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Catalytic Thioether and Thioacetal Formation using Bis(diphenylphosphino)methane Complexes of Platinum (II)

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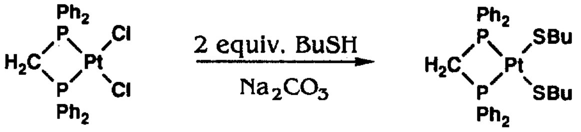
Abstract: Bis(diphenylphosphino)methane complexes of platinum (II) catalyze the formation of thioethers from thiols and alkyl halides and of thioacetals from thiols or dithiols and geminal dihalides.

Many methods are known for the formation of thioethers including desulphurization of disulphides, reduction of sulphoxides and sulphones, aryllithium or organocuprate addition to thiocarbonyl compounds;[1,2] the treatment of alkyl halides with sodium sulphide,[3] thiourea,[4] or thiocarbonates;[5] the use of electrophilic sulphur species;[6] the reaction of 2-alkylthio-1,3-benzoxazoles with sodium alkoxides;[7] the use of bis(tributyltin)sulphide as a sulphur transfer agent;[8] and the reaction of halides with thiosilanes;[9] but the most widely used method for the preparation of unsymmetrical thioethers is the alkylation of thiols with alkyl halides.[10] Commonly, thiols are treated with base – typically sodium hydride – to generate intermediate thiolate anions which are then treated with alkyl halides; perhaps the simplest variation of this method of preparation is that reported by Ono in 1980:[11] thioethers and thioacetals were prepared in excellent yields simply by stirring a mixture of thiol, DBU, and alkyl halide or geminal dihalide in benzene for one to five hours at room temperature.

The use of metal–diphosphine complexes as catalysts in reactions such as hydroformylation,[12] hydrogenation,[13] and decarbonylation[14] is well known.[15] The introduction of chiral diphosphine ligands in these complexes to effect asymmetric induction in such reactions has led to increased attention being focussed on catalytic procedures.[16] We have found that bis(diphenylphosphino)methane complexes of platinum (II) are capable of catalyzing thioether and thioacetal formation.[17]

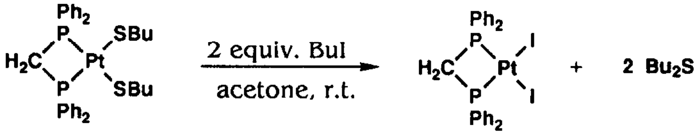
The most common chelating ligands used for complexation with platinum (II) are those of the general formula $Ph_2P(CH_2)_nPPh_2$.[18] These compounds form chelate complexes PtX_2L_2 which necessarily have the *cis* geometry for X. Comparison between the ligands $Ph_2P(CH_2)_nPPh_2$ for coordination to platinum (II) shows that monomeric complexes are formed when n=1 and 2, dimeric complexes when n=3, and trimers when n=4. Thiolates have been shown to form very strong bonds to platinum (II). Thiolate platinum (II) complexes have been known for nearly a century,[19] but the characterization and chemistry of these complexes has been difficult to study because of the strong tendency of the thiolato ligand to form bridges to a second platinum centre, resulting in the formation of insoluble bridged polymers.[20]

The usual method of preparation of thiolato complexes involves the reaction of halo platinum (II) complexes with the appropriate thiol and base in the presence of a base, or with the preformed alkali metal or thallium thiolate salt.[10] For example, Lai and Shaver have shown that bis(thiolate) platinum (II) complexes such as $[(Ph_3P)_2Pt(SR)_2]$, where R = ^{n}Pr, ^{i}Pr, or CH_2Ph, may be prepared by the reaction of $[(Ph_3P)_2PtCl_2]$ with thiols in the presence of the weak base triethylamine.[21] We have prepared the bis(diphenylphosphino)methane complex (1) in a similar manner from $[Pt(dppm)Cl_2]$ using sodium carbonate as the weak base (eq. 1).



(1) (Equation 1)

We were intrigued to find that complex (1) reacts readily with 1-iodobutane in acetone at room temperature to give dibutyl sulphide in good yield (eq. 2).



(1)

(Equation 2)

Further, we discovered that isolation of intermediate (1) is unnecessary for thioether formation, but most interesting was the finding that the platinum complex need not be used in stoicheiometric quantity — when a mixture of l-iodobutane, butanethiol, and sodium carbonate was boiled under reflux in the presence of a catalytic quantity of $[Pt(dppm)Cl_2]$ (5 mol%) in acetone solution for twenty-four hours, dibutyl sulphide was furnished in 80% yield. Simple work-up involved solvent removal, extraction of the residue into ether, and evaporation to dryness. The reaction was found to be very clean and quite general, and the formation of a variety of thioethers was effected using this method (table 1). No reaction was observed in the absence of catalyst except in the case of thiophenol.

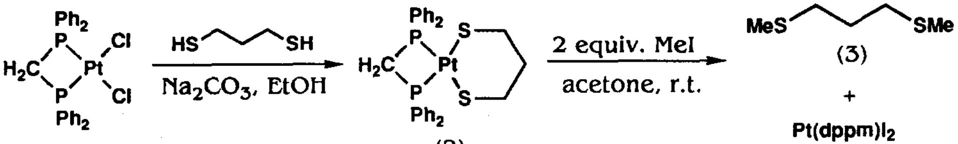
TABLE 1. Thioether Formation

Entry	Thiol	Alkyl Iodide	Thioether	Yield/%
a	BuSH	BuI	Bu_2S	80
b	$HS(CH_2)_3SH$	MeI[a]	$MeS(CH_2)_3SMe$	70
c	$HS(CH_2)_3SH$	EtI[a]	$EtS(CH_2)_3SEt$	90
d	PhSH	MeI	PhSMe	77
e	PhSH	EtI	PhSEt	80
f	$HO(CH_2)_3SH$	MeI	$HO(CH_2)_3SMe$	69
g	$HSCH(Me)CH_2CH(Me)SH$	MeI[a]	$MeSCH(Me)CH_2CH(Me)SMe$	80

a. Two equivalents

As can be seen from table 1, alkyl and aryl thiols react equally well (entries a – e), as do secondary thiols (entry g) and dithiols. Reaction of mercaptopropanol with iodomethane gave exclusive thioether formation (entry f), the alcohol functionality remaining unaffected.

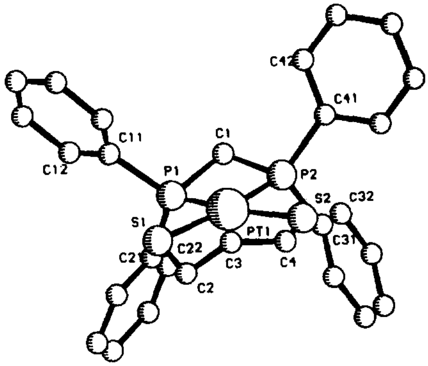
In order to determine the structure of the thiolate intermediate involved in the dithiol reactions, 1,3-propanedithiol was allowed to react with $[Pt(dppm)Cl_2]$ in ethanol in the presence of sodium carbonate. The isolated product (2) reacted readily with two equivalents of iodomethane to give the bis-thioether (3) (scheme 1). A single crystal X-ray structure determination carried out on (2) confirmed its mononuclear chelated structure (figure).[22]



(2)

(3)

Scheme 1



Figure

The structure of Pt(dppm)(SCH2CH2CH2S) with H atoms omitted. Selected bond lengths (Å) and angles (°) are: Pt-P(1) 2.236(3), Pt-P(2) 2.276(4), Pt-S(1) 2.332(4), Pt-S(2) 2.276(4), S(1)-C(2) 1.77(2), C(2)-C(3) 1.49(3), C(3)-C(4) 1.42(3), C(4)-S(2) 1.78(3)Å; P(1)-Pt-P(2) 72.6(1), P(1)-Pt- S(1), 96.3(1), P(2)-Pt-S(2) 92.7(1), S(1)-Pt-S(2) 98.4(1), P(1)-C(1)-P(2) 92.8(6)°

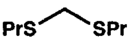
A particularly interesting application of this reaction is the synthesis of thioacetals. Diiodomethane was found to react successfully with thiols under our standard conditions in acetone or methanol solution to produce thioacetals in good yield (table 2); as no reaction of thiols with carbonyl groups is observed under these conditions, this method is complementary to the more usual acid catalysed thiol/ketone routes.

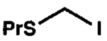
Table 2 shows that 1,3-dithianes can be prepared by this method under very mild conditions (entries e, h) from 1,3-propanedithiol, without the use of formaldehyde or an equivalent, or the need to pre-form thiolate anions.[23] However, as expected, 3-mercaptopropan-1-ol did not produce 1,3-oxathiane under the same conditions but gave displacement of halide ions by two molecules of thiol, as did mercaptoethanol, producing only dithioacetal. Entries e, f, and g in table 2 indicate that reactions proceed most efficiently for iodides and bromides, with chlorides being poor substrates. This pattern lends weight to the nucleophilic substitution mechanism outlined in scheme 3. Further, the reaction of one equivalent of propanethiol with diiodomethane (entry a) gave thioacetal (4) only, with no iodothioether (5) being detected. This observation can no doubt be attributed to the high susceptibility to nucleophilic attack of (5) resulting in its immediate consumption in the reaction mixture. Since species such as (5) are not isolable, this method cannot be used to form unsymmetrical thioethers.

TABLE 2 Thioacetal Formation

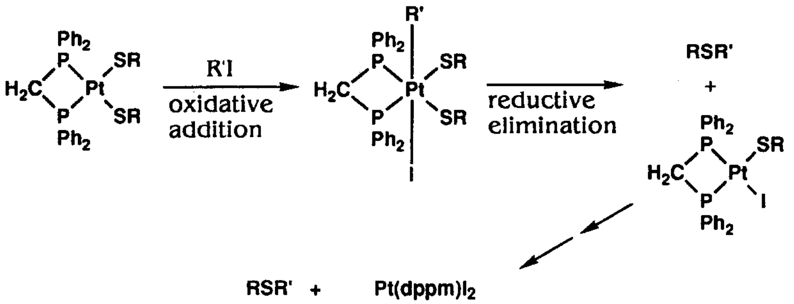
Entry	Thiol	Halide	Product	Yield/%
a	$^{n}PrSH$[a]	CH_2I_2	$(^{n}PrS)_2CH_2$	66
b	$^{n}PrSH$[b]	CH_2I_2	$(^{n}PrS)_2CH_2$	70
c	$HO(CH_2)_2SH$	CH_2I_2	$HO(CH_2)_2SCH_2S(CH_2)_2OH$	73
d	$HO(CH_2)_3SH$	CH_2I_2	$HO(CH_2)_3SCH_2S(CH_2)_3OH$	72
e	$HS(CH_2)_3SH$	CH_2I_2	1,3-dithiane	70
f	$HS(CH_2)_3SH$	CH_2Br_2	—[c]	
g	$HS(CH_2)_3SH$	CH_2Cl_2	no reaction	
h	$HS(CH_2)_2CH(Me)SH$	CH_2I_2	4-methyl-1,3-dithiane	70

a. one equivalent; yield based on $^{n}PrSH$
b. two equivalents
c. complex mixture of products


(4)

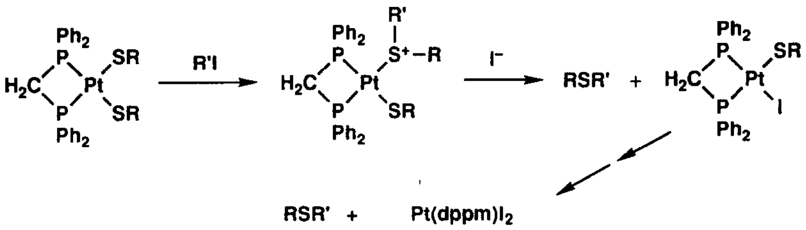

(5)

One possible mechanism for this platinum (II)-catalysed carbon-sulphur bond formation proceeds by initial oxidative addition[24] to give a bis(thiolate) platinum (IV) complex followed by reductive elimination as shown in scheme 2.



Scheme 2

An alternative mechanism, illustrated in scheme 3, involves nucleophilic displacement of the halide ion by a sulphur species of enhanced nucleophilicity, such as the bis-thiolate platinum (II) intermediate, or by thiolate formed from dissociation of this intermediate, followed by a replacement of the thioether by halide.



Scheme 3

Acknowledgment

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EXPERIMENTAL SECTION

General experimental details

Commercially available reagents were used as supplied unless otherwise stated. 1,3-Butanedithiol was prepared by the method of Cossar in 36% yield.[25]

Reactions were carried out in glassware which had been dried for several hours at 150-200 °C. The apparatus was assembled hot and allowed to cool while a rapid flow of argon was admitted. Reactions were maintained in an atmosphere of argon and reagents and solvents introduced *via* syringe, through a septum cap. Solvents were freshly distilled before use.

Flash column chromatography was carried out on Merck 9385 Kieselgel 60 (230-400 mesh), using hand bellows or an air-line to apply pressure to the column. Thin layer chromatography was carried out on glass- or aluminium- backed plates coated with a 0.25 mm layer of silica gel 60H containing fluorescer; compounds were visualized by u.v. irradiation or by spraying with dodecamolybdophosphoric acid (15% w/v in ethanol) or potassium permanganate (1% w/v in water) followed by charring.

Infrared spectra were recorded in the range 4000—600 cm^{-1} using Perkin Elmer 298 or 1720FT spectrophotometers and were calibrated against the 1602 cm^{-1} absorption of polystyrene. Solid samples were run as Nujol mulls or potassium bromide discs, and liquids as thin films. ^{1}H Nuclear magnetic resonance spectra were recorded using Bruker WM250 (250 MHz), Bruker AC200 (200 MHz), Perkin Elmer R34 (220 MHz), or Jeol PMX60 (60 MHz) spectrometers, using deuteriochloroform solutions and tetramethylsilane as internal standard. Electron impact (EI) and chemical ionisation (CI) mass spectra were recorded on a VG Micromass 7070E instrument.

Melting points were determined on a Reichert hot-stage apparatus and are uncorrected. Microanalyses were carried out by the Department of Chemistry microanalytical service.

[Pt(dppm)Cl$_2$] (1)

Concentrated HCl (12.5 ml) and a hot solution of diphenylphosphinomethane (dppm, 2.31 g, 6.03 mmol) were added to a warm solution of potassium tetrachloroplatinate (2.50 g, 6.03 mmol) in water (36 ml). The mixture was heated under reflux for 30 minutes and filtered. The white precipitate was washed with hot propanol (20ml), water (2 x 20ml), and cold propanol (20ml), and dried under vacuum to give [Pt(dppm)Cl$_2$] (1) (3.27 g, 84%); ν_{max} 300 cm^{-1} (Pt–Cl stretch). Found: C, 45.87; H 3.35; calc. for $C_{25}H_{22}Cl_2P_2Pt$: C, 46.17; H, 3.41%.

[Pt(dppm)(SCH$_2$CH$_2$CH$_2$S] (2)

A mixture of [Pt(dppm)Cl$_2$] (1) (1.0 g, 1.53 mmol), 1,3-propanedithiol (0.19 g, 0.21 ml, 1.75 mmol), and sodium carbonate (10 g) in ethanol (150 ml) was stirred overnight at room temperature under a nitrogen atmosphere. The resulting pale yellow suspension was filtered to give a yellow precipitate which was washed with water (100 ml) and dried to give [Pt(dppm)(SCH$_2$CH$_2$CH$_2$S] (2) (0.86 g, 82%). Found: C, 48.67; H, 3.96; calc. for $C_{28}H_{28}P_2PtS_2$: C, 49.04; H, 4.12%.

1,3-Propanedithiol dimethyl ether (3)

A mixture of [Pt(dppm)(SCH$_2$CH$_2$CH$_2$S] (2) (0.567 g, 0.83 mmol) and iodomethane (0.26 g, 0.11 ml, 1.82 mmol) was stirred overnight at room temperature under an argon atmosphere. The mixture was filtered to give a yellow precipitate. The filtrate was concentrated and purified by flash column chromatography using 15% ethyl acetate–petroleum ether as eluant to give 1,3-propanedithiol dimethyl ether (3) (0.074 g, 66%); δ ($CDCl_3$) 1.85 (2H, m), 7.05 (6H, s), and 2.55 (4H, t, *J* 7 Hz). Found: C, 43.25; H, 9.97; calc. for $C_5H_{14}S_2$: C, 43.43; H, 10.20%.

General procedure for catalytic thioether preparation

A mixture of the appropriate thiol (3 mmol), alkyl halide (3 mmol), [Pt(dppm)Cl_2] or [Pt(dppm)I_2] (0.15 mmol, 5 mol%), and sodium carbonate (0.65 g, 6 mmol) is heated under reflux in acetone solution for 24 hours under an argon atmosphere. The mixture is concentrated, extracted into ether, filtered, and re-concentrated *in vacuo* to give the thioether. Purification where necessary is effected by flash chromatography using ethyl acetate in petroleum ether (bp 40-60 °C) as eluant.

Dibutyl thioether (table 1, entry a)

Reaction of 1-iodobutane (0.34 ml, 3 mmol) and 1-butanethiol (0.27 ml, 3 mmol)) in the presence of [Pt(dppm)Cl_2] (5 mol%) by the above procedure gave dibutyl thioether, obtained as a colourless oil (80%); bp 50 °C (1 mmHg); δ (^{1}H, $CDCl_3$) 0.95 (6H, t, *J* 7 Hz), 1.50 (8H, m), and 2.50 (4H, t, *J* 7 Hz).

1,3-Propanedithiol dimethyl ether (3) (table 1, entry b)

Reaction of 1,3-propanedithiol (0.21 g, 0.14 ml, 2 mmol) and iodomethane (0.34 g, 2.4 equiv.) in the presence of [Pt(dppm)Cl_2] (0.13 g, 5 mol%) by the above procedure gave (3), obtained as a colourless oil (70%) with identical spectroscopic characteristics to the product obtained from the reaction above, of (2) with iodomethane.

1,3-Propanedithiol diethyl ether (table 1, entry c)

Reaction of 1,3-propanedithiol (0.32 g, 0.21 ml, 3 mmol) and iodoethane (1.03 g, 2.2 equiv.) in the presence of [Pt(dppm)Cl_2] (5 mol%) by the above procedure gave the title compound, obtained as a colourless oil (90%); δ (^{1}H, $CDCl_3$) 1.26 (6H, t, *J* 7.4 Hz), 1.80–1.94 (2H,m), 2.55 (4H, q, *J* 7.2 Hz), and 2.63 (4H, t, *J* 7.1 Hz). Found: C, 51.10; H, 9.79; calc. for $C_7H_{16}S_2$: C, 51.16; H, 9.81%.

Thioanisole (table 1, entry d)

Reaction of thiophenol (3 mmol) and iodomethane (3.3 mmol) in the presence of [Pt(dppm)Cl_2] (5 mol%) by the above procedure gave thioanisole, obtained as a colourless oil (77%); δ (^{1}H, $CDCl_3$) 2.40 (3H, s), and 7.1–7.3 (5H, m)

Ethyl phenyl thioether (table 1, entry e)

Reaction of bromoethane (0.36 ml, 3.3 mmol) and thiophenol (0.33 ml, 3 mmol) in the presence of [Pt(dppm)Cl_2] (5 mol%) by the above procedure gave the title compound, obtained as a colourless oil (80%); δ (^{1}H, $CDCl_3$) 1.30 (3H, t, *J* 7.3 Hz), 2.90 (2H, q, *J* 7.3 Hz), and 7.2–7.4 (5H, m). Found: C, 69.40; H, 7.19; calc. for $C_8H_{10}S$: C, 69.51; H, 7.29%.

3-Thiomethyl propanol (table 1, entry f)

Reaction of iodomethane (0.19 ml, 3 mmol) and 3-mercaptopropanol (0.28 g, 3 mmol) in the presence of [Pt(dppm)Cl_2] (5 mol%) by the above procedure gave 3-thiomethyl propanol, obtained as a pale yellow oil (69%); ν_{max} 3360 cm^{-1}; δ (^{1}H, $CDCl_3$) 1.80–1.95 (2H, m), 2.10 (3H, s), 2.60 (2H, t, *J* 7.3 Hz), 3.40 (1H, br s), and 3.75 (2H, t, *J* 6.7 Hz). Found: C, 45.14; H, 9.45; calc. for $C_4H_{10}OS$: C, 45.24; H, 9.49%.

Butyl propyl thioether (table 1, entry h)

Reaction of 1-iodobutane (0.34 ml, 3 mmol) and 1-propanethiol (0.28 ml, 3 mmol) in the presence of [Pt(dppm)Cl_2] (5 mol%) by the above procedure gave butyl propyl thioether, obtained as a colourless oil (87%); δ (^{1}H, $CDCl_3$) 0.92 (3H, t, *J* 7 Hz), 1.00 (3H, t, *J* 7 Hz), 1.35–1.50 (2H, m), 1.50–1.70 (4H, m), and 2.45–2.55 (4H, m). Found: C 63.52; H, 12.08; calc. for $C_8H_{16}S$: C, 63.57; H, 12.19%.

General procedure for catalytic thioacetal preparation

A mixture of diiodomethane (3 mmol), thiol (6 mmol, 2 equiv) or dithiol (3 mmol), [Pt(dppm)Cl_2] or [Pt(dppm)I_2] (0.15 mmol, 5 mol%), and sodium carbonate (1.30 g, 12 mmol) is heated under reflux in acetone solution for 24 hours under an argon atmosphere. Work up procedure is identical to that described above for simple thioether preparation.

Formaldehyde dipropyl thioacetal (table 2, entries a and b)

Reaction of diiodomethane (0.24 ml, 3 mmol) and 1-propanethiol (0.28 ml, 6 mmol) in the presence of [Pt(dppm)Cl_2] (5 mol%) by the above procedure gave formaldehyde dipropyl thioacetal, obtained as a colourless oil (entry a, 66%) or (entry b, 70%); b.p. 50 °C (1 mmHg); δ (^{1}H, $CDCl_3$) 1.0 (6H, t, *J* 7.3 Hz), 1.55–1.75 (4H, m), 2.65 (4H, t, *J* 7.3 Hz), and 3.70 (2H, s). Found: C, 51.09%; H, 9.79; calc. for $C_8H_{16}S_2$: C, 51.16; H, 9.81%.

Formaldehyde di-(2-hydroxyethyl) thioacetal (table 2, entry c)

Reaction of diiodomethane (0.40 ml, 5 mmol) and mercaptoethanol (0.35 ml, 5 mmol) in the presence of [Pt(dppm)Cl_2] (5 mol%) by the above procedure gave the title compound, obtained as a viscous yellow oil (73%); ν_{max} 3435 cm^{-1}; δ (^{1}H, $CDCl_3$) 2.65 (4H, t, *J* 6.7 Hz), 3.50–3.60 (4H, m), 3.75 (2H, s), and 4.75 (2H, t, *J* 5.5 Hz). Found: C, 34.21; H, 7.14; calc. for $C_5H_{12}O_2S_2$: C, 35.69; H, 7.19%.

Formaldehyde di-(3-hydroxypropyl) thioacetal (table 2, entry d)

Reaction of diiodomethane (0.24 ml, 3 mmol) and 3-mercaptopropanol (0.28 g, 3 mmol) in the presence of [Pt(dppm)Cl_2] (5 mol%) by the above procedure gave the title compound, obtained as a white crystalline solid (72%); ν_{max} 3440 cm^{-1}; δ (^{1}H, $CDCl_3$) 1.80–1.95 (4H, m), 2.80 (4H, t, *J* 7.3 Hz), 3.00 (2H, br s), 3.70 (2H, s), and 3.75 (4H, t, *J* 6.1 Hz). Found: C, 42.69; H, 8.20; calc. for $C_7H_{16}O_2S_2$: C, 42.82; H, 8.21%.

1,3-Dithiane (table 2, entry e)

Reaction of diiodomethane (0.27 ml, 3.3 mmol) and 1,3-propanedithiol (0.32 g, 0.21 ml, 3 mmol) in the presence of [Pt(dppm)Cl_2] (5 mol%) by the above procedure gave 1,3-dithiane, obtained as a white crystalline solid (70%); δ (^{1}H, $CDCl_3$) 2.05–2.25 (2H, m), 2.85–2.95 (4H, m), and 3.80 (2H, s).

4-Methyl-1,3-dithiane (table 2, entry h)

Reaction of diiodomethane (0.24 ml, 3 mmol) and 1,3-butanedithiol (0.35 ml, 3 mmol) in the presence of [Pt(dppm)Cl_2] (5 mol%) by the above procedure gave 4-methyl-1,3-dithiane, obtained as a pale yellow solid (70%); δ (^{1}H, $CDCl_3$) 1.25 (3H, d, *J* 7.3 Hz), 1.60–1.80 (1H, m), 2.15–2.25 (1H, m), 2.85–2.95 (3H, m), 3.60 (1H, d, *J* 13.4 Hz), and 4.15 (1H, d, *J* 13.4 Hz); m/z (NH_4^+, CI)134 (M^+). Found: C, 45.14; H, 7.57; calc. for $C_5H_{10}S_2$: C, 44.73; H, 7.51%.

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