Journal of Organometallic Chemistry, 282 (1985) 413–419
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

REACTION OF DIAZOMETHANE WITH THE PALLADIUM(II) CHLORIDE COMPLEXES OF 2,2,*N*,*N*-TETRAMETHYL-3-BUTEN-1-AMINE AND 2,2-DIMETHYL-3-BUTEN-1-YL METHYL SULFIDE. CARBENE INSERTION

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(Received August 21st, 1984)

Summary

Reaction of dichloro(2,2,*N*,*N*-tetramethyl-3-buten-1-amine)palladium(II) with diazomethane in ether/ethanol leads to the carbene insertion product, *a*-chloro-*b*-(chloromethyl)-*d*,*c*-(2,2,*N*,*N*-tetramethyl-3-buten-1-amine)palladium(II) and the analogous ethoxymethyl and methyl complexes. Similar treatment of dichloro(2,2-dimethyl-3-buten-1-yl methyl sulfide)palladium(II) gives the chloromethyl complex and a product of cyclopropanation.

Introduction

In an extension of our studies [1] of the reactions of the olefinic chelates dichloro(2,2,*N*,*N*-tetramethyl-3-buten-1-amine)palladium(II) (**1**) and dichloro(2,2-dimethyl-3-buten-1-yl methyl sulfide)palladium(II) (**2**), we have now treated these complexes with diazomethane. It was anticipated that if a carbene metal or related species were formed [2], a migratory insertion of the olefin of the ligand into this new metal–carbon bond might occur, especially since **2** reacts [1] with $HgPh_2$ to give the olefin arylation product **3**. The intermediacy of carbene-olefin-metal complexes has been invoked in olefin cyclopropanation [3,4] and metathesis [5], in Ziegler–Natta polymerization [6] and in the formation of metallocyclobutanes [5,7,8].

Results and discussion

Treatment of **1** in dichloromethane at 0°C with ethereal diazomethane (containing a small proportion of ethanol) led to the deposition of small quantities of

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0022-328X/85/$03.30

TABLE 1

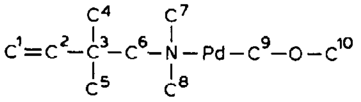
^{1}H NMR DATA (ppm) FOR COMPLEXES IN $CDCl_3$ AT AMBIENT TEMPERATURE

Compound	δ(C–Me)		δ(N–Me)		δ(N–CH_2)		δ(Olefinic)			δ(Pd–$CH_2(CH_3)$)	
	(a)	(e)	(a)	(e)	(a) [a]	(e) [a]	H(1) [b]	H(2) [b]	H(3) [b]	(1)	(2)
1	1.86	1.15	2.93	2.82	3.05	2.35	6.01	5.47	5.08	–	–
4	1.69	1.10	2.65	2.50	2.75	2.31	5.28	4.46	4.62	3.60 [c]	3.95 [c]
5 [d]	1.64	1.03	2.56	2.40	2.62	2.23	4.88	4.22	4.43	4.48 [e]	4.60 [e]
6	1.63	1.09	2.61	2.47	2.64	2.24	4.95	4.06	4.24	0.65	
7 [f]	1.66	1.06	2.57	2.42	2.62	2.23	4.88	4.22	4.43	4.48 [e]	4.51 [e]

[a] d (*J* 14 Hz). [b] *J*(H(1)/H(2)) 8–8.5 Hz/*J*(H(1)/H(3)) 15 Hz. [c] d(*J* 4 Hz). [d] δ(O–CH_2) 3.57 ppm, δ(CH_2–CH_3) 1.18 ppm. [e] d(*J* 2.5 Hz). [f] δ(O–Me) 3.36 ppm.

TABLE 2

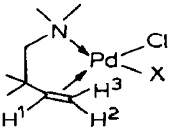
CARBON-13 NMR DATA (ppm) FOR COMPLEXES IN $CDCl_3$



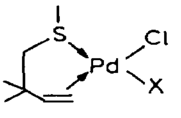
$$C^1{=}C^2{-}\underset{C^5}{\overset{C^4}{C^3}}{-}C^6{-}\underset{C^8}{\overset{C^7}{N}}{-}Pd{-}C^9{-}O{-}C^{10}$$

Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)
ligand	110.6	147.9	38.5	25.5	25.5	71.5	48.4	48.4	–	–
1	85.32	120.28	42.17	27.75	28.12	73.95	54.52	55.52	–	–
4	80.39	117.56	41.69	28.02	28.85	69.20	50.56	51.82	35.25	–
6	74.80	109.82	42.02	28.39	29.05	68.30	49.91	51.43	1.29	–
7	78.98	114.81	41.28	28.72	29.08	68.06	49.65	51.14	71.47	60.88

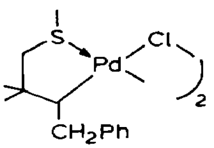
palladium(0) but apparently no polymer. Only three products, **4**–**6**, were detectable (and separated) by TLC. The major product, **4**, forms air-stable, almost colorless, crystals which analyzed for $C_9H_{19}Cl_2NPd$. The gross structure was readily deduced from its ^1H and ^{13}C NMR spectra (see Tables 1 and 2). Both spectra show that the olefinic ligand has survived and is still chelated, since the two *C*- and *N*-methyl groups are magnetically non-equivalent. Comparison of the ^{13}C spectrum of **4** with that of **1** reveals the presence, in the former, of a new resonance attributable to PdCH$_2$Cl and upfield shifts of 3–5 ppm for the resonances of the olefinic C's and the three NC's. In the ^1H spectrum of **4**, the chloromethyl group gives rise to a well-resolved AB quartet and the resonances attributable to the olefinic protons are well upfield of their shift positions [9] for **1** (or indeed for those of the free ligand). The *cis* configuration of the two carbon ligands, first suggested by the magnitude of the magnetic non-equivalence of the protons of the chloromethyl group, was firmly established by an X-ray crystallographic study [10].



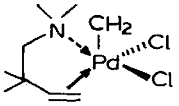
(**1**, X = Cl;
4, X = CH$_2$Cl;
5, X = CH$_2$OEt;
6, X = CH$_3$;
7, X = CH$_2$OMe)



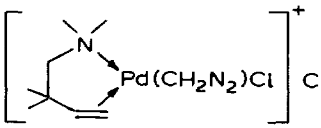
(**2**, X = Cl;
10, X = CH$_2$Cl)



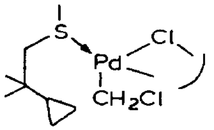
(**3**)



(**8**)



(**9**)



(**11**)

Complexes **5** and **6** were recovered from preparative TLC as pale yellow solids. Solutions of the former gradually deposit palladium(0) and it could not be crystallized for analysis. The latter, however, is almost as stable as **4** and, on crystallization, gave material which analyzed for $C_9H_{20}ClNPd$. The structures of these compounds were also readily assigned on the basis of their ^1H and ^{13}C NMR spectra (see Tables 1 and 2). Their stereochemistry can be inferred, tentatively, from the following observation. When the chloromethyl complex **4**, in dichloromethane, was treated with one molar equivalent of sodium methoxide in dry methanol, initially, small quantities of the methoxy analogue (**7**) of **5** were formed. However, as further amounts of **4** were consumed, a gradually increasing concentration of **6** was noted and palladium(0) started to precipitate. At completion, the only product isolable was **6** (56%).

As expected, treatment of **1** with ethanol-free ethereal diazomethane at 0°C gave only **4** and **6**. When this reaction was repeated at −60°C, with a limited quantity of diazomethane, the proportion of chloromethyl to methyl complex was markedly enhanced. The inference that the latter is formed, at least in part, from the former is supported by the observation that **4** gives **6** when exposed to diazomethane.

Presumably **4** is formed via an intermediate such as **8** or **9**, which could be intercepted by ethanol, rather than chloride, to give **5**. It also seems likely that **6** is formed from a metal-carbene, such as **8**, presumably by inter- or intra-molecular α-hydride abstraction [5,11] from a $PdCH_2Cl$ or $PdCH_2OCH_2CH_3$ moiety. Certainly, when partially deuteriated diazomethane was used in the reaction, some trideuteriated **6** was formed. Alternative sources of hydride *, such as $PdCH_2O\mathit{H}$ (cf.ref. 13) (which would be formed by attack of ubiquitous water on **8** or **9**) or $CH_3C\mathit{H}_2OCH_2CH_3$ and/or $CH_3C\mathit{H}_2OH$ appear unlikely in light of the following two experiments. (i) The $PdCH_3$ group in **6** recovered from treatment of **1** with diazomethane in the presence of D_2O was essentially undeuteriated. (ii) When the diazomethylation was carried out in the presence of methanol, the major product was **7**, but significantly, the proportion of **6** relative to **4** did not increase.

The major mechanistic pathway involved in the conversion of **4** into **6** with sodium methoxide in methanol may well be related to that just discussed. Although metal hydrides are known [14] to be generated in the presence of alkoxide/alcohol combinations, when **4** was treated with Na^+ OCD_3^-/CD_3OD in CD_2Cl_2, only ca. 30% of the product contained $PdCH_2D$, the remainder being undeuteriated. Presumably, **4** generates a carbene, which again abstracts hydride (cf. ref. 15) from $PdCH_2Cl$ or $Pd\mathit{CH}_2OCH_3$. It is noteworthy that complexes **4**, **6** and **7** are all much less susceptible than **1** [20] to methoxypalladation. This may result from the expected increase in electron density at the double bond when the chloride ligand is replaced by carbon (an effect which is apparently mirrored in the upfield shifts of the ^1H and ^{13}C olefinic resonances on going from **1** to **4**, **6** and **7**).

There is ample precedent [2,16] for the carbene insertion which converts **1** into **4**. However, haloalkylmetal complexes [2,16,17] are often unstable. Thus, the isolation of **4**–**7**, in which the carbon ligands are *cis*, is perhaps surprising in view of the knowledge that palladium(II) salts can catalyse the cyclopropanation of olefins with diazoalkanes [4] and that Pd–C bonds may suffer [18] insertion by olefins. Indeed, as noted above, reaction of **2** with $HgPh_2$ leads [1] to the product **3** of olefin insertion. This insertion probably requires cleavage of the metal–sulfur bond, thus allowing the olefin and metal–phenyl bond to become coplanar [19]. Complexes **4**–**7** lack this required geometry ** and can, presumably, achieve it less readily (than **2**), since the Pd–N bond is expected [1] to be less labile than the Pd–S bond.

When **2** was treated with diazomethane at −60°C, several products were detected by TLC and the two major ones were separated by this technique on a preparative scale. These complexes failed to crystallize and decompose slowly at room temperature. However, when first purified, they appear to be pure compounds which can be formulated with some confidence as **10** and **11** on the basis of their ^1H NMR spectra (see Table 1). The tentative assignment of stereochemistry to **10** rests on the similarity in the changes in chemical shift suffered by the olefinic protons on going from $\mathbf{1} \rightarrow \mathbf{4}$ (see Table 1) and $\mathbf{2} \rightarrow \mathbf{10}$ (see [9] and Experimental). A comparison of

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* An attempt at hydride-trapping, by having tetrachloromethane present [12] when **1** was treated with diazomethane, led to diminished yields of **4** and **6**, but no appreciable change in the proportions of these products.

** Certainly, **4** [10] and related complexes [1] do not have this geometry in the solid state. For example, in **4**, the plane containing the Pd and the olefinic carbon atoms makes an angle of about 80° with the coordination plane. ^1H NMR studies suggest [1] that similar geometries exist in solution.

the ^1H NMR spectra of **10** (at −60°C) and of **2** (at ambient temperature) also reveals that the latter, like the former [9], exists in solution as a mixture of isomers with the SCH_3 either pseudoequatorial (major isomer) or pseudoaxial to the chelate ring. However, for **10**, at ambient temperature, the spectrum is severely broadened due to rapid inversion at sulfur [9] and, at −60°C, the proportion of the minor isomer (45%) is markedly unhanced over that (22%) found [9] for **2** (at ambient temperature).

Experimental

Melting points were determined on the Kofler block and are uncorrected. Hydrogen-1 NMR spectra were obtained on a Varian EM360L or Bruker WH-400 (Southwestern Ontario NMR Centre) spectrometer for solutions in deuteriochloroform with tetramethylsilane as internal standard. The latter instrument was also used to obtain carbon-13 spectra, with the same solvent and internal standard. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. TLC plates were spread with Kieselgel G (Merck) and run in dichloromethane/methanol (49/1 or 99/1). Diazomethane was prepared [21] from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide and potassium hydroxide in aqueous ethanol and was distilled and trapped in diethyl ether at 0°C. For ethanol-free diazomethane, 2-(2-ethoxyethoxy)ethanol was substituted for ethanol. Partially deuteriated (ca. 50% D) diazomethane was prepared by this latter procedure using D_2O rather than H_2O as solvent for the potassium hydroxide. Except where noted otherwise, the reactions with diazomethane were conducted by adding the ethereal diazomethane dropwise to ice-cold solutions of the complexes in dichloromethane.

Reaction of dichloro(2,2,N,N-tetramethyl-3-buten-1-amine)palladium(II) (1) with diazomethane

(i) Complex **1** (190 mg) in dichloromethane (20 cm^3) was treated at 0°C with aliquots of diazomethane in diethyl ether (which contained small quantities of ethanol) until analytical TLC showed that no starting material remained. Preparative TLC of the product mixture gave three major bands. The least polar of these contained **4** (45 mg) which crystallized from chloroform/hexane as pale yellow rods, m.p. 136–138°C (dec.) (Found: C, 34.27; H, 5.94; N, 4.31. $C_9H_{19}NCl_2Pd$ calcd.: C, 33.93; H, 6.01; N, 4.36%.) The band of intermediate polarity gave **6** (14 mg) which crystallized as pale yellows rods from dichloromethane/hexane and had m.p. 120–121°C (Found: C, 37.80; H, 6.94; N, 4.86. $C_9H_{20}NClPd$ calcd.: C, 38.05; H, 7.10; N, 4.93%.) The most polar band yielded a pale yellow solid (**5**, 10 mg), solutions of which, in a variety of solvents, gradually precipitated palladium(0).

(ii) Using ethanol-free ethereal diazomethane at −65°C, **1** (219 mg) gave **4** (87 mg) and **6** (14 mg).

(iii) When **1** (140 mg) in dichloromethane (8 cm^3)/methanol (25 cm^3) was treated at 0°C with ethanol-free ethereal diazomethane, **7** (58 mg), **4** (37 mg) and **6** (< 1 mg) were isolated.

(iv) When **1** (142 mg) in dichloromethane (25 cm^3)/tetrachloromethane (25 cm^3) was treated at 0°C with ethanol-free ethereal diazomethane, **4** (20 mg) and **6** (13 mg) were isolated.

(v) Experiment (ii) was repeated using partially deuteriated diazomethane. Complex **6**, recovered by preparative TLC, contained substantial quantities of $PdCH_3$, $PdCH_2D$, $PdCHD_2$ and $PdCD_3$; ^1H NMR (400 MHz, acquired with a digital resolution of 0.735 Hz/pt): δ(ppm) 0.652 (CH_3), 0.634 (CH_2D), 0.617 (CHD_2); ^2H NMR (61.4 MHz; proton decoupled): δ (ppm) 0.63 (CH_2D), 0.61 (CHD_2), 0.59 (CD_3)

*Reaction of dichloro(2,2-dimethyl-3-buten-1-yl methyl sulphide)palladium(II) (**2**) with diazomethane*

The substrate **2** (129 mg) in dichloromethane (50 cm^3) was treated at −60°C with aliquots of ethanol-free ethereal diazomethane until analytical TLC showed that all substrate had reacted. Preparative TLC of the resulting complex mixture showed several bands, each of which gave a pale yellow oil. Two of these fractions accounted for the major proportion of the material recovered. One of the less polar bands gave **11** (21 mg); ^1H NMR: δ 0.2–0.6 (m, cyclopropyl H's), 0.94 (s, 2 × $C{-}CH_3$), 2.50 (s, $S{-}CH_3$), 2.94 (s,$S{-}CH_2$), 3.78 (s, $Pd{-}CH_2{-}Cl$). One of the more polar bands gave **10** (54 mg); ^1H NMR at −60°C: major isomer, δ 1.33 (s, $C{-}CH_3$), 1.49 (s, $C{-}CH_3$), 2.38 (s, $S{-}CH_3$), 2.50(d, J 12.1 Hz, S–CH), 3.03 (d, J 12.1 Hz, S–CH), 3.84 (br s, $Pd{-}CH_2{-}Cl$), 4.59 (d, J 15.2 Hz, olefinic H(3)), 4.69 (d, J 8.0 Hz, olefinic H(2)), 5.31 (dd, J 15.2 and 8.0 Hz, olefinic H(1)); minor isomer, δ 1.33 (s, $C{-}CH_3$), 1.76 (s, $C{-}CH_3$), 2.55 (s, $S{-}CH_3$), 2.66 (d, J 14.9 Hz, S–CH), 2.89 (d, J 14.9 Hz, S–CH), 3.94 (br s, Pd–CH–Cl), 3.98 (br s, Pd–CH–Cl), 4.40 (d, J 8.2 Hz, olefinic H(2)), 4.45 (d, J 15.3 Hz, olefinic H(3)), 5.43 (dd, J 15.3 and 8.2 Hz, olefinic H(1)).

Reactions with sodium methoxide

(i) An equivalent of sodium methoxide in anhydrous methanol was added in three aliquots (30 min apart) to a solution of **4** (28 mg) in dichloromethane (2 cm^3). The reaction was monitored by ^1H NMR and TLC. After the first addition, **4**, **7**, and **6** were present. After the second addition, palladium(0) started to precipitate and the proportion of **6** relative to **4** and **7** increased markedly. After the third addition the solution was filtered and the solvent evaporated to give a pale yellow solid (14 mg) which was substantially pure (NMR) **6** containing a small quantity (< 10%) of **7**.

(ii) The above experiment was repeated using $NaOCD_3/CD_3OD/CD_2Cl_2$. A careful integration was then run (at 400 MHz) for $PdCH_3$ vs. $PdCH_2D$ for the recovered **6**. The ratio of 9/2 corresponds to a product ratio (undeuteriated/monodeuteriated) of 3/1.

(iii) Under the conditions described in (i), both **6** and **7** showed (^1H NMR and TLC) negligible reaction during 2 h.

Acknowledgement

Financial support from NSERC Canada is gratefully acknowledged.

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