	C_8H_9ClPdS	34.45 (35.05)	3.25 (3.20)
(**2**)	60	Light yellow	$C_{11}H_9ClPdS$	41.95 (41.90)	2.90 (2.55)
(**3**)	81	White	$C_{13}H_{11}ClPdS$	45.75 (45.50)	3.25 (2.90)
(**5**)	97	Light yellow	$C_{10}H_{13}ClPdS_2$	35.40 (35.45)	3.85 (3.60)
(**6**)	82	White	$C_5H_{11}ClN_2PdS$	22.00 (22.70)	4.05[b] (4.20)
(**7**)	90	Yellow	$C_{16}H_{20}Cl_2PdS_2$	42.40 (42.15)	4.40 (4.35)
(**8**)	90	Yellow-orange	$C_{18}H_{24}Cl_2PdS_2$	44.90 (45.05)	5.00 (5.05)
(**9**)	52	Yellow	$C_9H_{11}ClPdS$	36.90 (38.10)	3.80 (3.70)
(**10**)	22	Yellow	$C_{11}H_{15}ClPdS$	41.15 (41.55)	4.70 (4.70)

[a] Calculated values in parentheses. [b] N, 10.05 (10.25).

Table 2. Proton n.m.r. data for compounds (**1**)—(**10**)

Compound	T/K	δ (J/Hz in $CDCl_3$)[a]
(**1**)	293	7.40—6.88 (m, 4 H, aromatic), 4.25 and 3.89 (2 d, 2 H, CH_2SMe, $^2J_{HH}$ = 14.2), 2.63 (s, 3 H, SMe)
(**2**)	293	7.66—6.66 (m, 12 H, aromatic), 2.75 and 3.00 (2 s, 6 H, SMe)
(**3**)	293	7.44—6.85 (m, 8 H, aromatic), 2.63 (sbr, 3 H, SMe)
(**5**)	333	6.95 (sbr, 3 H, aromatic), 4.25 (s, 4 H, CH_2SMe), 2.78 (s, 6 H, SMe)
	293	6.90 (s, 3 H, aromatic), 4.41 and 4.06 (2 sbr, 4 H, CH_2SMe), 2.75 (s, 6 H, SMe)
	243[b]	6.96 (sbr, 6 H, aromatic), 4.41 and 4.06 (2 d, 4 H, CH_2SMe, $^2J_{HH}$ = 15.6), 4.46 and 4.11 (2 d, 4 H, CH_2SMe, $^2J_{HH}$ = 15.1), 2.75 and 2.70 (2 s, 12 H, SMe)
(**6**)	293[b]	4.14 (sbr, 2 H, CH_2NMe), 3.17 (s, 6 H, NMe_2), 3.10 (s, 3 H, NMe)
	233[b]	4.16 and 3.92 (2 d, 2 H, CH_2NMe), $^2J_{HH}$ = 7.4), 3.15 (sbr, 6 H, NMe_2), 3.09 (sbr, 3 H, NMe)
(**7**)	293	7.86 (dd, 1 H, aromatic), $^2J_{HH}$ = 7.9, $^3J_{HH}$ = 2.2), 7.27 (m, 3 H, aromatic), 2.59 and 2.56 (2 s, 6H, Me)
(**8**)	293	7.27 (m, 3 H, aromatic), 2.81 (s, 6 H, Me), 2.40 (s, 3 H, SMe)
	176	7.28 (m, 3 H, aromatic), 3.08 and 2.47 (2 s, 6 H, Me), 2.35 (s, 3 H, SMe)
(**9**)	293	7.23—7.10 (m, 3 H, aromatic), 3.67 and 3.32 (2 d, 2 H, CH_2Pd, $^2J_{HH}$ = 13.2), 2.77 (s, 3 H, SMe), 2.41 (s, 3 H, Me)
(**10**)	293	7.93 and 7.34 (2 m, 5 H, aromatic), 2.84 (sbr, 2 H, CH_2SPh), 2.39 (s, 2 H, CH_2Pd), 1.11 (s, 6 H, CMe_2)

[a] s = Singlet, d = doublet, m = multiplet, and br = broad. [b] In CD_2Cl_2.

$[\{Pd(CH_2C_6H_3SMe\text{-}2\text{-}Me\text{-}3)(\mu\text{-}Cl)\}_2]$, (**9**). To a solution of palladium acetate (0.22 g, 1 mmol) in acetic acid was added 2,6-dimethylphenyl methyl sulphide (0.17 g, 1.1 mmol) in acetic acid (5 cm^3). The solution was heated at 90 °C for 0.5 h and then evaporated to dryness. The brown residue was washed with pentane (3 × 60 cm^3) and dried *in vacuo*. The resulting solid was dissolved in acetone (70 cm^3), and LiCl (0.1 g) was added. The solvent was removed under reduced pressure after stirring for 0.1 h, and complex (**9**) was extracted with dichloromethane–methanol (50:1, 400 cm^3). The extract was filtered through an alumina column (3 cm) to afford a yellow solution which was concentrated to *ca.* 4 cm^3. Addition of hexane (60 cm^3) afforded (**9**) which was filtered off, washed with hexane (3 × 50 cm^3), and dried *in vacuo* (0.15 g, 52%).

$[\{Pd(CH_2CMe_2CH_2SPh)(\mu\text{-}Cl)\}_2]$, (**10**). This compound was prepared by the same method as used for (**3**) (see above). Quantities used were: palladium acetate (1.35 g, 6 mmol), neopentyl phenyl sulphide (1.35 g, 7.5 mmol), and acetic acid (50 cm^3). The light yellow cyclopalladated complex (**10**) was recrystallized from dichloromethane–pentane. Yield: 0.42 g, 22%.

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