Preparation of (Chloromethyl)palladium(II) Derivatives from Complexes of Palladium Dichloride by Reaction with Diazomethane or Bis(chloromethyl)-mercury

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Treatment, with diazomethane, of a range of palladium dichloride and dibromide complexes containing chelating ligands has been examined. With all but one, the formation of a mono(halogenomethyl) product was observed. The methylene insertion products from complexes of palladium dichloride are relatively stable if at least one olefin or phosphine ligand is present, but with bis-amine or -sulphide ligands the insertion products could not be isolated. However, all of the insertion products showed at least some tendency to revert to the starting dichloro complexes by loss of the methylene moiety. Products of insertion into a Pd–Br bond are less readily formed than those of the corresponding chloride and the resulting bromomethyl derivatives are less stable than their chloromethyl analogues. Chloromethyl derivatives were also prepared from the dichloride by treatment with bis(chloromethyl)mercury (only one of the two chloromethyl groups is transferred) or from a preformed chloromethyl complex by ligand exchange.

In earlier studies, we found that certain complexes of palladium(II) chloride [1] and of platinum(II) chloride [2] when treated with diazomethane suffer carbene insertion into a metal–halogen bond and give mainly (halogenomethyl)metal complexes. The compounds used all contained either an olefinic sulphide or an olefinic amine as chelating ligands. Further work was carried out to explore the generality of this reaction with platinum(II) and palladium(II) halide complexes. A recent paper reports [3] our results for the platinum(II) derivatives, which, in those cases where products of insertion could be observed, gave either mono- or both mono- and bis-(halogenomethyl) products. In general, insertion only took place at platinum–halogen bonds that were *trans* to a group of high *trans* influence. The present paper deals mainly with the results obtained when a wider range of palladium(II) halide complexes of bidentate ligands were treated with diazomethane. We also report the preparation of some chloromethyl complexes of palladium(II) by transmetallation using bis(chloromethyl)mercury and by ligand exchange from preformed chloromethyl complexes.

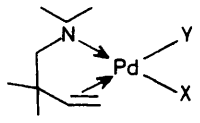
Results

In our initial work we treated [1] the palladium dichloride complex (**1a**) of 2,2,*N*,*N*-tetramethylbut-3-enylamine with ethereal diazomethane and obtained the product (**1b**) of methylene insertion along with the analogous methyl (**1c**) and ethoxymethyl (**1d**) complexes. Since the last arose from ethanol used for the generation [4] of the diazomethane, we thereafter utilised ethanol-free [5] diazomethane in our studies.

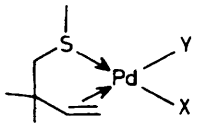
Treatment of the methylthio analogue (**2a**) of (**1a**) gave [1] the chloromethyl complex (**2b**) and a product (**3a**) resulting from cyclopropanation of (**2b**). We have re-examined this reaction and found two further products, the known [6] η-allyl complex (**4**) and the additional cyclopropyl species (**3b**). It appears likely that (**3b**) is a decomposition product of (**3a**) since solutions containing the latter, upon standing, give ^{1}H n.m.r. spectra in which signals for (**3a**) are gradually replaced by those for (**3b**). In addition, it has been shown that compound (**3a**) is formed *via* (**2b**). Indeed, deuterium labelling studies have demonstrated that in this transformation the chloromethyl group does not play an active role, since the CD_2Cl-containing analogue of (**2b**), (**2c**), reacts with diazomethane to give a product (**3c**) which lacks deuterium in the cyclopropane ring. More recently, the reactions of complexes of palladium dichloride containing chelating bis-olefin, -amine, -sulphide, and -phosphine ligands, and of two related complexes of palladium dibromide, with diazomethane have been investigated. The outcome of these studies is summarised below.

Treatment of [$PdCl_2$(cod)] (**5a**; cod = cyclo-octa-1,5-diene) at 0 °C with an excess of diazomethane led to the deposition of small amounts of palladium metal. Only two products, (**5b**) and (**5c**), were obtained in appreciable quantities when the reaction mixture was submitted to preparative t.l.c. The structure of the major product (**5b**), an air-stable pale yellow solid, was readily deduced from its elemental analysis and ^{1}H and ^{13}C n.m.r. spectra (see Experimental section). Both spectra contain resonances attributable to the chloromethyl group and to the diene ligand, in which the olefins are magnetically non-equivalent, as anticipated. The known [7] methyl analogue, (**5c**), was also recovered as a pale yellow solid. This compound appears to be less stable than (**5b**) in solution, depositing Pd^0 slowly. Its structure was again readily deduced from its ^{1}H n.m.r. spectrum, which is very similar to that of (**5b**) except for the resonances arising from the $PdCH_2Cl$ group in the latter and the $PdCH_3$ group in the former. In contrast to (**5a**), when dichloro(hexa-1,5-diene)palladium(II) [8] was treated with an excess of diazomethane much of the palladium was deposited as the metal and there was no evidence (t.l.c., ^{1}H n.m.r.) for the presence of products analogous to (**5b**) or (**5c**).

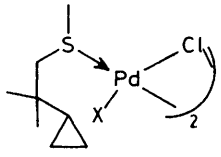
The low solubility of dichloro(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)palladium(II) (**6a**) in the normal range of solvents made the study of its reaction difficult. However, when a saturated solution of this complex in dichloromethane was treated with an excess of diazomethane the methylene insertion product (**6b**) was formed slowly. This compound was prepared more conveniently by displacement of cod from [$Pd(CH_2Cl)Cl$(cod)] (**5b**), with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine. The structure assigned to (**6b**) rests on analytical and ^{1}H and ^{13}C n.m.r. spectral data. Compound (**6b**) is air-stable as a solid, but in solution gradually reverts to (**6a**) during several days. When the more soluble diamine complex (**7a**) (see Experimental section for preparation) was treated with an excess of diazomethane at −60 °C a variety of products were detected by t.l.c. and, when the reaction mixture was warmed to



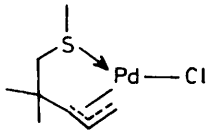
	X	Y
(1a)	Cl	Cl
(1b)	CH_2Cl	Cl
(1c)	Me	Cl
(1d)	CH_2OEt	Cl
(1e)	Br	Br
(1f)	CH_2Br	Br
(1g)	Me	Br



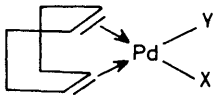
	X	Y
(2a)	Cl	Cl
(2b)	CH_2Cl	Cl
(2c)	CD_2Cl	Cl



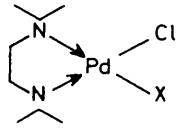
	X
(3a)	CH_2Cl
(3b)	Cl
(3c)	CD_2Cl



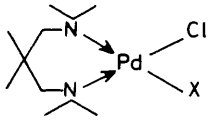
(4)



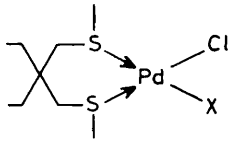
	X	Y
(5a)	Cl	Cl
(5b)	CH_2Cl	Cl
(5c)	Me	Cl
(5d)	Br	Br
(5e)	CH_2Br	Br



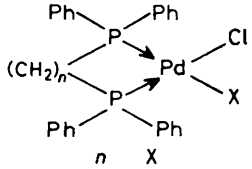
	X
(6a)	Cl
(6b)	CH_2Cl



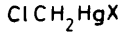
	X
(7a)	Cl
(7b)	CH_2Cl



	X
(8a)	Cl
(8b)	CH_2Cl



	n	X
(9a)	2	Cl
(9b)	3	Cl
(9c)	2	CH_2Cl
(9d)	3	CH_2Cl



	X
(10a)	CH_2Cl
(10b)	Cl

ambient temperature, substantial amounts of Pd^0 were deposited. A ^1H n.m.r. spectrum of the resulting product mixture revealed the presence of a major proportion of substrate in addition to resonances attributable to the methylene insertion product (**7b**). An attempt to recover this product by preparative t.l.c. led to the isolation of only (**7a**). Complex (**7b**) was obtained by reaction of the diamine[3] with $[Pd(CH_2Cl)Cl(cod)]$ in dichloromethane and identified by ^1H n.m.r. spectroscopy. The solid (obtained by precipitation with hexane) is air-stable but, upon dissolution, is converted back into (**7a**) during a few hours.

The complex (**8a**) of 4,4-diethyl-2,6-dithiaheptane[3] and palladium dichloride was prepared as a readily soluble substrate for treatment with diazomethane. In the event, reaction was relatively slow. Monitoring by t.l.c. and ^1H n.m.r. spectroscopy showed that, even after several hours of exposure to an excess of diazomethane, some substrate survived although some of the chloromethyl derivative (**8b**) was produced. Again, the latter was obtained more conveniently by ligand exchange from (**5b**). The product, (**8b**), although stable enough to permit its purification for analysis, is, like (**7b**), gradually converted back into the dichloride upon dissolution in deuteriochloroform.

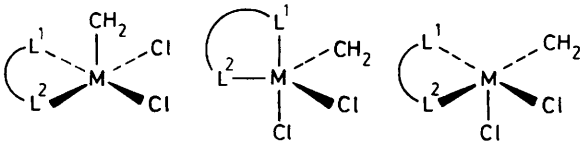
[1,2-Bis(diphenylphosphino)ethane]dichloropalladium(II), (**9a**), and [1,3-bis(diphenylphosphino)propane]dichloropalladium(II), (**9b**), also afforded products, (**9c**) and (**9d**) respectively, of methylene insertion upon exposure to an excess of diazomethane. Reaction in both cases was relatively rapid, and the products were purified by preparative t.l.c. followed by crystallisation. Both (**9c**) and (**9d**) are relatively stable in the dark in deuteriochloroform, but undergo detectable (^1H and ^{31}P n.m.r.) decomposition to the corresponding dichlorides over several days. Complex (**9c**) was also prepared from the cod complex (**5b**) by ligand exchange.

The reaction of two complexes, (**1e**) and (**5d**), of palladium dibromide with diazomethane was also investigated. In both cases the formation of insertion products was appreciably slower than for the chloro analogues. In the case of $[PdBr_2(cod)]$ (**5d**), a ^1H n.m.r. spectrum of the reaction mixture showed many responses in addition to those attributable to the methylene insertion product (**5e**). Purification by preparative t.l.c. led to extensive decomposition, but gave a substantially pure sample of (**5e**) in poor yield. This compound could not be crystallised for analysis, since it gradually precipitates Pd^0 upon dissolution. In the case of (**1e**), even after exhaustive diazomethane treatment at room temperature, some starting complex remained. However the reaction mixture gave ^1H n.m.r. signals attributable to substantial amounts of the bromomethyl species (**1f**) and its methyl analogue (**1g**). Attempts to separate these components by preparative t.l.c. led to the deposition of much Pd^0 and only small amounts of the substrate (**1e**) were recovered.

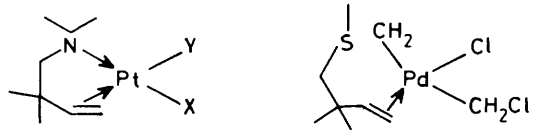
Transmetallation reactions using organomercurials provide a well established route to organometallic compounds. Surprisingly, there is apparently no report of the reaction of bis(chloromethyl)mercury, (**10a**), with transition-metal derivatives. In a series of experiments (for representative examples see Experimental section) complexes (**1a**), (**2a**), and (**5a**) were treated with (**10a**) in dichloromethane. In each case the (chloromethyl)palladium(II) species was formed. For example, monitoring by ^1H n.m.r. spectroscopy and t.l.c. revealed that at ambient temperature (*i*) (**1a**) and a large excess of (**10a**) gave a mixture of (**1b**) and chloro(chloromethyl)mercury (**10b**) in 1 h, (*ii*) (**2a**) and 1 mol equivalent of (**10a**) gave (**2b**) and (**10b**) in 3 d; and (*iii*) (**5a**) and 0.5 mol equivalent of (**10a**) required 4 d for reaction to be complete, giving (**5b**), (**10b**), and unreacted (**5a**).

Discussion

The results reported here and earlier[1] suggest that methylene insertion into one palladium halide bond may be expected when complexes of palladium dichloride (or dibromide) with bidentate ligands are treated with diazomethane. This contrasts with the analogous complexes of platinum where with complexes of bis-amine or -sulphide ligands no insertion products were observed while with bis-olefin or -phosphine ligands both

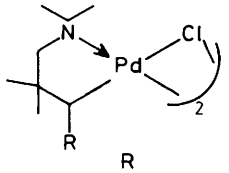


(11a) (11b) (11c)



(12a) X = Cl, Y = Cl
(12b) X = Cl, Y = CH_2Cl
(12c) X = CH_2Cl, Y = Cl

(13)



(14a) R = CH_2OH
(14b) R = CHO

mono- and bis-(chloromethyl) species were formed: exclusive monoinsertion was observed when only one end of the bidentate ligand was an olefinic or a phosphine function.

We have suggested[2,3] that these insertion processes proceed *via* a series of steps [complex + CH_2N_2 ⟶ square-pyramidal adduct (**11a**) ⟶ trigonal-bipyramidal species (**11b**) ⟶ square-pyramidal adduct (**11c**)] similar to those believed[9] to be involved in nucleophilic substitution reactions of square-planar complexes. Two observations concerning the present work on palladium complexes are consistent with such a scheme. First, insertion apparently takes place more rapidly and cleanly in the presence of ligands of high *trans* effect (*viz.* phosphine or alkene *vs.* amine or sulphide). Although the olefinic amine, (**1a**) and (**1e**), and olefinic sulphide, (**2a**), adducts gave products [(**1b**), (**1f**), and (**2b**) respectively] in which the halogenomethyl group is *trans* to the amine or sulphide ligand rather than *trans* to the olefin, it is likely that complexes of the latter type are labile intermediates in the formation of the former. Such a sequence of reactions has been observed[2] for dichloro(2,2,*N*,*N*-tetramethylbut-3-enylamine)platinum(II), (**12a**), for which the product (**12b**) of insertion *trans* to the olefinic ligand has been isolated and shown to undergo facile conversion into the isomer (**12c**). The greater kinetic lability of palladium complexes compared to analogous platinum derivatives[9] may preclude the observation of the intermediates in the former case. Secondly, insertion into the Pd–Cl bond appears to take place more readily than into the Pd–Br bond, in line with expectation[9] for the relative leaving abilities (Cl > Br) of the halogens in nucleophilic substitution reactions.

As noted earlier, only mono(halogenomethyl) complexes could be isolated from reactions of palladium derivatives, while certain platinum derivatives also gave bis(halogenomethyl) complexes. One, or both, of the following rationalisations may explain this difference. (*a*) Bis(halogenomethyl) complexes of palladium can form, but these are labile, and undergo rapid decomposition, *e.g.* with liberation of ethylene and regeneration of the dihalogenopalladium complex. We have found[10] that certain bis(chloromethyl)platinum(II) complexes readily undergo such a decomposition. (*b*) Reactions which compete with the second insertion may be more favourable, *e.g.* Lewis-acid-type catalysis of polymerisation or of ethylene formation.[11] Alternative types of competing reactions are found with the olefinic sulphide complex (**2a**), which gives, in addition to the chloromethyl derivative (**2b**), the cyclopropane-containing species (**3a**) and (**3b**). The last two complexes may result from displacement of the sulphide ligand in (**2b**) (*trans* to labilising CH_2Cl) by diazomethane to give the *trans*-chloromethyl(carbene) intermediate (**13**) in which the originally chelating ligand is monodentate. Reaction of the neighbouring carbene and olefin functions in (**13**) and reco-ordination of the sulphide ligand would give (**3a**), while the subsequent loss of CH_2 from the CH_2Cl group would give (**3b**). The η-allyl species (**4**) may also be formed along this pathway.

Several of the chloromethyl complexes reported in this paper, (**6b**), (**7b**), and (**8b**), have been found to suffer relatively facile 'excision' of the CH_2 moiety. Similar 'excisions' have also been observed[3] for some (chloromethyl)platinum(II) complexes. At present, the fate of the CH_2 moiety in these reactions has not been investigated. We plan to do so. One possibility is that excision simply involves reversal of the original insertion to regenerate the square-pyramidal species (**11a**), which subsequently loses carbene. Such a decomposition pathway could also provide a further possible explanation why bis(chloromethyl) species are not observed in reactions of dichloropalladium complexes with diazomethane, *viz.* loss of carbene from the appropriate intermediate is faster than rearrangement and insertion.

Apart from products of methylene insertion into the metal–halogen bond and of cyclopropanation, two other product types have been encountered in these reactions with diazomethane, namely methylpalladium and (ethoxymethyl)palladium species. These products result from attack of either hydride or ethanol on a carbene-type intermediate and, as mentioned above, the formation of ethers can of course be avoided by using ethanol-free diazomethane. Methylpalladium complexes have been detected by ^1H n.m.r. spectroscopy in the reaction products from (**1a**), (**5a**), and (**2a**) and have been isolated in the first two cases. In our earlier work[1] it had been noticed that the proportions of chloromethyl (**1b**) and methyl (**1c**) products formed from (**1a**) varied appreciably from one experiment to another and, in the present work, attempts were made to find conditions which favour one or the other product. Saturation of the reaction medium with water and prewashing of the glass reaction vessel with either strong acid or strong base had no obvious effect. However, running the reaction at −65 °C reduced the proportion of the methyl product (**1c**). Indeed, when ethereal diazomethane was added at −65 °C to a solution of (**1a**) and lithium chloride in acetone the production of (**1c**) was suppressed even further and only the chloromethyl derivative was detected in the product. Labelling studies[1,12] have shown that much of the hydride required for the production of (**1c**) does not come from solvent, ubiquitous water, or the diazomethane. Indeed, a prime suspect is the product (**14a**) of hydroxypalladation which would decompose to give (**14b**) and hydride (*cf.* ref. 13). Three separate pieces of evidence support this conclusion. First, methylpalladium derivatives have only been obtained from olefinic complexes. Secondly, in reactions where (**1c**) is produced, $CH_2{=}CHCMe_2CH_2NHMe_2^+$ can be detected by ^1H n.m.r. spectroscopy and, thirdly, in these reactions the product of oxidation (**14b**) can also be detected (and has been isolated in one case).

Bis(chloromethyl)mercury transferred only one of its chloromethyl groups to palladium when treated with a complex of palladium dichloride. This accords with previous results[14] for bis(organo)mercurials which show that transfer of the second organo group generally requires use of a catalyst such as

iodide. There are some advantages to preparing (chloromethyl)palladium derivatives by transmetallation using bis(chloromethyl)mercury as opposed to direct reaction with diazomethane. For example, once a batch of the relatively stable bis(chloromethyl)mercury has been made from mercury(II) chloride and diazomethane it can be used to produce (chloromethyl)palladium derivatives thus avoiding the tedium of preparing diazomethane on each occasion. The transmetallation also gives superior yields of (chloromethyl)palladium species partly because by-products such as (**1c**) or (**1d**) are not formed. Generally, chloro(chloromethyl)mercury is readily separable from the desired product by chromatography. An additional advantage arises if the substrate is very insoluble in diethyl ether [*e.g.* (**2a**)] since it often precipitates when it is dissolved in dichloromethane and the ethereal diazomethane is added. The transmetallation reaction avoids this problem since it can be carried out in dichloromethane alone. There are some apparent disadvantages to this procedure. First, if the stoicheiometric amount of bis(chloromethyl)mercury is used the reaction is quite slow, at least at ambient temperature. We have not investigated the outcome of carrying out these reactions at elevated temperatures. Secondly, it is well known that some individuals are hypersensitive to mercury derivatives.

Experimental

For general experimental details see ref. 3.

Reactions of Palladium Complexes with Diazomethane.—*Dichloro*(2,2,N,N-*tetramethylbut*-3-*enylamine*)*palladium*(II) (**1a**). Of the many reactions in which complex (**1a**) has been treated with diazomethane, the following represents a case in which the aldehyde (**14b**) was recovered from the product mixture. A solution of (**1a**) (310 mg) in a mixture of dichloromethane (20 cm^3) and methanol (60 cm^3) was cooled in ice and treated with a very large excess of diazomethane for 2 h. A ^1H n.m.r. spectrum (400 MHz) of the gum (335 mg) obtained on evaporating the solvent showed the presence of a complex mixture including an appreciable amount of $H_2C{=}CHCMe_2{-}CH_2NHMe_2^+$. This mixture was subjected to preparative t.l.c. (dichloromethane–methanol, 49:1) and afforded in order of increasing polarity complexes (**1b**) (7 mg), (**1c**) (26 mg), the methoxy analogue of (**1d**) (12 mg), (**1a**) (21 mg), and (**14b**) (11 mg), all of which were identified by analytical t.l.c. and ^1H n.m.r. spectroscopy (see refs. 1 and 13).

Complex (**1a**) (47 mg) was dissolved in acetone (20 cm^3) containing lithium chloride (150 mg). The solution was then cooled to −65 °C and treated with an excess of ethanol-free diazomethane. After 2 h the solvent was removed on a rotary evaporator and the residue extracted with dichloromethane. The dried extract gave a solid (55 mg) upon evaporation which was essentially the pure (^1H n.m.r. spectroscopy) chloromethyl complex (**1b**).

Dichloro(2,2-*dimethylbut*-3-*en*-1-*yl methyl sulphide*)*palladium*(II) (**2a**). Preparative t.l.c. of the mixture obtained from the reaction of complex (**2a**) (129 mg) in dichloromethane (80 cm^3) with a small excess (monitored by t.l.c.) of ethanol-free diazomethane at −60 °C gave a number of bands, all but three of which yielded minor amounts of material. The least polar of the three major bands gave complex (**3a**) (21 mg), the band of intermediate polarity gave (**2b**) (54 mg), and the most polar band gave (**4**) (23 mg). All three compounds were identified by analytical t.l.c. and ^1H n.m.r. spectroscopy (see refs. 1 and 6).

In a reaction almost identical to the above, but in which the product mixture stood at room temperature for 5 d before separation by preparative t.l.c., the least polar of the three major bands gave (**3b**) (25 mg) as a pale oil. This product could not be induced to crystallise but had δ_H 0.2—0.5 and 0.8—0.9 (m, 5 H, cyclopropyl H), 0.94 (s, 6 H, CMe_2), 2.45 (s, 3 H, SMe), and 2.94 (br s, 2 H, SCH_2). The other two major bands gave complexes (**2b**) (43 mg) and (**4**) (25 mg).

Reaction of complex (**2c**) (130 mg, for preparation see below) in dichloromethane at −60 °C with an excess of ethanol-free diazomethane for 2 h yielded a product (138 mg), a ^1H n..m.r. spectrum of which showed it to be a mixture of mainly (**3c**) and a minor amount of (**3b**). Signals due to the latter increased in intensity when the solution (in deuteriochloroform) was allowed to stand at room temperature. After 3 d the mixture was subjected to preparative t.l.c. (dichloromethane) and gave, as a less polar band, complex (**3c**) (17 mg) and, a more polar band, (**3b**) (23 mg). The integrated intensities for the cyclopropyl resonances in the ^1H n.m.r. spectra of both of these products corresponded to five protons, while the CH_2Cl and CHDCl resonances for (**3c**) integrated for less than 10% of 1 H [*i.e.* similar to that for the substrate (**2c**)].

Dichloro(*cyclo-octa*-1,5-*diene*)*palladium*(II) (**5a**). Preparative t.l.c. (dichloromethane–methanol, 99:1) of the solution obtained by treating complex (**5a**) (41 mg) with an excess of diazomethane in diethyl ether at 0 °C gave three major bands. The least polar of these was the chloromethyl complex (**5b**) (20 mg) which crystallised from dichloromethane–hexane as pale yellow rods, m.p. 118—125 °C (decomp.) [δ_H 2.5—2.8 (m, 8 H, CH_2CH_2), 4.10 (s, 2 H, CH_2Cl), 5.40 (m, 2 H, olefinic H), and 5.98 (m, 2 H, olefinic H); δ_C 27.9 (allylic C), 30.9 (allylic C), 43.4 (PdC), 108.8 (olefinic C), and 123.8 p.p.m. (olefinic C) (Found: C, 36.0; H, 4.55. $C_9H_{14}Cl_2Pd$ requires C, 36.1; H, 4.7%)]. The band of intermediate polarity yielded the known[7] methylpalladium complex (**5c**) (12 mg), which was identified from its ^1H n.m.r. spectrum. The most polar band yielded substrate, (**5a**) (5 mg).

Dichloro(*hexa*-1,5-*diene*)*palladium*(II). When this complex[8] (40 mg) was treated with an excess of ethanol-free diazomethane, large amounts of Pd^0 were precipitated. The solvent was removed on a rotary evaporator and a ^1H n.m.r. spectrum of the very small portion of the residue that dissolved in deuteriochloroform showed it to consist mainly of carbitol [2-(2′-ethoxyethoxy)ethanol] (carried over during the preparation of the diazomethane). The remainder of the black residue (28 mg) did not dissolve in any common organic solvent.

Dichloro(N,N,N′,N′-*tetramethylethylenediamine*)*palladium*(II) (**6a**). Upon heating in refluxing dichloromethane (100 cm^3), 48 mg of this rather insoluble complex dissolved. The resulting solution was then treated at 25 °C with an excess of ethanol-free diazomethane for 2 h. The yellow solid (49 mg) remaining upon evaporation of the solvent consisted (^1H n.m.r. spectroscopy) of a mixture of substrate (**6a**) and the chloromethyl complex (**6b**). An attempt to separate the products by preparative t.l.c. resulted in the recovery of only (**6a**). Complex (**6b**) was obtained by ligand exchange as follows. Treatment of [$Pd(CH_2Cl)Cl(cod)$] (**5b**) (24 mg) with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (9 mg) in dichloromethane gave (**6b**) (14 mg) which crystallised from solution upon addition of hexane [m.p. 175—178 °C (decomp.); δ_H 2.55 (t, 2 H, NCH_2, J = 5.2), 2.58 (s, 6 H, NMe_2), 2.80 (s, 6 H, NMe_2), 2.82 (t, 2 H, NCH_2, J = 5.2 Hz), and 3.62 (s, 2 H, CH_2Cl); δ_C 31.6 (PdC), 48.5 (NMe_2), 50.5 (NMe_2), 58.1 (NCH_2), and 63.6 p.p.m. (NCH_2) (Found: C, 27.55; H, 5.85; N, 8.75. $C_7H_{18}Cl_2N_2Pd$ requires C, 27.35; H, 5.9; N, 9.1%)]. Complex (**6b**) is gradually converted into the dichloro complex (**6a**) upon standing in deuteriochloroform solution for several days.

Dichloro(N,N,N′,N′,2,2-*hexamethylpropane*-1,3-*diamine*)*palladium*(II) (**7a**). This complex was prepared as follows. 2,2,*N*,*N*,*N*′,*N*′-Hexamethylpropane-1,3-diamine (158 mg) was added to a stirred solution of bis(benzonitrile)dichloropalladium(II) (383 mg) in dichloromethane. An excess of hexane was added and the red-brown precipitate was collected and

crystallised from dichloromethane–hexane (twice). This gave yellow crystals (124 mg) of *dichloro*(2,2,N,N,N′,N′-*hexamethylpropane*-1,3-*diamine*)*palladium*(II) (**7a**), m.p. 119—123 °C (decomp.); δ_H 1.20 (s, 6 H, CMe_2), 2.17 (s, 4 H, CH_2), and 2.93 (s, 12 H, NMe_2); δ_C 27.13 (CMe_2), 35.50(?) (4 °C), 55.91 (NMe_2), and 73.93 p.p.m. (NCH_2) (Found: C, 32.25; H, 6.6; N, 8.3. $C_9H_{22}Cl_2N_2Pd$ requires C, 32.2; H, 6.6; N, 8.35%).

Complex (**7a**) (40 mg) was treated with an excess of ethanol-free diazomethane at −60 °C for 2 h. Upon warming to ambient temperature small amounts of Pd^0 precipitated. The residue, obtained by evaporation of the solvent, contained substrate and the chloromethyl complex (**7b**) (^{1}H n.m.r. spectroscopy), but only substrate (19 mg) was recovered from preparative t.l.c.

Treatment of [$Pd(CH_2Cl)Cl(cod)$] (**5b**) (18 mg) with hexamethylpropanediamine (9 mg) in dichloromethane at 0 °C and then evaporation of the solvent (and displaced cod) *in vacuo* at ambient temperature gave a pale brown gum (15 mg). This was essentially pure (^{1}H n.m.r. spectroscopy) chloromethyl complex (**7b**) contaminated with small amounts of (**7a**). The former had δ_H 1.19 (s, 6 H, CMe_2), 2.28 (s, 2 H, NCH_2), 2.53 (s, 2 H, NCH_2), 2.65 (s, 6 H, NMe_2), 2.80 (s, 6 H, NMe_2), and 3.71 (s, 2 H, CH_2Cl). Upon standing in solution in deuteriochloroform the resonances arising from (**7b**) were entirely replaced by those for (**7a**) within 24 h.

Dichloro(4,4-*diethyl*-2,6-*dithiaheptane*)*palladium*(II) (**8a**). This complex was prepared by adding 4,4-diethyl-2,6-dithiaheptane[3] (125 mg) to a stirred solution of bis(benzonitrile)dichloropalladium(II) (192 mg) in dichloromethane (40 cm^3). The resulting solution was reduced in volume and then hexane was added. This gave an orange precipitate which was crystallised (twice) from dichloromethane–hexane to give yellow crystals (145 mg) of *dichloro*(4,4-*diethyl*-2,6-*dithiaheptane*)*palladium*(II) (**8a**), m.p. 225—228 °C (decomp.); δ_H 0.89 (t, 6 H, CH_2Me, J = 7.5), 1.54 (q, 4 H, CH_2Me, J = 7.5 Hz), and 2.74 (br s, 10 H, SCH_2 and SMe); δ_C 7.34 (CH_2Me), 23.75 (SMe), 40.21 (CH_2Me), and 43.37 p.p.m. (SCH_2) (Found: C, 29.2; H, 5.30. $C_9H_{20}Cl_2PdS_2$ requires C, 29.25; H, 5.45%).

Complex (**8a**) (55 mg) in dichloromethane was treated with an excess of diazomethane at ambient temperature for 3 h. The product mixture, which contained (t.l.c. and ^{1}H n.m.r. spectroscopy) both substrate and the methylene insertion product (**8b**), was subjected to preparative t.l.c. and gave a less polar fraction (19 mg) consisting mainly of (**8b**) along with some (**8a**) and a more polar fraction (19 mg) containing only (**8a**).

A pure sample of complex (**8b**) was obtained by ligand exchange. 4,4-Diethyl-2,6-dithiaheptane (18 mg) was added to [$Pd(CH_2Cl)Cl(cod)$] (14 mg) in deuteriochloroform (1 cm^3). Hexane (4 cm^3) was added and the crystalline precipitate collected and recrystallised from dichloromethane–hexane. This gave pale yellow crystals (8 mg) of *chloro*(*chloromethyl*)(4,4-*diethyl*-2,6-*dithiaheptane*)*palladium*(II) (**8b**), m.p. 114—115 °C; δ_H 0.88 (t, 6 H, CH_2Me, J = 7.4), 1.54 (q, 4 H, CH_2Me, J = 7.4 Hz), 2.47 (s, 3 H, SMe), 2.62 (s, 3 H, SMe), 2.69 (s, 2 H, SCH_2), 2.83 (br s, 2 H, SCH_2), and 3.89 (s, 2 H, CH_2Cl) (Found: C, 31.35; H, 5.85. $C_{10}H_{22}Cl_2PdS_2$ requires C, 31.3; H, 5.8%). This complex (**8b**) upon standing in deuteriochloroform was converted into the dichloro complex (**8a**) within 2 d (^{1}H n.m.r. spectroscopy).

[1,2-*Bis*(*diphenylphosphino*)*ethane*]*dichloropalladium*(II) (**9a**). This complex (60 mg) in dichloromethane (30 cm^3) was treated with an excess of ethanol-free diazomethane at −60 °C. The residue from evaporation of the solvent was subjected to preparative t.l.c. (methanol–dichloromethane, 1:49) and gave only one major band (R_f 0.7) which contained an almost colourless solid (55 mg). Crystallisation of this solid from dichloromethane–diethyl ether gave [1,2-*bis*(*diphenylphosphino*)*ethane*]*chloro*(*chloromethyl*)*palladium*(II) (**9c**) (23 mg), m.p. 280—282 °C (decomp.); δ_H 1.57 (s, H_2O, see analysis), 2.3—2.6 (m, 4 H, CH_2CH_2), 3.59 (dd, 2 H, CH_2Cl, J = 2.2 and 6.5 Hz), and 7.2—8.0 (m, 20 H, aromatic H); $\delta_P(CH_2Cl_2)$ 36.03 (d, $^2J_{PP}$ = 29.7) and 57.02 p.p.m. (d, $^2J_{PP}$ = 29.7 Hz) (Found: C, 53.4; H, 4.55. $C_{27}H_{26}Cl_2P_2Pd{\cdot}H_2O$ requires C, 53.35; H, 4.65%).

[1,3-*Bis*(*diphenylphosphino*)*propane*]*dichloropalladium*(II) (**9b**). Treatment of this complex (20 mg) in dichloromethane (20 cm^3) at −60 °C with an excess of diazomethane gave a product (22 mg) which consisted (t.l.c. and ^{1}H n.m.r. spectroscopy) mainly of the chloromethyl complex (**9d**). This compound had been obtained earlier by displacing cod from (**5b**) (27 mg) with 1,3-bis(diphenylphosphino)propane (34 mg). The resulting product was crystallised from dichloromethane–hexane to give almost colourless crystals (27 mg) of [1,3-*bis*(*diphenylphosphino*)*propane*]*chloro*(*chloromethyl*)*palladium*(II) m.p. 300—303 °C (decomp.); δ_H 2.2—2.7 (m, 6 H, $CH_2CH_2CH_2$), 3.42 (dd, 2 H, CH_2Cl, J = 2 and 8 Hz), 5.25 (CH_2Cl_2, see analysis), and 7.3—7.9 (m, 20 H, aromatic H); $\delta_P(CH_2Cl_2)$ −4.65 (d, $^2J_{PP}$ = 57) and 20.90 p.p.m. (d, $^2J_{PP}$ = 57 Hz) (Found: C, 53.7; H, 4.3. $C_{28}H_{28}Cl_2P_2Pd$. 0.4 CH_2Cl_2 requires C, 53.65; H, 4.55%).

Dibromo(*cyclo-octa*-1,5-*diene*)*palladium*(II) (**5d**). Treatment of complex (**5d**) (37 mg) in dichloromethane (20 cm^3) with an excess of ethanol-free diazomethane at ambient temperature for 3 h gave a product consisting (t.l.c., ^{1}H n.m.r. spectroscopy) mainly of substrate and the methylene insertion product (**5e**) and several other unidentified minor products. This mixture was subjected to preparative t.l.c. (dichloromethane–methanol, 59:1) which gave two major bands. The more polar of these was essentially pure substrate (4 mg) while the less polar consisted mainly of the bromomethyl complex (**5e**) (16 mg); δ_H 2.4—2.9 (m, 8 H, allylic H), 3.87 (s, 2 H, CH_2Br), 5.51 (m, 2 H, olefinic H), and 6.02 (m, 2 H, olefinic H). Attempts to crystallise this product led to the deposition of Pd^0.

Dibromo(2,2,N,N-*tetramethylbut*-3-*enylamine*)*palladium*(II) (**1e**). Treatment of this complex[15] (55 mg) in dichloromethane (30 cm^3) with a large excess of ethanol-free diazomethane for 4 h at 25 °C achieved only partial consumption (t.l.c.) of the substrate. Removal of the solvent *in vacuo* gave a dark oil, containing a small amount of Pd^0. A ^{1}H n.m.r. spectrum of the material that dissolved in deuteriochloroform contained signals derived from a major proportion of the bromomethyl complex (**1f**) and smaller amounts of its methyl analogue (**1g**) and substrate (**1e**). Complex (**1f**) had δ_H 1.07 (s, 3 H, CMe), 1.67 (s, 3 H, CMe), 2.32 (d, 1 H, NCH_2, J = 14), 2.53 (s, 3 H, NMe), 2.68 (s, 3H, NMe), 2.75 (d, 1 H, NCH_2, J = 14), 3.22 (d, 1 H, CH_2Br, J = 2.5), 3.83 (d, 1 H, CH_2Br, J = 2.5), 4.46 (d, 1 H, $CH{=}CH_2$, J = 8), 4.64 (d, 1 H, $CH{=}CH_2$, J = 15), and 5.34 (m, 1 H, $CH{=}CH_2$, J = 8 and 15 Hz). The methyl analogue (**1g**) had δ_H 0.67 (s, 3 H, PdMe), 1.03 (s, 3 H, CMe), 1.57 (s, 3 H, CMe), 2.21 (d, 1 H, NCH_2, J = 13), 2.42 (s, 3 H, NMe), 2.59 (s, 3 H, NMe), 2.63 (d, 1 H, NCH_2, J = 13), 4.05 (d, 1 H, $CH{=}CH_2$, J = 8), 4.24 (d, 1 H, $CH{=}CH_2$, J = 15), and 4.90 (m, 1 H, $CH{=}CH_2$, J = 8 and 15 Hz). When this solution was allowed to stand at ambient temperature the resonances arising from complexes (**1f**) and (**1g**) diminished in intensity (those from the former more rapidly) and a palladium mirror formed on the tube. An essentially pure sample (t.l.c. and ^{1}H n.m.r. spectroscopy) of the methyl complex (**1g**) was formed by treating the dibromo compound (**1e**) in dichloromethane at −60 °C with 1 mol equivalent of methylmagnesium bromide. This product was reasonably stable (^{1}H n.m.r. spectroscopy) as a solid but could not be crystallised for analysis since it gradually deposits palladium metal when dissolved.

Reactions of Palladium Complexes with Bis(*chloromethyl*)*mercury* (**10a**).—This compound was prepared by treating[16] mercury(II) chloride with an excess of diazomethane in diethyl ether. The product had δ_H 3.53 [s, Hg satellites, ^2J(Hg–H) = 62

Hz]. The perdeuterio analogue of (**10a**) was prepared using CD_2N_2 (from Deutero-Diazald^R, Aldrich).

Dichloro(2,2,N,N-*tetramethylbut*-3-*enylamine*)*palladium*(II) (**1a**). (*i*) Treatment of complex (**1a**) 19 mg, 0.063 mmol) with bis(chloromethyl)mercury (**10a**) (21 mg, 0.070 mmol) in dichloromethane (20 cm^3) at ambient temperature for 16 h gave a mixture in which *ca.* 50% of (**1a**) had been converted into its chloromethyl analogue (**1b**) (^1H n.m.r. evidence). The reaction mixture was then allowed to stand in dichloromethane for a further 28 h. Preparative t.l.c. of the resulting product mixture gave two major fractions. The less polar product (13 mg) was chloro(chloromethyl)mercury (**10b**); δ_H 3.85 [s, Hg satellites, ^2J(Hg–H) = 118 Hz]. The more polar component was the (chloromethyl)palladium complex (**1b**) (19 mg).

(*ii*) Reaction of complex (**1a**) (171 mg, 0.56 mmol) with bis(chloromethyl)mercury(1.107g,3.7mmol)indichloromethane (40 cm^3) at ambient temperature was complete within 1 h. The reaction mixture was subjected to column chromatography over silica gel (49 g), elution with dichloromethane–methanol (49:1) giving a pale yellow solid (151 mg) which was the fairly pure (t.l.c.) chloromethyl complex (**1b**). Preparative t.l.c. of this material gave pure (**1b**) (147 mg) (t.l.c., ^1H n.m.r. spectroscopy).

Dichloro(2,2-*dimethylbut*-3-*en*-1-*yl methyl sulphide*)*palladium*(II) (**2a**). (*i*) Reaction of complex (**2a**) (40 mg, 0.13 mmol) with bis(chloromethyl)mercury (39 mg, 0.13 mmol) in dichloromethane (20 cm^3) at ambient temperature was essentially complete (t.l.c.) after 3 d. Preparative t.l.c. of the product mixture gave two fractions. The less polar fraction contained chloro(chloromethyl)mercury (14 mg) while the more polar one contained the (chloromethyl)palladium complex (**2b**) (29 mg) which was identified by ^1H n.m.r. spectroscopy.

(*ii*) A further experiment was carried out that was very similar to the one reported above except that an excess of the mercury reagent (**10a**) was used. Thus, when complex (**2a**) (106 mg, 0.35 mmol) in dichloromethane (30 cm^3) was treated with (**10a**) (183 mg, 0.61 mmol) the reaction was complete (t.l.c.) within 1 d. Separation of the components of the product mixture by column chromatography followed by preparative t.l.c. furnished pure (**2b**) (84 mg).

(*iii*) When complex (**2a**) (172 mg, 0.56 mmol) was treated with bis([$^2H_2$]chloromethyl)mercury (625 mg, 2.1 mmol) the reaction was complete within 2 h. The partially deuteriated (chloromethyl)palladium complex (**2c**) (116 mg), recovered as above for (**2b**), gave a ^1H n.m.r. spectrum identical to that for (**2b**) except for the absence of the resonance arising from $PdCH_2$ and the presence of a very small signal (*ca.* 5% of 1 H) assignable to PdCDH.

Dichloro(*cyclo-octa*-1,5-*diene*)*palladium*(II) (**5a**). Reaction of complex (**5a**) (42 mg, 0.15 mmol) with bis(chloromethyl)mercury (22 mg, 0.073 mmol) in dichloromethane (20 cm^3) at ambient temperature appeared to be complete (t.l.c.) after 4 d. Preparative t.l.c. of the resulting mixture gave three major fractions. In order of increasing polarity these contained (t.l.c., ^1H n.m.r. spectroscopy) chloro(chloromethyl)mercury (7 mg), the (chloromethyl)palladium complex (**5b**) (11 mg), and substrate (**5a**) (13 mg).

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References

1 R. McCrindle and D. W. Sneddon, *J. Organometallic Chem.*, 1985, **282**, 413.
2 R. McCrindle, G. Ferguson, G. J. Arsenault, A. J. McAlees, B. L. Ruhl, and D. W. Sneddon, *Organometallics*, 1986, **5**, 1171.
3 R. McCrindle, G. J. Arsenault, R. Farwaha, M. J. Hampden-Smith, R. E. Rice, and A. J. McAlees, *J. Chem. Soc., Dalton Trans.*, 1988, 1773.
4 T. J. de Boer and H. J. Backer, *Recl. Trav. Chim. Pays-Bas*, 1954, **73**, 229.
5 T. J. Boer and H. J. Backer, *Org. Synth.*, 1963, Coll. vol. 4, 250.
6 R. McCrindle, E. C. Alyea, G. Ferguson, S. A. Dias, A. J. McAlees, and M. Parvez, *J. Chem. Soc., Dalton Trans.*, 1980, 137.
7 M. Rudler-Chauvin and H. Rudler, *J. Organomet. Chem.*, 1977, **134**, 115.
8 P. J. Hendra and D. B. Powell, *Spectrochim. Acta*, 1961, **17**, 909.
9 See, for example, J. D. Atwood, 'Inorganic and Organometallic Reaction Mechanisms,' Brooks/Cole Publishing Company, Monterey, California, 1985, ch. 2.
10 R. McCrindle, G. J. Arsenault, M. J. Hampden-Smith, R. E. Rice, and A. J. McAlees, unpublished work.
11 See R. McCrindle, G. J. Arsenault, R. Farwaha, M. J. Hampden-Smith, and A. J. McAlees, *J. Chem. Soc., Chem. Commun.*, 1986, 943.
12 G. J. Arsenault, Ph.D. Thesis, University of Guelph, 1986.
13 R. McCrindle and A. J. McAlees, *J. Chem. Soc., Dalton Trans.*, 1983, 127.
14 See J. Vicente, M. T. Chicote, J. Martin, M. Artigao, X. Solans, M. Font-Altaba, and M. Aguilo, *J. Chem. Soc., Dalton Trans.*, 1988, 141.
15 R. McCrindle, E. C. Alyea, S. A. Dias, and A. J. McAlees, *J. Chem. Soc., Dalton Trans.*, 1979, 640.
16 D. Seyferth, *Chem. Rev.*, 1955, **55**, 1155.

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