Formation and Decomposition of an α-Alkoxyalkyl Complex of Palladium(II)

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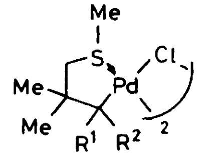
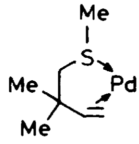
The α-methoxyalkyl species [{PdCl[CH(OMe)CMe_2CH_2SMe]}$_2$] decomposes in solution to give complexes containing the acetal $MeSCH_2CMe_2CH(OMe)_2$ or the corresponding aldehyde. The reaction requires water, is acid-catalysed, and produces hydrogen. A mechanism involving protonation of the metal atom, either initially or in a subsequent step, is proposed. Under certain conditions, the acyl complex [{PdCl[C(=O)CMe_2CH_2SMe]}$_2$] or complexes of the ester $MeSCH_2CMe_2CO_2Me$ or acid $MeSCH_2CMe_2CO_2H$ are produced.

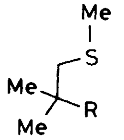
We have reported[1] that the product, (**1**), of methoxypalladation of dichloro(2,2-dimethylbut-3-enyl methyl sulphide)palladium(II), (**2**), undergoes relatively slow decomposition in solution. The major decomposition pathway leads to complexes containing the acetal $MeSCH_2CMe_2CH_2CH(OMe)_2$ (**3**), or the corresponding aldehyde (**4**). An important intermediate in this process is the α-methoxyalkylpalladium(II) derivative (**5**) which can also be generated by reaction of $MeSCH_2CMe_2CH_2CH$(Cl)OMe with bis(dibenzylideneacetone)palladium(0). To our knowledge, no other α-alkoxyalkylpalladium(II) derivative has been detected directly. The mechanism of formation of compound (**3**) from (**4**) remained unclear, with two aspects of the conversion being particularly intriguing: first, the efficiency with which a methoxy group is transferred from one ligand molecule to another and, secondly, the stoicheiometry of the process, which requires one additional mol equiv. of oxygen atoms. We have now prepared the analogue, (**6**), of (**5**) and studied its decomposition in an attempt to shed some light on the mechanism of the reaction.



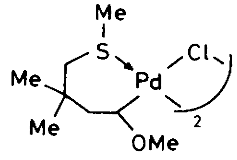
(**1**) R^1 = CH_2OMe, R^2 = H
(**6**) R^1 = OMe, R^2 = H
(**12**) R^1 = OH, R^2 = H
(**16**) R^1 + R^2 = O



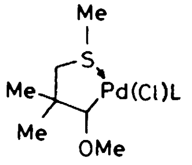
(**2**)



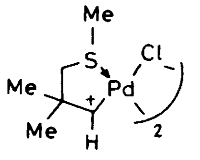
R
(**3**) $CH_2CH(OMe)_2$
(**4**) CH_2CHO
(**7**) CHO
(**8**) $CH(OMe)_2$
(**9**) CH_2OMe
(**13**) CO_2Me
(**14**) CO_2H
(**15**) COCl
(**17**) CH(OMe)Cl
(**18**) $CH(OMe)O_2CMe$



(**5**)



(**10**)



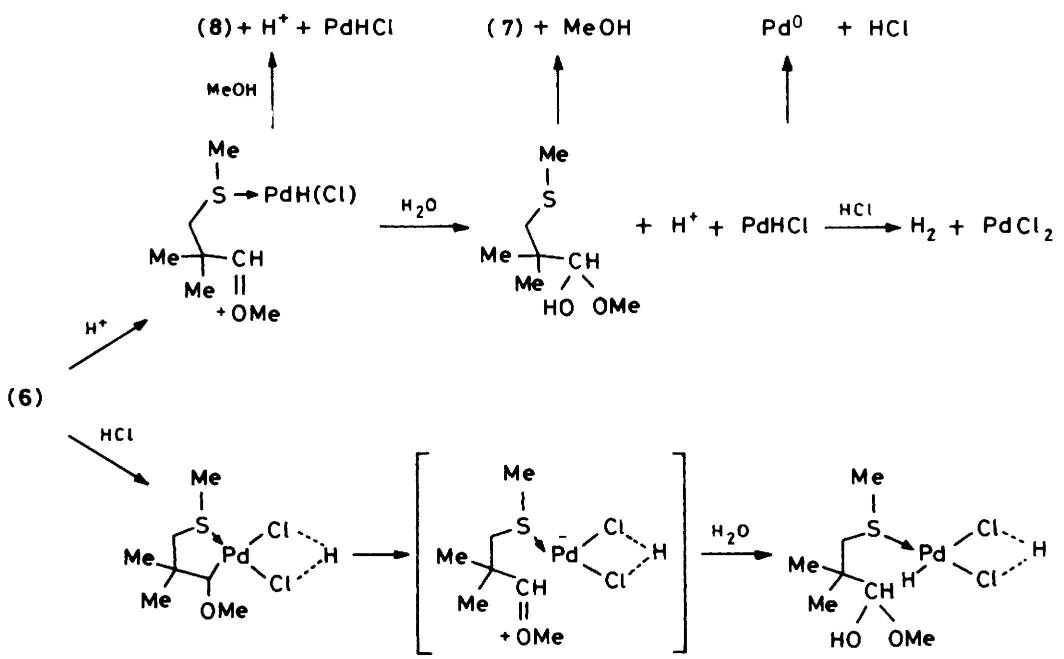
(**11**)

Results and Discussion

The α-methoxyalkylpalladium(II) derivative (**6**) was chosen for study, mainly because it lacks hydrogen atoms β to the metal thus avoiding the possibility of decomposition *via* β-hydride elimination[1] and thence vinyl ether complexes. Accordingly, a solution of $MeSCH_2CMe_2CH$(Cl)OMe in deuteriochloroform (which had been dried over molecular sieves) was treated with solid bis(dibenzylideneacetone)palladium(0). Rapid dissolution, and discharge of the intense colour, of this complex occurred giving a pale yellow solution. Initially, ^1H n.m.r. spectra of this solution were consistent with the presence of essentially pure derivative (**6**). Over several hours, however, the signals arising from (**6**) were replaced by a series of signals consistent with the presence of mainly sulphur-bonded complexes of the aldehyde (**7**) and acetal (**8**). This was confirmed by comparison of these spectra with ones obtained from solutions containing palladium(II) chloride and authentic samples of compounds (**7**)[2] and (**8**). During the decomposition of compound (**6**) about half of the palladium present precipitated as Pd^0. In an attempt to confirm the presence of traces of methanol in the final solution, the ^1H n.m.r. spectrum was rerun after the addition of a small quantity of this alcohol. Unexpectedly, much of the methanol was consumed quite rapidly and the concentration of complexed acetal (**8**) increased at the expense of complexed (**7**). Thus, one cannot rule out the possibility that compound (**8**) is formed from (**6**) *via* (**7**) rather than directly. In any event, the similarities in the ease of decomposition of compounds (**5**) and (**6**), and in the structures of the products, may indicate that they decompose by a similar mechanism. If this is the case, since (**6**) cannot suffer β-hydride elimination, enol ether species may play[1] little or no role in the decomposition of (**5**) either.

As indicated above, the formation of compounds (**7**) and (**8**) from (**6**) requires 1 mol equiv. of oxygen atoms, likely sources being air and/or adventitious water. The former possibility was ruled out by the following experiment. When a solution of compound (**6**) was prepared in deuteriochloroform as before and then carefully degassed and sealed in an n.m.r. tube, the build-up of complexes of (**7**) and (**8**) was again observed during 24 h. Despite attempts to exclude water we have not been able to prevent this decomposition, although when an excess of chloroether is used the ^1H n.m.r. signals arising from compound (**6**) persist for considerably longer periods. We attribute this to the scavenging effect of the chloroether for water.

The results reported above suggest that the major decomposition pathway may involve the following net reactions: (**6**) + $H_2O \longrightarrow 2HPdCl$ + (**7**) + (**8**); $2HPdCl \longrightarrow Pd^0 + PdCl_2 + H_2$. Indeed, when the decomposition was allowed to proceed in a closed container, a build-up of pressure was noted during the



Scheme. Possible routes for the conversion of complex (**6**) into (**7**), (**8**), Pd⁰, $PdCl_2$, and H_2

reaction and, at completion, a mass-spectral analysis of the head-space gas showed the presence of a substantial quantity of H_2. We have, however, been unable to detect the presence of the presumed hydride intermediate(s). Products of reduction of the dibenzylideneacetone were not detectable by n.m.r. or t.l.c., and dimethyl fumarate, a compound that has been used[3] to trap hydride from palladium-mediated reactions, survived when added to the reaction mixture. Furthermore, it is noteworthy that any palladium hydride species formed did not cleave the Pd–C bond of the initial adduct (**6**), since the ^1H n.m.r. spectra of the product mixtures did not contain resonances attributable to the methyl ether (**9**). In an attempt to achieve this last reaction, N-benzyl-1,4-dihydronicotinamide was introduced. Instead of producing the methyl ether, the complex (**6**) was rendered considerably more stable. Further investigation showed that this stability was due to basic decomposition products from the amide and that a similar result could be obtained by carrying out the oxidative addition in the presence of either triethylamine or pyridine (py). In both cases, two palladium complexes were obtained by preparative t.l.c., the dimer (**6**) and a product of dimer cleavage [**10**; L = (**7**) or py respectively]. Complexes (**10**) could not be purified by crystallisation. On the other hand, compound (**6**) crystallised readily and the resulting material appears to be stable when stored in a refrigerator. The ^1H n.m.r. spectra of a solution of crystallised (**6**) in deuteriochloroform showed little change over 2 d at room temperature. However, when a small amount of hydrogen chloride was added to this solution the complex decomposed quite rapidly to give the products observed previously.

It thus appears that both water and acid are necessary for the decomposition of complex (**6**), the latter probably being generated by reaction of the chloroether with adventitious water during the formation of (**6**). It seems likely that protonation of (**6**) is a key step in its decomposition and, of the various possible sites of attack, the following two appeared to warrant serious consideration. First, protonation of the oxygen atom might lead *via* the carbocation (**11**) to an α-hydroxyalkyl species (**12**) which could then decompose to the aldehyde compound (**7**) and a palladium hydride by β-hydride elimination. We consider this mechanism unlikely since, when complex (**6**) was allowed to decompose in the presence of a substantial quantity of CD_3OD, the unreacted substrate had not suffered exchange of OCH_3 by OCD_3. As expected, this decomposition was accelerated by the addition of HCl. We favour an alternative pathway, involving heterolytic cleavage of the Pd–C bond, and triggered either by protonation of the palladium atom or by generation of an intermediate in which the electrophilic character of the palladium is increased. Possible routes are summarised in the Scheme. Protonation of the metal atom of a palladium alkyl species would be expected to facilitate nucleophilic attack at the α-carbon atom. Certainly, among the published reports[4] of this type of reaction there are cases where the attachment of a Lewis acid, such as $CuCl^+$ (ref. 5) or $[Pb(O_2CMe)_3]^+$,[6] to the palladium atom may facilitate the process. Indeed, this type of acid catalysis of Pd–C bond cleavage may be widespread and operative in some Wacker-type processes.

When $CDCl_3$ solutions of the decomposition products of complex (**6**) were kept at room temperature for several weeks under air the ^1H n.m.r. signals arising from complexes of (**7**) and (**8**) were replaced* by ones consistent with the presence of 2:1 complexes of methyl 2,2-dimethyl-3-methylthiopropanoate (**13**) and the corresponding acid (**14**) with $PdCl_2$. The 2:1 complex of the ester (**13**) was isolated by preparative t.l.c. Metal acyl species were considered as possible intermediates in the palladium-mediated conversion of compound (**7**) into (**13**) and therefore the carboxylic acid chloride (**15**) was treated with bis(dibenzylideneacetone)palladium(0) to give the acyl complex (**16**), which was purified by preparative t.l.c. Careful study of ^1H n.m.r. spectra of solutions at intermediate stages of the decomposition of complex (**6**) did reveal signals attributable to species such as (**16**), and, in one experiment where HCl in D_2O was added to the reaction mixture an appreciable quantity of

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* A concomitant decrease in the magnitude of the ^1H n.m.r. signals arising from the olefinic protons of the dibenzylideneacetone [released during the formation of (**6**)] was observed.

(**16**) built up and was recovered by preparative t.l.c. Indeed, when the 1:1 complex of the aldehyde (**7**) and PdCl$_2$ was kept in deuteriochloroform for several days appreciable amounts of (**16**) were formed. However, complex (**16**) resists exposure to small quantities of methanol in CDCl$_3$ solution, even in the presence of protic acids. There have been several reports[7] of the formation of chelated metal acyl species from aldehydes bearing a ligand atom on a γ-carbon, in some cases possibly *via* a mechanism involving electrophilic attack of the metal on the aldehyde C–H bond. The relatively ready formation of complex (**16**) from (**6**) in the presence of aqueous HCl, presumably *via* intermediate S-bound complexes of (**7**), may constitute further evidence for the electrophilic character of this reaction for palladium, particularly in view of the observation[8] that cyclometallation of benzyl sulphides with palladium(II) salts occurs readily only with the more electrophilic derivatives.

Experimental

Melting points were determined with a Kofler hot-stage apparatus. Proton n.m.r. spectra were recorded on a Bruker WH-400 (Southwestern Ontario NMR Centre) or Varian EM360L spectrometer for solutions in [^{2}H]chloroform (which was dried by treatment with 4A molecular sieves). Elemental analyses were obtained from Galbraith Laboratories, Knoxville, Tennessee, U.S.A. T.l.c. plates were spread with Kieselgel G (Merck). Components were more clearly visible on analytical plates when exposed to iodine vapour.

Aldehyde (**7**), *Acetal* (**8**), *and Chloroether* (**17**).—A mixture of the aldehyde[2] (**7**) (4.79 g), trimethyl orthoformate (4.0 cm^3), and a small amount (30 mg) of toluene-*p*-sulphonic acid hydrate was heated at 35 °C for 2.5 h. The solution was then stirred with excess anhydrous sodium carbonate, filtered, and distilled at a water pump (b.p. 80—81 °C) to give the acetal (**8**) (5.44 g); δ 0.97 (6 H, s, CMe), 2.08 (3 H, s, SMe), 2.48 (2 H, s, SCH$_2$), 3.47 (6 H, s, OMe), and 3.98 (1 H, s, OCHO). Acetyl chloride (0.418 g) was added to acetal (**8**) (0.477 g) in a dry flask and, after 1 h at room temperature, the excess of acetyl chloride and the methyl acetate formed were removed on the rotary evaporator. The resulting chloroether (**17**) (0.489 g) was essentially pure (^{1}H n.m.r.); δ 1.08 (6 H, s, CMe), 2.10 (3 H, s, SMe), 2.60 (2 H, s, SCH$_2$), 3.48 (3 H, s, OMe), and 5.40 (1 H, s, ClCHO). Another sample (1.21 g) of compound (**17**) was prepared by treating the hemiacetal acetate[2] (**18**) (1.12 g) with thionyl chloride (0.41 cm^3) in carbon tetrachloride (40 cm^3) for 30 min. In this case, the removal of by-products required a lengthy period on the rotary evaporator at *ca.* 50 °C.

Generation and Decomposition of the α-Methoxyalkyl Complex (**6**).—(*i*) Bis(dibenzylideneacetone)palladium(0)[9] (203 mg, 0.353 mmol) was added to a solution of the chloroether (**17**) (65 mg, 0.36 mmol) in deuteriochloroform (1.5 cm^3). Rapid dissolution and discharge of the intense colour of the complex occurred to give a yellow solution which gave a ^{1}H n.m.r. spectrum containing resonances attributable to dibenzylideneacetone and complex (**6**) (see below). On standing (36 h), a palladium mirror (15 mg) formed on the walls of the tube and the ^{1}H n.m.r. spectrum of the solution was essentially identical to that obtained when palladium(II) chloride (0.1 mmol) was dissolved in a solution of compounds (**7**) (0.1 mmol) and (**8**) (0.1 mmol) in deuteriochloroform. After standing at room temperature for 6 d the ^{1}H n.m.r. spectrum of the original mixture contained an additional set of resonances. The solution was then heated to 50 °C for 10 d, during which time the new signals grew in intensity and the original set disappeared. The product mixture was subjected to preparative t.l.c. (benzene–methanol, 97:3). A band of intermediate polarity contained the 2:1 complex (89 mg) of methyl 2,2-dimethyl-3-methylthiopropanoate (**13**) with PdCl$_2$, which crystallised from dichloromethane–hexane and had m.p. 93—94 °C; δ 1.35 (6 H, s, CMe), 2.40 (3 H, s, SMe), 3.19 (2 H, s, SCH$_2$), and 3.67 (3 H, s, OMe) (Found: C, 33.3; H, 5.8. C$_{14}$H$_{28}$Cl$_2$O$_4$PdS$_2$ requires C, 33.5; H, 5.6%).

(*ii*) The experiment reported in (*i*) was repeated, except that after the initial mixing the tube was degassed (using three freeze–evacuate–thaw cycles) and then sealed. Monitoring of the reaction by ^{1}H n.m.r. spectroscopy showed no significant difference from the experiment run in air, except that a new signal was present in early spectra, and during the course of the reaction it grew in intensity and shifted upfield to 1.7 p.p.m. Addition of a small quantity of methanol enhanced the intensity of this peak and it was no longer present when the solvent was evaporated and the residue redissolved in deuteriochloroform.

(*iii*) Experiment (*i*) was repeated, this time in a small flask (5 cm^3) sealed with a rubber septum. After 48 h a sample of the head-space gas was injected into a VG7070F mass spectrometer *via* the septum reservoir. An intense signal at *m*/*e* 2 was observed. While the sample was being withdrawn from the reaction flask, it was noted that the pressure therein exceeded ambient.

(*iv*) Solid bis(dibenzylideneacetone)palladium(0) (90 mg, 0.16 mmol) and then *N*-benzyl-1,4-dihydronicotinamide (33 mg, 0.16 mmol) were added to a solution of the chloroether (**17**) (29 mg, 0.16 mmol) in deuteriochloroform. During 3 h a yellow solid precipitated from the solution and the signals due to the nicotinamide were lost from the ^{1}H n.m.r. spectrum of the solution. After 3 d at room temperature a dark precipitate was present but the ^{1}H n.m.r. signals arising from the α-methoxyalkyl complex (**6**) had diminished only slightly in intensity. The solution was filtered and evaporated and the residue submitted to preparative t.l.c. (dichloromethane–ethyl acetate, 49:1). The least polar band contained mainly dibenzylideneacetone (61 mg). The band of intermediate polarity contained the methoxy complex (**6**) (13 mg) (see below) and the most polar band contained material (11 mg) which gave ^{1}H n.m.r. resonances similar to those expected for a combination of (**6**) and (**7**), and is probably attributable to [**10**; L = (**7**)].

(*v*) When experiment (*iv*) was repeated replacing the nicotinamide with triethylamine a similar yield of products was obtained after preparative t.l.c.

(*vi*) When experiment (*iv*) was repeated using pyridine as the base, preparative t.l.c. of the products gave the following fractions. The least polar fraction (58 mg) contained dibenzylideneacetone and uncomplexed (**7**). The fraction (4 mg) of intermediate polarity contained complex (**6**) and the most polar one (30 mg) consisted of oily (**10**; L = py); δ 1.08 (3 H, s, CMe), 1.37 (3 H, s, CMe), 2.53 (3 H, s, SMe), 2.60 (2 H, m, SCH$_2$), 3.40 (3 H, br s, OMe), 3.97 (1 H, br s, Pd–CH), 7.30 (2 H, m, H$_m$), 7.72 (1 H, m, H$_p$), and 8.80 (2 H, m, H$_o$). This oil could not be induced to crystallise.

(*vii*) The reaction procedure outlined in experiment (*i*) was repeated, but soon after mixing the reactants (*ca.* 15 min) the solvent was evaporated and the residue submitted to preparative t.l.c. (dichloromethane–ethyl acetate, 49:1). The major band of intermediate polarity yielded complex (**6**) (38 mg), which crystallised from dichloromethane–hexane as pale yellow rosettes, m.p. 114—115 °C; δ (60 MHz; ambient temperature) 1.03 (3 H, s, CMe), 1.37 (3 H, s, CMe), 2.52 (3 H, s, SMe), 2.58 (2 H, m, SCH$_2$), 3.55 (3 H, s, OMe), and 4.03 (1 H, s, Pd–CH); δ (400 MHz; −30 °C) (major isomer) 1.05 (3 H, s, CMe), 1.29 (3 H, s, CMe), 2.54 (3 H, s, SMe), 2.64 (1 H, d, SCH, *J* = 11), 2.68 (1 H, d, SCH, *J* = 11 Hz), 3.61 (3 H, s, OMe), and 4.08 (1 H, s, Pd–CH); (minor isomer) 1.05 (3 H, s, CMe), 1.63 (3 H, s, CMe), 2.13 (1 H, d, SCH, *J* = 13), 2.64 (3 H, s, SMe), 3.12 (1 H, d, SCH, *J* = 13 Hz), 3.56 (3 H, s, OMe), and 4.08 (1 H, s, Pd–CH) (Found: C, 28.95; H, 4.9. $C_{14}H_{30}Cl_2O_2Pd_2S_2$ requires C, 29.1; H, 5.25%).

The ^1H n.m.r. spectrum of a solution of crystallised (**6**) in deuteriochloroform which had been kept at room temperature for 3 d was identical to that of the freshly prepared solution. After 3 d, hydrogen chloride gas was bubbled through the solution for 1 min. Monitoring of the resulting solution by ^1H n.m.r. revealed that complex (**6**) then decomposed as before [see experiment (*i*)].

[$^2H_4$]Methanol (20 µl) was added to a solution of complex (**6**) (18 mg) in deuteriochloroform (1 cm^3). After 18 h no reaction had occurred (^1H n.m.r. evidence) and hydrogen chloride gas was bubbled through the solution for 1 min. Monitoring by ^1H n.m.r. revealed that during *ca.* 20 h complex (**6**) was converted into the 2:1 complex of the acetal (**8**) (partially deuteriated) and $PdCl_2$. When approximately 60% of complex (**6**) had reacted, integration of the Pd–C*H* resonance *vs.* the CHOCH_3 resonance for unreacted (**6**) gave a ratio of 1:3.

A solution of HCl in D_2O (0.1 cm^3, 1 mol dm^{-3}) was added to a solution of complex (**6**) (35 mg) in deuteriochloroform. After 36 h a palladium mirror was present and a ^1H n.m.r. spectrum was run. This showed resonances attributable to the acyl complex (**16**) and to complexes formed from (**6**) by dimer cleavage. Preparative t.l.c. (dichloromethane–methanol, 99:1) of the products afforded a major fraction (13 mg) of intermediate polarity, which was essentially pure (**16**) (see below). A more polar fraction (8 mg) gave a ^1H n.m.r. spectrum which contained resonances attributable to complex (**16**) and complexed (**7**) (cleaved dimer?).

The Acyl Complex (**16**).—An authentic sample of the acyl complex was prepared as follows. Aldehyde (**7**)[2] (1.33 g) was added dropwise, with stirring, to an ice-cold suspension of silver oxide, prepared[10] by adding sodium hydroxide (1.6 g) to a solution of silver nitrate (3.5 g) in water (60 cm^3). After 1 h the mixture was filtered, the filtrate acidified with concentrated hydrochloric acid, and the resulting solution extracted with diethyl ether (2 × 30 cm^3). Evaporation of the combined extracts gave substantially pure acid (**14**) (1.43 g); δ 1.28 (6 H, s, CMe), 2.13 (3 H, s, SMe), 2.72 (2 H, s, SCH_2), and 10.63 (1 H, s, OH). A mixture of the acid (103 mg) and oxalyl chloride (1 cm^3) was allowed to stand at room temperature overnight and the excess of oxalyl chloride was then distilled out *in vacuo*. The acid chloride, (**15**), formed had δ (in carbon tetrachloride) 1.34 (6 H, s, CMe), 2.13 (3 H, s, SMe), and 2.75 (2 H, s, SCH_2). It was dissolved in dichloromethane (2 cm^3) and treated with bis(dibenzylideneacetone)palladium(0) (356 mg). The colour of this complex was discharged immediately and the solvent was then evaporated. The crude product (420 mg) was submitted to preparative t.l.c. (dichloromethane–methanol, 99:1) and afforded a fraction (138 mg) of intermediate polarity, which crystallised from chloroform as almost colourless prisms of complex (**16**), m.p. 157—159 °C (decomp.); $\nu_{max.}$ 1 710 and 1 745 cm^{-1}; $\lambda_{max.}(CH_2Cl_2)$ at 350 (ε 4 000), 292 (5 500), and 260 nm (4 000 dm^3 mol^{-1} cm^{-1}); δ 1.14 (6 H, s, CMe), 2.20 (2 H, s, SCH_2), and 2.67 (3 H, s, SMe) (Found: C, 26.4; H, 4.1. $C_{12}H_{22}Cl_2O_2Pd_2S_2$ requires C, 26.4; H, 4.05%). This compound darkens on exposure to light, but a solution of it in deuteriochloroform containing a small quantity of methanol resisted (^1H n.m.r. evidence) heating, in the dark, at 53 °C for 1 week.

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