Preparation and Crystal Structure Analysis of a Vinyl Ether Chelate, Dichloro[4-methoxy-2,2,*N*,*N*-tetramethylbut-(*Z*)-3-enylamine]palladium(II), and its Conversion into Di-μ-chloro-bis[3-(dimethylamino)-1-formyl-2,2-dimethylpropyl-*C*,*N*]dipalladium(II)

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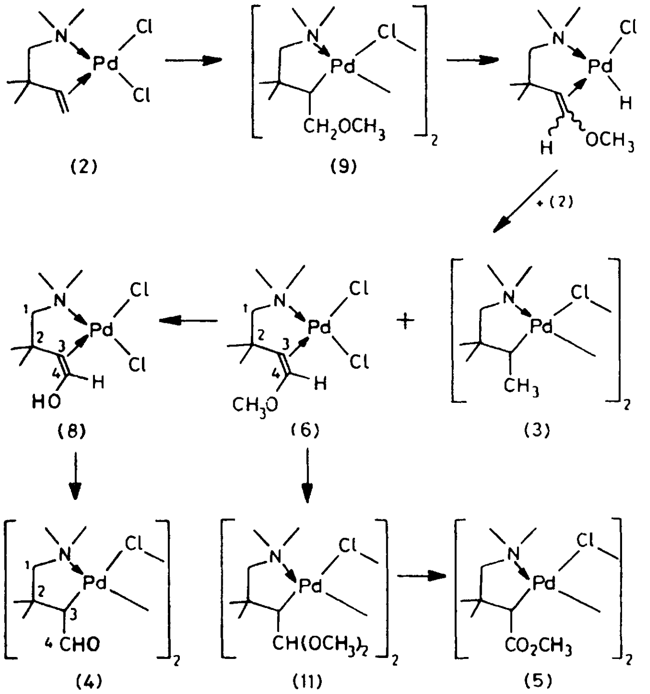
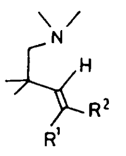
Reaction of either *cis*- (1a) or *trans*-4-methoxy-2,2,*N*,*N*-tetramethylbut-3-enylamine (1b) with PdCl$_2$·2PhCN afforded only the *cis*-vinyl ether chelate [PdCl$_2$(NMe$_2$CH$_2$CMe$_2$CH=CHOMe)], (6). Crystals of (6) are monoclinic, space group $P2_1/n$, with eight molecules in a unit cell of dimensions a = 14.241(3), b = 14.744(2), c = 13.508(1) Å, and β = 111.53(1)°. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations to R = 0.024 8 for 3 981 reflections with $I > 3\sigma(I)$. The two independent molecules have essentially the same conformation and dimensions. In each molecule, the Pd co-ordination is close to square planar with *cis* Cl atoms. The five-membered chelate rings have envelope conformations with quaternary carbon C(2) at the flap. The olefin configuration is *cis*. Principal bond lengths are Pd–Cl (*trans* to olefin) 2.321(1) and 2.330(1), Pd–Cl (*cis* to olefin) 2.298(1) and 2.296(1), Pd–N 2.082(2) and 2.089(2), Pd–C(3) 2.135(3) and 2.139(3), Pd–C(4) 2.266(3) and 2.249(3), C=C 1.363(5) and 1.378(4), C(sp^2)–O 1.336(4) and 1.341(4), O–CH$_3$ 1.436(5) and 1.442(4) Å. It has been shown that (6) is also formed, along with di-μ-chloro-bis[4-(dimethylamino)-3,3-dimethylbut-2-yl-*C*,*N*]dipalladium(II) (3), when dichloro[2,2,*N*,*N*-tetramethylbut-3-enylamine]palladium(II) (2) is allowed to react with di-μ-chloro-bis[4-(dimethylamino)-3,3-dimethyl-1-methoxybut-2-yl-*C*,*N*]dipalladium(II) (9). The last, (9), was generated by reaction of (2) with sodium methoxide. The conversion of (6) into di-μ-chloro-bis[3-(dimethylamino)-1-formyl-2,2-dimethylpropyl-*C*,*N*]dipalladium(II) (4) was investigated and found to proceed *via* a vinyl alcohol complex (8).

We have suggested[1] that complexes of 4-methoxy-2,2,*N*,*N*-tetramethylbut-3-enylamine (1) are key intermediates in the reaction of dichloro(2,2,*N*,*N*-tetramethylbut-3-enylamine)palladium(II) (2) with methanol in the presence of base to give products in which the ligand has been reduced (3) and oxidised [(4) and (5)] (see Scheme). In order to test the validity of this scheme, both *cis* (1a) and *trans* (1b) vinyl ethers have now been prepared and found to react with bis(benzonitrile)dichloropalladium(II) to give the same complex (6). The formation of this complex (6) from (2) has been achieved as has its conversion into (4).

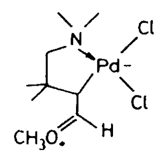


SCHEME Routes to products obtained by base-promoted reaction of dichloro(2,2,*N*,*N*-tetramethylbut-3-enylamine)palladium(II) with methanol

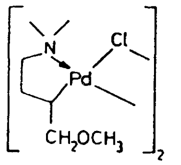


(1a) R' = OCH$_3$, R^2= H

(1b) R' = H, R^2 = OCH$_3$



(7)



(10)

RESULTS AND DISCUSSION

The *cis* ligand (1a) contaminated with minor amounts of the *trans* isomer (1b) was obtained by reaction of 3-dimethylamino-2,2-dimethylpropanal with the Wittig reagent generated from (methoxymethyl)triphenylphosphonium chloride. Treatment of (1a) with mercury(II) acetate established an equilibrium in which (1b) was the predominant component. These isomers are readily distinguishable on the basis of their n.m.r. spectra (see Table 1). The ^{1}H n.m.r. spectra observed on addition of an equimolar amount of either (1a) or (1b) to a solution of PdCl$_2$·2PhCN were identical and were consistent with the presence of a single isomer (6) of the expected complex, which was subsequently obtained in crystalline form. Co-ordination of the double bond was confirmed

TABLE 1

Hydrogen-1 n.m.r. data (p.p.m., Hz observed) for ligands and complexes at ambient temperature

Compound	Solvent	C–Me	N–Me	N–CH_2	O–Me	C(3)–H	C(4)–H	$J(H^3–H^4)$
(1a)	$CDCl_3$	1.08	2.28	2.28	3.53	4.24	5.73	7.0
(1b)	$CDCl_3$	1.00	2.28	2.12	3.38	4.84	6.25	13.2
(6)	$(CD_3)_2CO$	1.18, 1.78	2.58, 2.97	2.56,[a,b] 3.47[b]	4.32	4.49[a]	7.48	4.5
(9)	$(CD_3)_2CO$	0.94, 1.50	2.78, 2.84	2.28,[c,d] 3.18[d]	3.41	*e*	*e*, 3.51[f]	see *f*

[a] $J(H^1–H^3)$ = 1.5. [b] $J_{gem.}$ = 13.0. [c] $J(H^1–H^3)$ = 1.8. [d] $J_{gem.}$ = 12.2. [e] Obscured by N–Me resonances. [f] dd (X part of ABX system, splittings 6,12).

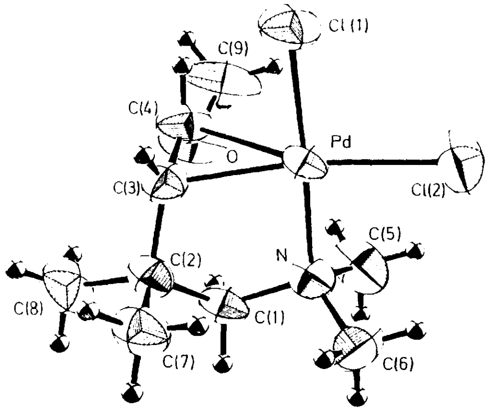


FIGURE 1 View of molecule 1 of (6) showing the crystallographic numbering scheme

by its i.r. spectrum which showed a strong band at 1 522 cm^{-1} in place of the one in (1a) at 1 665 cm^{-1} which is usually associated with ν(C=C). The spin–spin coupling constant (Table 1) for the olefinic protons suggests *cis* geometry for the double bond. Further notable features of the ^1H n.m.r. spectrum are the very low-field shifts of the ethereal methyl group and one of the olefinic protons. These observations and the apparent ease of *trans* to *cis* isomerisation of (1b) on co-ordination to palladium led us to consider that metal–olefin bonding might be envisaged to involve a significant contribution from the canonical form (7) (*cf.* ref. 2). Accordingly, an *X*-ray crystallographic study of the structure of (6) was undertaken.

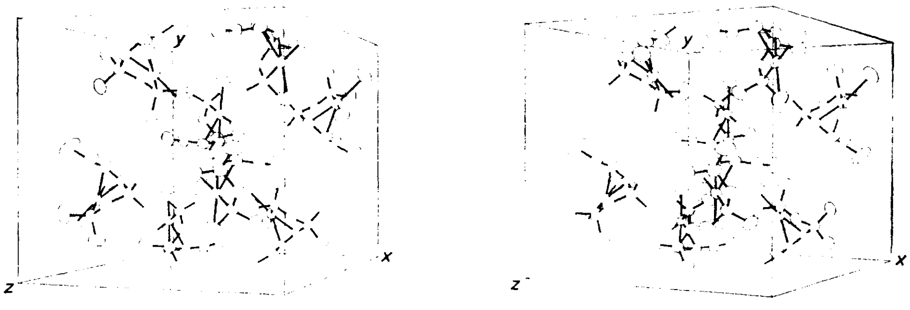


FIGURE 2 Stereoview of the unit-cell contents of (6)

There are two independent molecules of (6) in the asymmetric unit of the crystal structure (details are in the Experimental section). The molecular structure for one of the molecules and the crystallographic numbering scheme is given in Figure 1.* Figure 2 is a stereo pair showing the molecular packing. The final values of the positional parameters with their estimated standard deviations are in Table 2, and Table 3 gives selected interatomic distances, bond angles, and torsion angles. Table 4 gives details of mean-plane calculations. The two independent molecules of (6) have essentially the same conformation in the solid state as shown by the torsion angle and bond length data (Table 3). The palladium co-ordination is approximately square planar with *cis* angles at Pd in the range 83.3—94.1(1)°. The five-membered chelate ring Pd,N,C(1),C(2),C(3) has an envelope conformation with the quaternary carbon atom C(2) at the flap and lying 0.54 (molecule 1) and 0.51 Å (molecule 2) from the best plane through Pd,N,C(1),C(3). Similar conformations have been found for the rings in (8) [3] and (4).[1] The Pd–Cl bond lengths (Table 3) show a *trans* influence, with those *trans* to olefin 0.02—0.03 Å longer than those *trans* to nitrogen. This bond length difference is slightly smaller than that found [3] for the corresponding vinyl alcohol complex (8) (0.05—0.06 Å) and markedly smaller than that found in the aldehyde complex (4),[1] consistent with a trend to increased Pd–C(3) σ-bond character.

The plane containing Pd and olefinic carbons C(3) and C(4) makes an angle of 74.9° (molecule 1) or 76.0° (molecule 2) with the $PdCl_2N$ co-ordination plane. The Pd–olefin interaction is asymmetric with the mean Pd–C(3) distance (2.14 Å) much shorter than the mean Pd–C(4) distance (2.26 Å) and the midpoint of the olefin

* In the crystallographic discussion, for clarity, the numbering scheme in (6) is used and the two independent molecules we designate 1 and 2. For the crystallographic numbering scheme used in Table 2 and Figure 1 the numbers 1 and 2 have been added to the atom labels, *e.g.* C(1) in molecule 1 is labelled C(11), C(1) in molecule 2 is labelled C(21), *etc.*

TABLE 2

Final fractional co-ordinates ($\times 10^5$ for Pd, $\times 10^4$ for O,N,C, $\times 10^3$ for H) for (6) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Pd(1)	105 624(2)	29 493(2)	64 031(2)
Pd(2)	8 771(2)	16 773(2)	17 842(2)
Cl(11)	9 763(1)	3 544(1)	4 730(1)
Cl(12)	9 310(1)	1 858(1)	6 079(1)
Cl(21)	−535(1)	1 020(1)	563(1)
Cl(22)	325(1)	3 090(1)	1 019(1)
O(1)	11 266(2)	4 623(2)	7 796(2)
O(2)	2 615(2)	478(2)	1 842(2)
N(1)	11 372(2)	2 411(2)	7 899(2)
N(2)	2 104(2)	2 242(2)	3 009(2)
C(11)	12 351(2)	2 908(2)	8 395(2)
C(12)	12 750(2)	3 291(2)	7 573(3)
C(13)	11 891(2)	3 746(2)	6 705(2)
C(14)	11 227(3)	4 356(2)	6 837(3)
C(15)	10 793(3)	2 513(4)	8 617(3)
C(16)	11 566(4)	1 424(3)	7 813(3)
C(17)	13 199(3)	2 563(3)	7 068(3)
C(18)	13 567(3)	3 988(3)	8 131(3)
C(19)	10 427(4)	5 161(4)	7 802(4)
C(21)	2 704(2)	1 508(2)	3 737(3)
C(22)	2 093(3)	681(2)	3 785(3)
C(23)	1 389(2)	450(2)	2 661(2)
C(24)	1 665(2)	355(2)	1 790(3)
C(25)	2 782(3)	2 737(3)	2 576(4)
C(26)	1 723(3)	2 908(3)	3 608(4)
C(27)	1 456(4)	820(3)	4 476(3)
C(28)	2 823(4)	−117(3)	4 246(3)
C(29)	2 732(3)	539(3)	828(3)
H(131)	1 187(3)	380(3)	604(3)
H(141)	1 078(3)	471(3)	628(3)
H(231)	82(3)	20(3)	257(3)
H(241)	128(3)	13(3)	114(3)
H(111)	1 225	340	881
H(112)	1 284	250	885
H(151)	1 066	314	869
H(152)	1 118	227	930
H(153)	1 017	219	832
H(161)	1 194	135	736
H(162)	1 094	111	753
H(163)	1 195	119	850
H(171)	1 374	227	761
H(172)	1 344	284	657
H(173)	1 269	213	671
H(181)	1 383	424	764
H(182)	1 410	370	869
H(183)	1 329	446	841
H(191)	1 052	532	852
H(192)	982	482	750
H(193)	1 038	570	740
H(211)	323	132	350
H(212)	300	175	444
H(251)	303	233	219
H(252)	333	299	315
H(253)	242	321	212
H(261)	129	261	389
H(262)	136	338	314
H(263)	228	316	417
H(271)	189	97	518
H(272)	110	28	448
H(273)	99	130	420
H(281)	245	−64	428
H(282)	328	3	494
H(283)	319	−23	380
H(291)	342	63	94
H(292)	235	103	43
H(293)	250	−1	45

bond considerably above the $PdCl_2N$ plane (0.37 Å, molecule 1; 0.58 Å, molecule 2). In (8) the mean Pd–C(3) distance is 2.11 Å while in (4) it is 2.036(4) Å, again consistent with increasing σ-bond character in the sequence (6) < (8) < (4). This trend is further reflected

TABLE 3

Interatomic distances (Å), angles (°), and torsion angles (°) for (6)

	Molecule 1	Molecule 2
(*a*) Bond lengths		
Pd–Cl(1)	2.298(1)	2.296(1)
Pd–Cl(2)	2.321(1)	2.330(1)
Pd–N	2.082(2)	2.089(2)
Pd–C(3)	2.135(3)	2.139(3)
Pd–C(4)	2.266(3)	2.249(3)
N–C(1)	1.497(4)	1.500(4)
N–C(5)	1.494(4)	1.491(5)
N–C(6)	1.494(4)	1.495(4)
C(1)–C(2)	1.529(4)	1.514(4)
C(2)–C(3)	1.507(4)	1.520(5)
C(2)–C(7)	1.531(5)	1.534(5)
C(2)–C(8)	1.528(5)	1.541(5)
C(3)–C(4)	1.363(5)	1.378(4)
C(4)–O	1.336(4)	1.341(4)
C(9)–O	1.436(5)	1.442(4)
C(3)–H(31)	0.89(3)	0.85(4)
C(4)–H(41)	0.94(4)	0.90(4)
(*b*) Angles		
Cl(1)–Pd–Cl(2)	90.6(1)	89.7(1)
Cl(1)–Pd–N	176.3(1)	174.4(1)
Cl(1)–Pd–C(3)	93.6(1)	94.1(1)
Cl(1)–Pd–C(4)	85.1(1)	86.6(1)
Cl(2)–Pd–N	91.9(1)	92.5(1)
Cl(2)–Pd–C(3)	169.4(1)	173.2(1)
Cl(2)–Pd–C(4)	154.5(1)	149.7(1)
N–Pd–C(3)	83.6(1)	83.3(1)
N–Pd–C(4)	93.9(1)	94.1(1)
C(3)–Pd–C(4)	35.9(1)	36.5(1)
Pd–N–C(1)	109.9(2)	110.0(2)
Pd–N–C(5)	110.5(2)	111.0(2)
Pd–N–C(6)	110.4(2)	109.0(2)
C(1)–N–C(5)	107.8(3)	108.4(3)
C(1)–N–C(6)	110.1(3)	110.6(3)
C(5)–N–C(6)	108.0(3)	107.9(3)
N–C(1)–C(2)	112.9(2)	114.3(3)
C(1)–C(2)–C(3)	108.5(3)	108.5(3)
C(1)–C(2)–C(7)	113.1(3)	113.3(3)
C(1)–C(2)–C(8)	108.0(3)	108.6(3)
C(3)–C(2)–C(7)	108.5(3)	108.5(3)
C(3)–C(2)–C(8)	109.8(3)	109.4(3)
C(7)–C(2)–C(8)	108.9(3)	108.5(3)
Pd–C(3)–C(2)	108.3(2)	109.2(2)
Pd–C(3)–C(4)	77.3(2)	76.1(2)
C(2)–C(3)–C(4)	126.6(3)	125.8(3)
Pd–C(4)–C(3)	66.8(2)	67.4(3)
Pd–C(4)–O	112.7(3)	112.1(2)
C(3)–C(4)–O	122.6(3)	122.7(3)
C(4)–O–C(9)	115.5(3)	115.1(3)
H(31)–C(3)–Pd	99(2)	100(3)
H(31)–C(3)–C(2)	123(2)	119(3)
H(31)–C(3)–C(4)	107(2)	113(3)
H(41)–C(4)–Pd	102(2)	101(3)
H(41)–C(4)–C(3)	124(2)	127(3)
H(41)–C(4)–O	113(2)	110(3)

(*c*) Intermolecular contacts ⩽3.5 Å for non-hydrogen atoms and ⩽2.5 Å involving only hydrogen atoms

Cl(3) ··· C(19)^{I}	3.40	Cl(2) ··· C(25)^{II}	3.50

I, $1 - x$, $1 - y$, $1 - z$; II, $\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$

	Molecule 1	Molecule 2
(*d*) Torsion angles		
C(3)–Pd–N–C(1)	5.3	5.4
Pd–N–C(1)–C(2)	−29.1	−28.2
N–C(1)–C(2)–C(3)	45.7	43.0
C(1)–C(2)–C(3)–Pd	−38.6	−35.9
C(2)–C(3)–Pd–N	18.9	17.2
C(2)–C(3)–C(4)–O	−0.0	−1.4
N–Pd–C(3)–C(4)	−105.8	−106.3
N–Pd–C(4)–O	−43.7	−44.7
C(3)–C(4)–O–C(9)	−171.0	−167.6

TABLE 4

Mean-plane data for (6)

(*a*) Displacements (Å) of the atoms from the various planes. An asterisk indicates that the atom was included in the plane equation calculation

	Plane 1			Plane 2			Plane 3		
Atom	Molecule 1		Molecule 2	Molecule 1		Molecule 2	Molecule 1		Molecule 2
Pd	0	*	0	0.035	*	0.065	0.031	*	0.031
Cl(1)	−2.231		−2.245	−0.016	*	−0.031	0.016		−0.087
Cl(2)	0.069		0.104	−0.007	*	−0.001	0.304		−0.130
N	1.991		1.991	−0.018	*	−0.034	−0.043	*	−0.044
C(1)	2.362		2.359	−0.057		−0.014	0.037	*	0.038
C(2)	1.177		1.197	−0.833		−0.591	−0.544		−0.508
C(3)	0	*	0	−0.292		−0.079	−0.024	*	−0.025
C(4)	0	*	0	1.022		1.239	1.273		1.279
Midpoint C(3)–C(4)				0.365		0.580			

(*b*) Plane equations: in the form $aX + bY + cZ = d$ where X, Y, and Z are the fractional co-ordinates given in Table 2

$$\text{Plane 1}\begin{cases}\text{Molecule 1} & -0.731X - 3.493Y + 12.445Z = 6.166\\ \text{Molecule 2} & 10.627X + 6.345Y + 2.683Z = 2.475\end{cases}$$

$$\text{Plane 2}\begin{cases}\text{Molecule 1} & -9.782X + 9.106Y + 8.219Z = -2.419\\ \text{Molecule 2} & 11.413X - 2.119Y - 11.269Z = -1.430\end{cases}$$

$$\text{Plane 3}\begin{cases}\text{Molecule 1} & -8.430X + 10.410Y + 7.818Z = -0.859\\ \text{Molecule 2} & 11.569X - 2.589Y - 11.015Z = -1.416\end{cases}$$

in the mean C(3)–C(4) distances 1.370(5) Å in (6), 1.39(2) Å in (8), and 1.460(8) Å in (4) and in the mean C(4)–O distances 1.339(4) Å in (6), 1.32(1) Å in (8), and 1.234(8) Å in (4). The remaining distances and angles are not significantly different from those found [1,3] in related systems. A significant contribution of canonical form (7) to the bonding in (6) would be consistent with the *X*-ray structural results as well as the ready isomerisation of ligand (1b) during complex formation and the low-field positions of certain of the proton resonances (Table 1) for (6). Ready isomerisation of simple enol ethers on complexation with Pd^{II} and Pt^{II} has been noted previously,[4] and σ-bonded species analogous to (7) have been proposed [5] as intermediates in the platinum(II)-catalysed *cis–trans* isomerisation of vinyl ethers.

To our knowledge, the literature records only one report [4] concerning vinyl ether complexes of Pd^{II}, and no structural work has been reported for such a compound. The details of the metal–olefin interaction found for (6), however, compare very closely with those described [6] for the platinum(II) vinyl ether complex *cis*-dichloro[(*R*)-α-methylbenzylamine][(*S*)-1,2,2-trimethylpropyl (*R*)-vinyl ether]platinum(II). Indeed, comparison of the structural data given [6] for the latter compound with those reported [7] for the platinum(II) vinyl alcohol complex, acetylacetonatochloro(1,2-η-vinyl alcohol)platinum(II), shows the same trend in bonding already indicated for the palladium(II) analogues, (6) and (8). Interestingly, data on the dimeric platinum(II) complexes, $[\{PtCl_2(CH_2{=}CX_2)\}_2]$ (X = OMe [8] or NMe_2 [9]), in which one olefinic carbon now carries two potentially electron-donating groups, indicate essentially σ-bonded (*via* the CH_2 group), zwitterionic structures, although surprisingly, the latter report [9] claims that solutions of the bis(dimethylaminoethylene) complex also contain the π-bonded form as a separate, detectable species.

With the ^1H n.m.r. spectrum of (6) in hand, attempts were made to detect this complex in the course of reaction of (2) with methanol in the presence of base (potassium carbonate or triethylamine). However, the only products detected by ^1H n.m.r. were those, (3), (4), and (5), previously described.[1] This failure is not surprising in the light of subsequent results (see below) which indicate that (6) itself undergoes rapid reaction in methanol in the presence of base. For this reason we decided to add one equivalent of sodium methoxide to (2) in the hope of generating an essentially quantitative yield of (9) which might then be converted into (6) by reaction with a further amount of (2). Indeed, ^1H n.m.r. spectra (Table 1) indicated fairly rapid and complete formation of (9) when (2) was reacted with sodium methoxide. Solutions of (9) are reasonably stable when stored in a refrigerator, but deposit palladium at higher temperatures. The relative instability of (9), when compared with the methoxypalladation adduct (10) derived [10] from dichloro(*N*,*N*-dimethylbut-3-enylamine)-palladium(II), may arise from steric compression between one or both of the geminal methyl groups and the methoxymethyl group in the former. Hydrogen-1 n.m.r. monitoring at ambient temperature of a solution of (9) to which (2) had been added showed a steady build-up of peaks ascribable to (6), (3), and (4). Concomitant deposition of palladium was noted. When this reaction was carried out in $CDCl_3$–CD_3OD (see

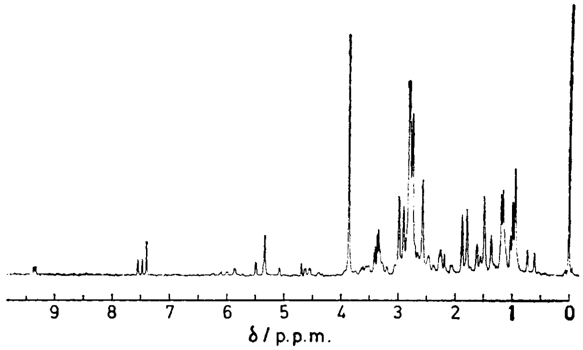


FIGURE 3 ^1H n.m.r. spectrum of the mixture formed on adding a solution of (2) in $CDCl_3$ to a solution of trideuterio(–OCD_3) (9) in CD_3OD and standing for 2 h at ambient temperature

Figure 3), no incorporation of deuterium was detected in the olefinic positions of (6) or in the secondary methyl group of (3). These findings suggest that the earlier portion of the proposed [1] reaction scheme is reasonable and that hydrogen transfer is not mediated by solvent-derived protons.

A study of the conversion of (6) into (4) was next carried out. Since (4) was obtained [1] even when (2) was reacted with triethylamine and methanol under apparently anhydrous conditions we considered the possibility that conversion of (6) into (4) might involve the formation of dimethyl ether, methyl chloride, or methane. However, we have been unable to detect any of these possible products in reactions giving (4). It therefore seems likely that traces of water are involved in this conversion. When deuterium oxide was added to a solution of (6) in $(CD_3)_2CO$ little or no change occurred in the ^1H n.m.r. spectrum. However, upon addition of a weak base, *N,N*-dimethylaniline (0.5 equivalents), a peak due to methanol and a set of peaks ascribable (see below) to an equilibrium mixture of vinyl alcohol complex (8) and aldehyde (4) {*cf.* $[PtCl(acac)(CH_2CHOH)]$ [11]} (acac = acetylacetonate) appeared and grew steadily. After 0.5 h, approximately half of the substrate had undergone reaction. The resonances attributable to the protons on C(3) and C(4) for the equilibrating species were very broad. As more base was added these resonances moved to higher and lower field respectively and the rate of loss of (6) increased. Ultimately, with excess of base the spectrum matched that of the aldehyde (4) in which the C(3) and C(4) protons appear as clean doublets. In our original work [1] on this compound the aldehyde proton was observed to give rise to a slightly broadened singlet in $CDCl_3$. Since this resonance appears as a clean doublet (J = 1.7 Hz) in $(CD_3)_2CO$ it was felt that the broadening observed in $CDCl_3$ might be caused by the presence of traces of acid in the solvent. Accordingly, we have studied the changes resulting in the ^1H n.m.r. spectrum of (4) in $(CD_3)_2CO$ upon dropwise addition of a solution of HCl in the same solvent. Most notably, the aldehyde proton doublet progressively broadens and moves to higher field, ultimately resharpening to a clean doublet (J = 4.8 Hz) at *ca.* δ 7.7. This change reflects the conversion of (4) into a vinyl alcohol complex (8), which we have now isolated [3] as a stable crystalline product.

Hydrogen-1 n.m.r. spectra of (6) in CD_3OD showed little or no change over a period of 10 days. When 1,5-diazabicyclo[5.4.0]undec-5-ene or triethylamine (1—2 equivalents) was added to such solutions and the spectra re-run, the peaks due to (6) had disappeared. The resulting spectra were fairly complex but contained resonances attributable to both (8) and (4), the proportion of the latter increasing with increasing amount of base added. Formation of these products presumably depends on the presence of traces of water. We have been unable to locate peaks ascribable to the acetal (11), particularly a low-field resonance expected for the C(4) proton. A small amount of ester (5) was detected in these reaction mixtures by thin-layer chromatography.

EXPERIMENTAL

General details have been reported.[12]

*4-Methoxy-2,2-*N,N*-tetramethylbut-3-enylamines* (1).—Phenyl-lithium was prepared by reaction of bromobenzene (31.4 g, 0.2 mol) with lithium (1.5 g) in diethyl ether (200 cm^3). Most of the ether was distilled out and replaced by tetrahydrofuran and (methoxymethyl)triphenylphosphonium chloride (68.5 g, 0.2 mol) was added in portions with stirring under N_2. The resulting mixture was stirred for 3 h at 20 °C and then 3-(dimethylamino)-2,2-dimethylpropanal (25.8 g, 0.2 mol) was added in one portion. After stirring at reflux for 24 h, the mixture was cooled and diethylene glycol (200 cm^3) added. Tetrahydrofuran was distilled out at ambient pressure and then crude product was recovered by distillation at the water-pump. This material was purified by heating (100 °C) with sodium (3 g) to remove traces of hydroxylic contaminants and then redistilled at the water-pump to give a fraction (15.6 g) of b.p. 56—58 °C. ^1H N.m.r. (Table 1) showed this to be 85% *cis* (1a), 15% *trans* (1b), $\nu_{max.}$ (liquid film), 1 665s, 1 110s, 1 048s, and 747m, br cm^{-1} (Found: M, 157.147 2. $C_9H_{19}NO$ requires M, 157.146 7).

Mercury(II) acetate (3 mg) was added to a portion (202 mg) of this product in dry methanol (0.25 cm^3). Isomerisation, (1a)—(1b), was monitored by ^1H n.m.r. Equilibrium appeared to have been attained after 6 d at ambient temperature. The methanol was distilled off and the residue taken up in C_6D_6 (1 cm^3) and passed through a short plug of alumina (Fisher; basic, activity I). ^1H N.m.r. integration indicated a *trans* (1b) : *cis* (1a) ratio of 10 : 1.

*Dichloro[4-methoxy-2,2,*N,N*-tetramethylbut-(*Z*)-3-enylamine]palladium*(II) (6).—A slight excess of ligand [mainly (1a) or mainly (1b)] was added to a solution of $PdCl_2{\cdot}2PhCN$ in acetone. In either case only (6) was detected by ^1H n.m.r. The adduct was recovered by evaporation of the acetone and purified by crystallisation from methanol. The product had m.p. 161.5—162.5 °C, $\nu_{max.}$ (Nujol mull) 1 522s, 1 080s, 763m, 730s, 725(sh), and 687m cm^{-1} (Found: C, 31.65; H, 5.95; N, 4.1. $C_9H_{19}Cl_2NOPd$ requires C, 32.3; H, 5.75; N, 4.2%).

Crystal Data for (6).—$C_9H_{19}Cl_2NOPd$, M = 334.5, Monoclinic, a = 14.241(3), b = 14.744(2), c = 13.508(1) Å, β = 111.53(1)°, U = 2 638.3 Å^3, Z = 8, D_c = 1.68 g cm^{-3}, $F(000)$ = 1 344, Mo-K_α radiation, λ = 0.710 69 Å, μ = 16.4 cm^{-1}, space group $P2_1/n$ from systematic absences.

Accurate cell parameters were obtained by a least-squares refinement of the setting angles of 12 reflections (with θ in the range 10—20°) measured on a Hilger and Watts four-circle Y290 diffractometer. Intensity data were collected in our usual way [1] with a small (0.30 × 0.25 × 0.22 mm) crystal to a maximum θ of 25° and 4 652 unique data were obtained. After corrections for Lorentz, polarization effects, and absorption, the data with $I > 3\sigma(I)$ (3 981) were labelled observed and used in structure solution and refinement. All calculations were carried out on the Amdahl V5 computer with our programs for data reduction; the SHELX [13] program system was used in subsequent calculations.

Structure Solution and Refinement.—The co-ordinates of the Pd atoms were obtained from an analysis of a three-dimensional Patterson function and the remaining non-hydrogen atoms were located in a heavy-atom-phased Fourier summation. Refinement was by full-matrix least-squares calculations initially with isotropic and then with anisotropic vibration parameters. A difference map computed at an intermediate stage in the refinement revealed maxima (0.3—0.7 e Å^{-3}) in positions expected for all the hydrogen atoms; these were then allowed for in geometrically idealised positions (C–H, 0.95 Å) and included in the final rounds of calculations. The positional and isotropic thermal parameters of the hydrogens bonded to the olefinic C atoms were allowed to refine; for the remaining H atoms, only an overall isotropic thermal parameter was refined. In the final three refinement cycles a weighting scheme of the form $w^{\frac{1}{2}} = 1/(\sigma^2F + pF^2)^{\frac{1}{2}}$ was employed where the final p parameter was 1.7×10^{-4}. Scattering factors used in the structure factor calculations were taken from refs. 14 and 15 and allowance was made for anomalous dispersion.[16] Refinement converged with $R = 0.024\,8$ and $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0.027\,3$ for the 3 981 reflections with $I > 3\sigma(I)$. A final difference map was devoid of any significant features. The structure factor listing and table of thermal parameters have been deposited as Supplementary Publication No. SUP 22956 (28 pp.).*

Reaction of (2) *with Sodium Methoxide*.—Sodium methoxide, prepared by dissolving sodium metal (4.7 mg) in dry methanol (2 cm^3), was added to an ice-cooled solution of (2) (61 mg) in dichloromethane (2 cm^3) and the mixture kept at 0 °C for 30 min. Some slight darkening occurred during this period. The solvents were removed *in vacuo* and the residue extracted with $(CD_3)_2CO$. An ^{1}H n.m.r. spectrum (see Table 1) was run on the filtered extract. This solution was stable for several hours at 0 °C but noticeable palladium deposition occurred at ambient temperature.

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.