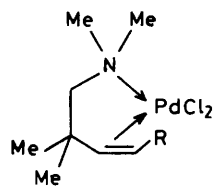
Decomposition of the Product of Methoxypalladation of Dichloro(2,2-dimethylbut-3-enyl methyl sulphide)palladium(II). Identification of an α-Alkoxyalkylpalladium(II) Intermediate

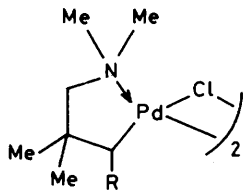
Robert McCrindle* and Alan J. McAlees
Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

The methoxypalladation product $[\{PdCl[CH(CH_2OMe)CMe_2CH_2SMe]\}_2]$ from the title complex (3) undergoes relatively slow decomposition in solution *via* at least two pathways. The major pathway leads to complexes containing the acetal $MeSCH_2CMe_2CH_2CH(OMe)_2$ or the corresponding aldehyde. An important intermediate in this pathway is the α-methoxyalkylpalladium(II) derivative $[\{PdCl[CH(OMe)CH_2CMe_2CH_2SMe]\}_2]$ which has also been generated by reaction of $MeSCH_2CMe_2CH_2CH(Cl)OMe$ with bis(dibenzylideneacetone)palladium(0). The minor pathway involves hydride transfer between ligand molecules and leads to complexes containing both oxidised and reduced ligands. More efficient hydride transfer is observed when the product $[\{PdCl[CH(CH_2Ph)CMe_2CH_2SMe]\}_2]$ from reaction of (3) with $HgPh_2$ is treated with $MeSCH_2CMe_2CH{=}CH_2$.

We have reported [1] that in the methoxypalladation of dichloro(2,2,*N*,*N*-tetramethylbut-3-enylamine)palladium(II) (1a) the initially formed complex (2a) undergoes further reactions which lead to (2b)—(2d). More recent studies [2] have shown that vinyl ether and vinyl alcohol complexes, (1b) and (1c), play a role in the latter reactions. The present paper describes the methoxypalladation of dichloro(2,2-dimethylbut-3-enyl methyl sulphide)palladium(II) (3) to give complex (4) (see Scheme), subsequent reaction of which leads largely to different types of products, containing the acetal (5a) or the corresponding aldehyde (5b).



(1a) R = H
(1b) R = OMe
(1c) R = OH



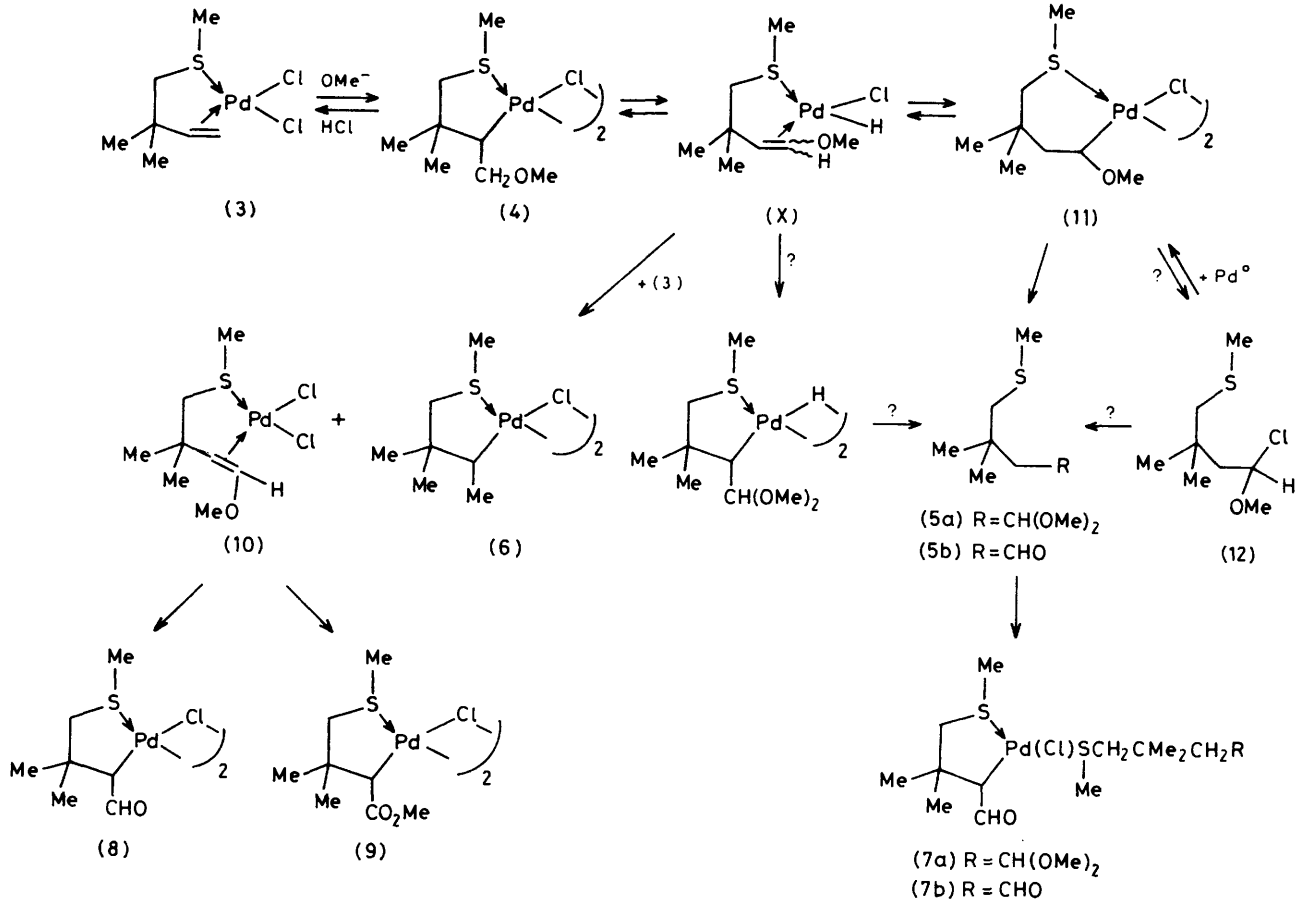
(2a) R = CH_2OMe
(2b) R = Me
(2c) R = CHO
(2d) R = CO_2Me

Results and Discussion

When a suspension of complex (3) was stirred in methanol containing 1 mol equivalent of ethyldi-isopropylamine at ambient temperature for 4 d it dissolved, to give a murky yellow solution from which palladium gradually precipitated. This palladium amounted to about 50% of that initially present. Preparative t.l.c. of the material from the supernatant gave di-μ-chloro-bis[(1,2,2-trimethyl-3-methylthiopropyl-C^1,*S*)palladium(II)] (6), a fraction showing ^{1}H n.m.r. resonances attributable to the moieties $CH_2CH(OMe)_2$, CH_2CHO, $CH{=}CH_2$ (unco-ordinated), and $PdCHCH_3$, and a fraction consisting largely of a complex (7a) containing the acetal (5a). When the reaction was repeated at lower temperature (10 °C) and examined by analytical t.l.c. shortly after all of (3) had gone into solution, essentially one product, (4), less polar than the substrate, was present. Attempts to purify this material by preparative t.l.c. at 0 °C gave a fraction containing largely (4), but contaminated with significant amounts of the aldehyde complex (8) and/or related species (see legend to the Scheme). When a deuteriochloroform solution of this fraction was allowed to stand for several days, changes in its ^{1}H n.m.r. spectrum were observed analogous to those described below for a purer sample of complex (4). Significantly, the amount of complex (8) did not appear to increase. In the course of this decomposition a small amount of *regenerated* olefin complex (3) was precipitated along with some palladium. Repeated preparative t.l.c. of the mixture recovered from the supernatant gave the dimeric species (6), (8), and (9) and the monomeric products (7a) and (7b).

A substantially pure sample of the methoxypalladation product (4), obtained from treatment of complex (3) with 1 mol equivalent of sodium methoxide, was then allowed to decompose in $CDCl_3$. After 4 d, when decomposition appeared to be complete, a ^{1}H n.m.r. spectrum revealed the presence of relatively small amounts of the vinyl ether complex (10), *S*-bonded $MeSCH_2CMe_2CH_2CHO$, and products containing the moieties $PdCHCH_3$ [*cf.* (6)] and $PdCHCO_2Me$ [*cf.* (9)] along with substantial quantities of *S*-bonded $MeSCH_2CMe_2CH{=}CH_2$ and $MeSCH_2CMe_2CH_2CH(OMe)_2$ (5a). The last accounted for (^{1}H n.m.r. integration) *ca.* 75% of the methoxy-groups present, the remainder being ascribable to complexes (9), (10), and free methanol. This behaviour contrasts with that of the nitrogen analogue (2a) which decomposes over several hours, rather than days, to give a mixture containing mainly complexes (1a), (1b), (2b), and (2c).

During the decomposition of complex (4), and prior to the growth of resonances arising from co-ordinated (5a), a transient set of resonances was observed. The peak positions, multiplicities, and relative intensities of these (see Experimental section) suggested the presence of the moiety $CH_2CH(OMe)Pd$ and led us to speculate that complex (11) (or a monomeric analogue) was responsible for these signals. The direct observation of such a compound is particularly interesting since α-alkoxyalkylpalladium species are believed [3] to be intermediates in the formation of vinyl ethers and/or acetals from olefins by alkoxypalladation. To our knowledge no such species has been detected directly. Since the relative



Scheme. Dimeric species are shown for simplicity although the mixtures presumably contain, in addition, mixed dimers and monomers formed by their cleavage

instability of complex (11) precluded its separation from the reaction mixture, we decided to attempt to generate it by reaction of $MeSCH_2CMe_2CH_2CH(Cl)OMe$ (12) with $[Pd(dba)_2]$ [4] (dba = dibenzylideneacetone). Compound (12) was prepared by treating acetyl chloride with the acetal (5a) which was in turn obtained from the product (5b) of homologation of $MeSCH_2CMe_2CHO$.[5]

When the stoicheiometric amount of solid $[Pd(dba)_2]$ was added to compound (12) in $CDCl_3$ immediate reaction occurred to give a yellow solution. Initially, the ^1H n.m.r. spectrum of this solution showed mainly resonances similar to those observed for the transient intermediate formed during decomposition of (4) although they tended to be somewhat broader. On standing, palladium was deposited, and monitoring by ^1H n.m.r. indicated a build-up of signals arising from comparable amounts of *S*-co-ordinated compounds (5a) and (5b) along with much weaker resonances which could be ascribed to the vinyl ether complex (10) and methyl ester [*cf.* (9)]. The results of preparative t.l.c. on this mixture confirmed that there was no other significant product.

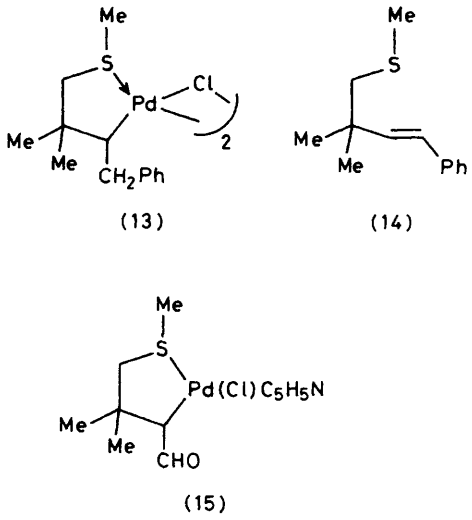
The conversion of 2 mol of complex (11) into (5a) and (5b) requires an additional 1 mol of oxygen atoms. Likely sources are: (*i*) adventitious water; and/or (*ii*) hydroxy-species formed by air oxidation of intermediates containing Pd–H bonds. If only adventitious water were involved the net reaction could be summarised as: (11) + H_2O ⟶ (5a) + (5b) + 2*x*(HPdCl). The last could decompose entirely to Pd^0 with liberation of HCl or disproportionate to Pd^0, $PdCl_2$, and H_2.[6] In the case of air oxidation, deposition of Pd^0 could be explained thus: (11) + $\frac{1}{2}O_2$ ⟶ (5a) + (5b) + Pd^0 + $PdCl_2$. Since at least half of the palladium could be recovered in palladium(II)-containing products the first of these three mechanisms cannot be an exclusive pathway. However, the present evidence does not permit a decision as to the relative importance of the various possibilities.

Formation of acetal (5a) requires transfer of methoxyl from one ligand molecule to another. The relative efficiency of this process is particularly striking. Such transfer could conceivably be mediated by palladium or involve free methanol which subsequently attacks externally. When complex (11) was allowed to decompose in $CDCl_3$ in the presence of 4A molecular sieves, co-ordinated (5a) and (5b) were still formed but the onset of deposition of palladium was markedly delayed and a significantly greater proportion of vinyl ether complex (10) was observed. This would be consistent with the involvement of external attack in the formation of compounds (5a) and (5b). Indeed, when complex (11) was allowed to decompose in $CDCl_3$ containing a small drop of CD_3OD the main product obtained initially was complexed (5a), largely containing the moiety $CH_2CH(OCH_3)OCD_3$ (^1H n.m.r.). Free methanol (CH_3O), co-ordinated (5b), and a trace of methyl ester [*cf.* (9)] were also present. The absence of deuterium at C^2 is consistent with earlier observations [7] on the methoxypalladation of ethylene to give dimethyl acetal. Interestingly, when the reaction was allowed to stand for several weeks a new resonance assignable to $CHDCH(OR)_2$ (R = CH_3 or CD_3) gradually built up. This presumably reflects an exchange reaction catalysed by acid arising from

decomposition of complex (11). The formation of compounds (5a) and (5b) could therefore conceivably result (see Scheme) from (*i*) nucleophilic attack of methanol or water on (or internal transfer of co-ordinated OCH_3 or OH to) a co-ordinated vinyl ether species, *e.g.* (X), followed by reductive elimination of the resulting palladium–alkyl species and Pd–H, or (*ii*) reaction of methanol or water with an α-methoxyalkylpalladium derivative [*cf.* (11)], with Pd^0 acting as leaving group. The former explanation seems unlikely in view of the fact that alkoxypalladation normally requires basic conditions while the present reaction mixture is expected to be somewhat acidic.* The second explanation would accord with the idea [3] that Pd^0 will leave a carbon carrying strongly electron-releasing substituents. While the precise mechanism by which such a displacement might occur is not yet clear, two reasonable pathways can be envisaged. These would involve reversible decomposition of complex (11) with formation, in one case, of the oxocarbenium ion, $MeSCH_2CMe_2CH_2CH{=}\overset{+}{O}Me$, and in the other, of the chloroether, (12), followed by irreversible reaction of either with methanol or water.

As mentioned previously, the major decomposition pathway followed by complex (4) differs significantly from that followed by its nitrogen-containing analogue (2a). The results of the present investigation suggest that an intermediate such as (11) plays a role in the former. The formation of complex (11) can be most simply rationalised by postulating that the Pd–S bond in intermediate (X) (see Scheme) is sufficiently labile that Pd–H is given the opportunity to re-add in the opposite sense [to give (11) rather than (4)] to the vinyl ether while it is co-ordinated *via* the olefin only. A similar pathway should be less favourable for complex (2a) since Pd^{II}–N bonds are expected [8] to be less labile than Pd^{II}–S bonds. Thus, in the present case, hydride transfer from the postulated intermediate (X), with subsequent formation of complexes (6) and (10), does not compete favourably with re-addition to give (11). This could be ascribed to a lack of significant amounts of hydride acceptors [*e.g.* (3)], and/or an inherently greater rate for the pathway involving Pd–H addition. Indeed, when complex (4) was stirred in methanol–dichloromethane with a suspension of (3), which is only slightly soluble in this medium, relatively larger amounts of complexes (6) and (8) were recovered by preparative t.l.c. than from (4) when it was allowed to decompose alone. However, even under these conditions, significant amounts of acetal (5a) were still generated.

The above observations led us to investigate the possibility of facilitating hydride transfer, as opposed to re-addition, in a compound closely related to (4). This possibility has now been realised with the finding that addition of $MeSCH_2CMe_2CH{=}CH_2$ to di-μ-chloro-bis[(1-benzyl-2,2-dimethyl-3-methylthiopropyl-C^1,*S*)palladium(II)] (13) gives the known (6) and (*E*)-2,2-dimethyl-4-phenylbut-3-enyl methyl sulphide (14). Complex (13), formation of which was confirmed by ^1H n.m.r., was obtained by treating (3) with diphenylmercury. It is less stable than the methyl analogue (6), solutions of (13) in $CDCl_3$ depositing palladium fairly rapidly at ambient temperature. The formation of complex (13) involves an olefin arylation analogous to those reported by Heck and co-workers.[9] The structure of compound (14) was confirmed by comparison of its ^1H n.m.r. spectrum with that of the mixture of *cis* and *trans* isomers obtained from a Wittig reaction of $MeSCH_2CMe_2CHO$.



Experimental

M.p.s were determined with a Kofler hot-stage apparatus. Proton n.m.r. spectra were recorded on Bruker WP-60 or Varian EM360L spectrometers for solutions in [^2H]chloroform. 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.

Methoxypalladation of Dichloro(2,2-dimethylbut-3-enyl methyl sulphide)palladium(II) (3).—A suspension of complex (3) [10] (62 mg) in methanol–dichloromethane (1.5 cm^3, 1 : 2 v/v) containing ethyldi-isopropylamine (26 mg) was stirred for 4 d at ambient temperature, during which time palladium metal (8.4 mg) precipitated. The material recovered from the pale yellow filtrate was subjected to preparative t.l.c. (methanol–dichloromethane, 3 : 97 v/v) which gave three major fractions. The least polar, *di-μ-chloro-bis*[(1,2,2-*trimethyl*-3-*methylthiopropyl*-C^1,S)*palladium*(II)], (6) (3.5 mg), had m.p. 130—132 °C (decomp.) from dichloromethane–hexane; δ(45 °C, broadened at ambient) 0.96 (d, J = 7.2, 3 H, CH*Me*), 0.99 (s, 3 H, CMe), 1.32 (s, 3 H, CMe), 2.48 (d, J = 12.5, 1 H, CH_2S), 2.53 (s, 3 H, SMe), 2.68 (d, J = 12.5, 1 H, CH_2S), and 2.89 (q, J = 7.2 Hz, 1 H, C*H*Me) (Found: C, 30.65; H, 5.5. $C_{14}H_{30}Cl_2Pd_2S_2$ requires C, 30.8; H, 5.55%). The fraction (25 mg) of intermediate polarity was a mixture, the ^1H n.m.r. of which showed resonances attributable to the moieties $CH_2CH(OMe)_2$, CH_2CHO, $CH{=}CH_2$ (unco-ordinated), and $PdCHCH_3$. The most polar fraction (15 mg) appeared (^1H n.m.r.) to consist largely of a single component (7a) (see below).

Generation and Decomposition of the Methoxypalladation Product (4).—(*i*) A suspension of complex (3) (0.615 g, 2.00 mmol) in methanol (30 cm^3) containing ethyldi-isopropylamine (0.259 g, 2.00 mmol) was stirred for 3 h at 10 °C during which time the substrate dissolved giving a murky yellow solution. Analytical t.l.c. (methanol–dichloromethane, 1 : 49 v/v) showed mainly one product which had lower polarity than (3). Preparative t.l.c. (methanol–dichloromethane, 1 : 99 v/v) at 0 °C afforded a fraction (0.521 g) which contained (^1H n.m.r.) the methoxypalladation product (4) contaminated

* The formation of small amounts of product(s) containing the methyl ester function does suggest that methoxy- or hydroxypalladation of a vinyl ether [1] is feasible under these conditions. If external nucleophilic attack is involved, such a reaction should take place more readily on, for example, the dichloro-complex (10) than on the presumably less electrophilic hydrido-species (X).

with the aldehyde (8). When a sample of this material was allowed to decompose at ambient temperature for 4 d in $CDCl_3$, ^1H n.m.r. indicated a build-up of resonances attributable to the moieties $CH_2CH(OMe)_2$, CH_2CHO, $CH{=}CH_2$ (unco-ordinated), $PdCHCH_3$, and CH=CHOMe [co-ordinated; δ 4.18 (s, 3 H, OMe), 4.58 (br d, J = 5, 1 H, C*H*=CHOMe), and 7.61 (d, J = 5 Hz, 1 H, CH=C*H*OMe)], while palladium and a small amount of crystalline material were deposited. A ^1H n.m.r. spectrum of a solution of these crystals in $C_6D_5NO_2$ allowed their identification as complex (3).[10] Preparative t.l.c. (methanol–dichloromethane, 1 : 49 v/v) of the mixture recovered from the supernatant gave the least polar component (6) in pure form. The remainder was divided into two fractions, each of which was subjected to further preparative t.l.c. using the same solvent. The less polar fraction yielded two recognisable components. The less polar of these, probably the ester complex (9) [δ 1.07 (s, 3 H, CMe), 1.27 (br s, 3 H, CMe), 2.50 (s, 3 H, SMe), 3.00 (br s, 1 H, C*H*CO_2Me), and 3.62 (s, 3 H, CO_2Me)], was obtained in small quantities as a yellow gum which failed to crystallise. The more polar, the *aldehyde* complex (8), had m.p. 168—170 °C (decomp.) from dichloromethane–hexane [δ 1.15 (s, 3 H, CMe), 1.30 (br s, 3 H, CMe), 2.30 (s, 3 H, SMe), 2.59 (d, J = 11, 1 H, CH_2S), 3.39 (d, J = 11 Hz, 1 H, CH_2S), 3.63 (br s, 1 H, C*H*CHO), and 9.46 (br s, 1 H, CHO) (Found: C, 29.3; H, 4.55. $C_{14}H_{26}Cl_2O_2Pd_2S_2$ requires C, 29.3; H, 4.55%)]. Rechromatography of the most polar, major, fraction from the initial plates gave fairly clean samples of the less polar complex (7a) and of (7b). Purer samples were obtained by further preparative t.l.c. in a different solvent mixture (ethyl acetate–dichloromethane, 1 : 2 v/v) in which their relative polarities were reversed. Both were obtained as yellow gums which could not be induced to crystallise. The acetal complex (7a) had δ 1.11 (s, 6 H, CMe in acetal), 1.19 (s, 3 H, CMe), 1.24 (br s, 3 H, CMe), 1.66 [d, J = 5.3, 2 H, C*H*$_2$CH(OMe)$_2$], 2.41 (br s, 6 H, SMe), 3.25 (s, 6 H, OMe), 3.40 (br s, 1 H, C*H*CHO), 4.41 [t, J = 5.3 Hz, 1 H, C*H*(OMe)$_2$], and 9.29 (br s, 1 H, CHO). The related aldehyde complex (7b) had δ 1.18 (s, 3 H, CMe), 1.23 (s, 9 H, CMe), 2.38 (br s, 6 H, SMe), 2.41 (d, J = 2.4, 2 H, C*H*$_2$CHO), 3.39 (br s, 1 H, C*H*CHO), 9.37 (br s, 1 H, CHC*H*O), and 9.79 (t, J = 2.4 Hz, 1 H, CH_2C*H*O).

The ligands (5a) and (5b) were liberated from the complexes by treatment with slightly more than the stoicheiometric quantity of pyridine in carbon tetrachloride. The products were separated on short columns of Kieselgel G, the ligands being eluted with carbon tetrachloride and identified by comparison of their ^1H n.m.r. spectra with those of authentic samples (see below). Washing with methylene chloride and then acetone gave first a small amount of pyridine and then complex (15), identical (^1H n.m.r.) with a sample prepared from (8); δ 1.14 (s, 3 H, CMe), 1.32 (br s, 3 H, CMe), 2.28 (br s, 3 H, SMe), 2.57 (d, J = 11, 1 H, CH_2S), 3.42 (br s, 1 H, C*H*CHO), 3.48 (d, J = 11 Hz, 1 H, CH_2S), 7.33 (t, 2 H, H_β), 7.65 (d, 1 H, H_δ), 8.66 (d, 2 H, H_α), and 9.20 (br s, 1 H, CHO). Attempts to crystallise (15), which was obtained as a yellow gum, led to its decomposition.

(*ii*) A substantially pure sample of complex (4) was prepared by mixing a solution of (3) in dichloromethane with one containing sodium methoxide (1 equivalent) in dry methanol and then removing the precipitated sodium chloride and solvent. This product had δ 1.08 (s, 3 H, CMe), 1.28 (br s, 3 H, CMe), 2.52 (s, 3 H, SMe), 3.37 (s, 3 H, OMe), and 2.5—3.8 (overlapping multiplets, 5 H). It could not be induced to crystallise.

When the decomposition of this material in $CDCl_3$ was monitored by ^1H n.m.r. the build-up of resonances ascribable to acetal (5a)-containing product(s) was preceded by the development of particularly significant resonances at δ 1.45—1.85 (m, 2 H), 3.51 (s, 3 H), and 4.66 (dd, $J_{obs.}$ = 3.2 and 1.6 Hz, 1 H). These resonances, ascribed to the moiety CH_2CH(OMe)Pd, subsequently declined, and eventually disappeared, while those arising from (5a) built up. Other resonances showed the presence of the moieties CH_2CHO, $CH{=}CH_2$ (unco-ordinated), and CH=CHOMe (co-ordinated). No complex (8), or a monomeric analogue, was detected.

Preparation of 3,3-*Dimethyl*-4-*methylthiobutanal* (5b) *and the Corresponding Dimethyl Acetal* (5a) *and Chloroether* (12).—Tetrahydrofuran (150 cm^3) and then (methoxymethyl)diphenylphosphine oxide [11] (21.9 g) were added at ambient temperature to a solution of lithium dicyclohexylamide, which had been prepared from dicyclohexylamine (18.1 g) and butyl lithium [62.5 cm^3 of a 1.6 mol dm^{-3} solution in hexane to which tetrahydrofuran (20 cm^3) had been added with cooling]. 2,2-Dimethyl-3-methylthiopropanal [5] (11.8 g) was added dropwise, with stirring, to the resulting orange-brown solution to give a pale yellow mixture which was then stirred overnight at ambient temperature. Hydrochloric acid (4 mol dm^{-3}, 50 cm^3) was then added dropwise with stirring and the resulting precipitate of amine hydrochloride was filtered off and washed with diethyl ether and ethyl acetate. Most of the solvent was distilled from the combined filtrate and washings. The residue was redissolved in ether and the solution dried (Na_2SO_4). After removal of the ether, the residual gum was subjected to distillation (Kugelrohr, water pump). The distillate (40—150 °C) (6.1 g) proved (^1H n.m.r.) to be essentially pure 3,3-*dimethyl*-4-*methylthiobutanal* (5b); δ 1.09 (s, 6 H, CMe), 2.03 (s, 3 H, SMe), 2.30 (d, J = 2.4, C*H*$_2$CHO), 2.46 (s, 2 H, CH_2S), and 9.69 (t, J = 2.4 Hz, 1 H, CHO). The corresponding 2,4-*dinitrophenylhydrazone* had m.p. 84—87 °C (Found: C, 47.95; H, 5.75; N, 17.2. $C_{13}H_{18}N_4O_4S$ requires C, 47.85; H, 5.55; N, 17.15%).

The aldehyde (5.95 g) was added to calcium chloride [0.8 g in methanol (3.0 g)] with stirring. The resulting mixture was left at ambient temperature for 2 d with occasional stirring. The two layers thus formed were separated, the lower aqueous layer was extracted with benzene, and this extract was combined with the upper layer. The combined organic phase was then dried (K_2CO_3), filtered, and distilled initially at ambient pressure and finally at a water pump to give the acetal (5a) (4.7 g, b.p. 92—95 °C); δ 0.95 (s, 6 H, CMe), 1.52 [d, J = 5.4, 2 H, C*H*$_2$CH(OMe)$_2$], 2.03 (s, 3 H, SMe), 2.34 (s, 2 H, CH_2S), 3.14 (s, 6 H, OMe), and 4.28 [t, J = 5.4 Hz, 1 H, C*H*(OMe)$_2$].

The acetal (5a) (577 mg) was treated [12] with freshly distilled acetyl chloride (300 mg). After 30 min at ambient temperature, methyl acetate and unreacted acetyl chloride were removed on a rotary evaporator leaving substantially pure (^1H n.m.r.) chloroether (12): δ 0.99 (s, 6 H, CMe), 2.08 (m, 2 H, C*H*$_2$CH), 2.08 (s, 3 H, SMe), 2.44 (s, 2 H, CH_2S), 3.45 (s, 3 H, OMe), and 5.56 (X of ABX, $J + J$ = 11.4 Hz, 1 H, CH_2C*H*).

Reaction of the Chloroether (12) *with Bis(dibenzylideneacetone)palladium*(0).—When the palladium(0) complex [4] (58 mg) was added to a solution of the chloroether (12) (21 mg) in dry $CDCl_3$ (0.8 cm^3) rapid dissolution and discharge of the intense colour of the complex occurred to give a pale yellow solution. In the ^1H n.m.r. spectrum of this solution the major peaks, other than those attributable to dibenzylideneacetone, derived from the α-methoxyalkylpalladium derivative (11): δ 1.13 (br s, 6 H, CMe), 1.4—1.8 (m, 2 H, C*H*$_2$CH), 2.41 (s, 3 H, SMe), 3.55 (s, 3 H, OMe), and 4.73 (dd, $J_{obs.}$ = 3.2 and 1.6 Hz, 1 H, CH_2C*H*). On standing the solution darkened, palladium was deposited, and ^1H n.m.r. resonances attributable to the moieties $CH_2CH(OMe)_2$,

CH_2CHO, and CH=CHOMe (co-ordinated) gradually built up over several hours. Preparative t.l.c. (methanol–methylene chloride, 1 : 99 v/v, run twice) afforded five bands. The least polar (49 mg) was mainly dibenzylideneacetone. The second fraction (1 mg) had an R_f on analytical t.l.c. and a ^1H n.m.r. spectrum attributable to the ester complex (9). The third fraction (6 mg) was probably $[PdCl_2(MeSCH_2CMe_2CH_2CHO)_2]$ and had δ 1.25 (s, 6 H, CMe), 2.39 (s, 3 H, SMe), 2.55 (d, J = 2.2, 2 H, CH_2CHO), 3.02 (s, 2 H, CH_2S), and 9.76 (t, J = 2.2, 1 H, CHO). The fourth fraction (5 mg) was a mixture having ^1H n.m.r. resonances attributable to $CH_2CH(OMe)_2$, CH_2CHO, and PdCHCHO. The ^1H n.m.r. spectrum of the most polar fraction (8 mg) was very similar to that observed (see above) for complex (7a).

Phenylation of Complex (3) *and Hydride Transfer therefrom to 2,2-Dimethylbut-3-enyl Methyl Sulphide.*—Solutions of complex (3) (31 mg) and of diphenylmercury (36 mg) in dichloromethane were mixed and kept in a refrigerator overnight. The solvent was then evaporated and the residue extracted with $CDCl_3$. The ^1H n.m.r. of this solution showed no olefinic resonances. 2,2-Dimethylbut-3-enyl methyl sulphide (20 mg) was added and its subsequent reaction monitored by ^1H n.m.r. The resonances of the added ligand shrank over a period of 12 h while those attributable to the moiety CH=CHPh [δ 6.27 (br s, 2 H)] and to species related to (6) grew steadily. The latter had δ 0.97 (s, 3 H, CMe), 0.98 (d, J = 7.2 Hz, 3 H, CH*Me*), 1.27 (s, 3 H, CMe), and 2.50 (s, 3 H, SMe). The solution remaining when reaction was apparently complete was evaporated and the residue was treated with pyridine (10 mg) in carbon tetrachloride (0.5 cm^3). The resulting solution was filtered through a short column of Kieselgel G, which was then washed with a further portion (0.5 cm^3) of the same solvent. The ^1H n.m.r. of this solution showed it to contain only two components, the minor of which was 2,2-dimethylbut-3-enyl methyl sulphide and the major, (*E*)-2,2-dimethyl-4-phenylbut-3-enyl methyl sulphide (14), which had δ(CCl_4) 1.14 (s, 6 H, CMe), 2.03 (s, 3 H, SMe), 2.45 (s, 2 H, CH_2S), 6.07 (d, J = 16, 1 H, olefinic), 6.12 (d, J = 16 Hz, 1 H, olefinic), and 7.11 (narrow m, 5 H, aromatic).

Preparation of a Mixture of cis *and* trans *Isomers of 2,2-Dimethyl-4-phenylbut-3-enyl Methyl Sulphide.*—2,2-Dimethyl-3-methylthiopropanal (3.91 g) was added to the Wittig reagent prepared from benzyltriphenylphosphonium chloride (11.5 g) and sodium ethoxide (from 0.92 g sodium in 50 cm^3 absolute ethanol). The resulting mixture was stirred for 2 d at ambient temperature under nitrogen. Most of the ethanol was then distilled out and the residue was extracted with hexane. The amber oil recovered from this extract was distilled (Kugelrohr, water pump, 140—150 °C) to give a colourless distillate (5.12 g). The ^1H n.m.r. spectrum showed this to be a mixture of *cis* and *trans* isomers (approximate ratio 5 : 2, respectively): δ(*cis*) 1.00 (s, 6 H, CMe), 2.00 (s, 3 H, SMe), 2.43 (s, 2 H, CH_2S), 5.49 (d, J = 12.7, 1 H, PhCH=C*H*), 6.39 (d, J = 12.7 Hz, 1 H, PhC*H*=CH), and 7.10 (narrow m, 5 H, aromatic); δ(*trans*) 1.17 (s, 6 H, CMe), 2.03 (s, 3 H, SMe), 2.51 (s, 2 H, CH_2S), 6.15 (d, J = 16.2, 1 H, olefinic), 6.17 (d, J = 16.2 Hz, 1 H, olefinic), and 7.10 (narrow m, 5 H, aromatic) (Found: C, 75.5; H, 8.85. $C_{13}H_{18}S$ requires C, 75.65; H, 8.80%).

Acknowledgements

Financial support from NSERC Canada (to R. M.) is gratefully acknowledged.

References

1 E. C. Alyea, S. A. Dias, G. Ferguson, A. J. McAlees, R. McCrindle, and P. J. Roberts, *J. Am. Chem. Soc.*, 1977, **99**, 4985.
2 R. McCrindle, G. Ferguson, M. A. Khan, A. J. McAlees, and B. L. Ruhl, *J. Chem. Soc., Dalton Trans.*, 1981, 986.
3 P. M. Henry, *Adv. Organomet. Chem.*, 1975, **13**, 398.
4 Y. Takahashi, Ts. Ito, S. Sakai, and Y. Ishii, *Chem. Commun.*, 1970, 1065.
5 R. McCrindle, A. J. McAlees, and D. K. Stephenson, *J. Chem. Soc., Perkin Trans. 1*, 1981, 3070.
6 F. R. Hartley, ' The Chemistry of Platinum and Palladium,' Wiley, New York, 1973, p. 62.
7 I. I. Moiseev and M. N. Vargaftik, *Izv. Akad. Nauk SSSR*, 1965, 759.
8 F. R. Hartley, ' The Chemistry of Platinum and Palladium,' Wiley, New York, 1973, p. 220.
9 R. F. Heck, *J. Am. Chem. Soc.*, 1971, **93**, 6896 and refs. therein.
10 R. McCrindle, E. C. Alyea, S. A. Dias, and A. J. McAlees, *J. Chem. Soc., Dalton Trans.*, 1979, 640.
11 S. Trippett, *J. Chem. Soc.*, 1961, 2813; C. Earnshaw, C. J. Wallis, and S. Warren, *J. Chem. Soc., Chem. Commun.*, 1977, 314.
12 C. A. Buehler and D. E. Pearson, ' Survey of Organic Syntheses,' Wiley-Interscience, New York, 1970, p. 310.

Received 24th May 1982; *Paper* 2/860