Base-Promoted Reaction of Dichloro(2,2,*N*,*N*-tetramethyl-3-buten-1-amine)palladium with Methanol. A Novel Route to a 2-Oxoalkylpalladium Complex and Its X-Ray Analysis

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Abstract: Dichloro(2,2,*N*,*N*-tetramethyl-3-buten-1-amine)palladium (**1**) reacts with methanol in the presence of base to give a mixture of products, the principal components of which have been separated by preparative thin layer chromatography and identified by IR and ^{1}H NMR (60 and 220 MHz) spectroscopy as dimeric palladium complexes in which both reduction (**2**) and oxidation (**3** and **4**) of the ligand has occurred. The reaction differs from previously reported reactions of chelating olefins in proceeding beyond the oxypalladation step. The reaction pathway also departs from that postulated for the Wacker reaction and similar processes in not leading, via isomerization, to an α-oxypalladium intermediate. Routes to these products (**2-4**) are suggested. X-ray analysis of the major isomer of the largest fraction isolated establishes its structure as a 2-oxoalkylpalladium complex (**3a**). The crystals are tetragonal, $P4_2/n$, $a = 16.535$ (4), $c = 7.956$ (2) Å, $Z = 4$. The structure was solved by conventional methods and refinement gave an R_1 of 0.034 for 2045 independent reflections. In the centrosymmetric dimeric molecule each Pd atom is in a square-planar configuration in a five-membered chelate ring that has an envelope conformation. Principal bond lengths are Pd-Cl (trans to C) 2.476 (1), Pd-Cl (trans to N) 2.335 (1), Pd-C 2.036 (4), Pd-N 2.076 (4) Å. The x-ray data along with spectroscopic evidence establish that a significant interaction exists between the palladium atom and the carbonyl carbon atom C(5) (Pd···C(5) 2.662 (6) Å, ∠C(5)-C(1)-Pd 97.9 (3)°).

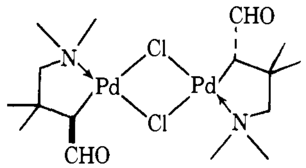
In the course of a study of palladium complexes of chelating olefinic ligands,[1] we have found that reaction of dichloro(2,2,*N*,*N*-tetramethyl-3-buten-1-amine)palladium (**1**)[1] with methanol and 1 molar equiv of base (triethylamine or anhydrous potassium carbonate) at 0 °C or room temperature[2] gives a mixture of compounds including complexes which result from both reduction (**2**) and oxidation (**3** and **4**) of the ligand bound to palladium. This reaction is closely related to previously reported oxypalladation reactions of chelating olefins[3] and to the Wacker reaction and similar processes.[4] However, it differs from both the former, in which reaction does not proceed beyond the oxypalladation step, and the latter, where the corresponding intermediate suffers isomerization to an α-oxyalkylpalladium intermediate.

Results

The principal products have been separated by preparative thin layer chromatography. The pale yellow band due to the least polar product (**2**) darkens rapidly if left on the plate, and palladium is deposited from solutions of **2** on standing. The ^{1}H NMR spectrum (60 MHz) of this product, including a doublet attributable to a secondary methyl group, accords with its formulation as **2**, although the quartet expected for the associated methine proton is obscured in both this spectrum and that run at 220 MHz. In the latter, one of the two peaks assigned to the quaternary methyl groups shows splitting presumably due to the presence of isomers. NMR spectra of samples of **2** which had deposited palladium upon standing showed that partial conversion into **1** had occurred.

The IR and ^{1}H NMR spectra (60 and 220 MHz) of the yellow product (**4**) from the next band clearly indicate the presence of a methoxycarbonyl group. Again, in the NMR spectra the resonance due to the methine proton is obscured and the quaternary methyl resonances show splitting at 220 MHz due to the presence of isomers.

Since the breadth and appearance of the third band on TLC suggested inhomogeneity, it was divided into three fractions before extraction. The ^{1}H NMR spectra of the extracts (**3**) at 60 MHz were virtually identical, the most significant feature being a low-field resonance assignable to an aldehyde proton. The presence of an aldehyde function was confirmed by the IR bands at 1635 and 2730 cm^{-1}. However, 220-MHz ^{1}H NMR spectra showed that two components were present in each fraction (Figure 1), the relative proportion of the minor component[5] increasing in the more polar fractions. Crystallization of the material from the least polar, and major, fraction gave orange-yellow crystals of the major isomer (**3a**), mp 164-166 °C dec, whose structure was determined by a single crystal x-ray analysis (details are in the Experimental Section). The molecule (Figure 2) is a centrosymmetric dimer. Final atomic coordinates are in Table I, and principal molecular dimensions are in Table II. All hydrogen atoms were located in a final difference synthesis and together with the observed dimensions unequivocally establish the structure and stereochemistry of the major isomer of **3**; this is shown as **3a**.



3a

Discussion

The crystal structure of **3a** contains discrete dimeric molecules (Figure 2) separated by normal van der Waals distances. The palladium atom has a slightly distorted square-planar coordination in which the cis angles at Pd are in the range 84.5 (2)-95.6 (1)° (Table II). Within the precision of the data the palladium is not significantly displaced from the plane of the four atoms bonded to it.

The Pd-Cl bonds show a marked trans effect; thus Pd-Cl trans to C(1) (2.476 (1) Å) is significantly longer than that trans to N (2.335 (1) Å). Similar bond length patterns have been found previously, e.g., (N)Pd-Cl 2.309 (3)[6] and (C)-Pd-Cl 2.403 (1) Å.[7] The centrosymmetric four-membered Pd_2Cl_2 ring is necessarily planar.

The conformation of the five-membered ring formed by the ligand and palladium is best described as an envelope in which

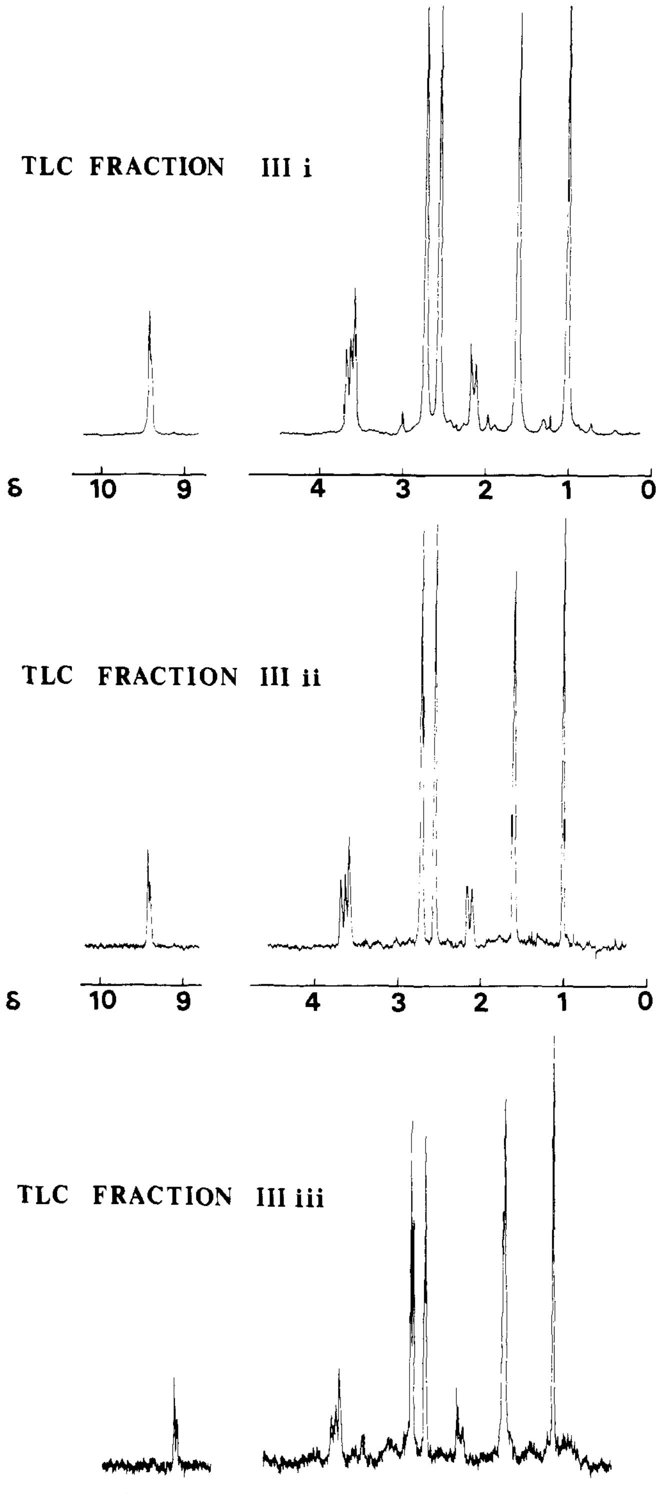


Figure 1. The 220-MHz ^1H NMR spectra of fractions IIIi, IIIii, and IIIiii (two isomers of **3**).

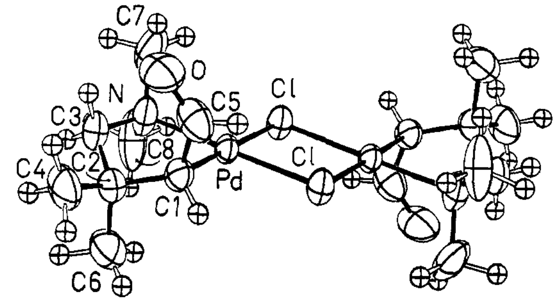


Figure 2. A view of molecule **3a** projected down the *c* axis. The standard deviations of the bond lengths are: Pd-Cl, 0.001; Pd-C, Pd-N, 0.004; C-C, C-N, C-O, 0.006-0.008 Å.

Table I. Final Fractional Coordinates (× 10^5 for palladium, chlorine, 10^3 for hydrogens, and 10^4 for the others)

	x/a	*y/b*	*z/c*
Pd	49667 (2)	40182 (2)	7673 (4)
Cl	54167 (7)	52542 (6)	18332 (13)
C(1)	5325 (3)	3414 (3)	2868 (6)
C(2)	5487 (3)	2538 (3)	2376 (7)
C(3)	4793 (4)	2268 (3)	1276 (8)
C(4)	5514 (4)	1992 (4)	3934 (9)
C(5)	4634 (4)	3612 (4)	3931 (8)
C(6)	6313 (4)	2501 (4)	1517 (11)
C(7)	3664 (4)	2927 (4)	−177 (14)
C(8)	4899 (7)	2696 (4)	−1667 (9)
N	4572 (3)	2891 (2)	−37 (6)
O	4054 (3)	3167 (3)	4243 (7)
H(1)	580 (3)	369 (3)	344 (6)
H(3A)	492 (4)	185 (4)	45 (8)
H(3B)	431 (4)	220 (4)	228 (8)
H(5)	466 (6)	414 (5)	453 (10)
H(4A)[a]	604	207	472
H(4B)	561	150	307
H(4C)	500	186	471
H(6A)	642	186	132
H(6B)	675	273	241
H(6C)	638	282	34
H(7A)	336	302	101
H(7B)	352	233	−64
H(7C)	346	337	−107
H(8A)	555	266	−170
H(8B)	469	315	−254
H(8C)	465	212	−202

[a] Methyl hydrogens have same standard deviations as the carbon atoms to which they are attached.

C(2) is 0.61 Å below the plane containing C(1), C(3), N, and Pd. The geometry around the nitrogen atom is close to tetrahedral (∠C(3)-N-C(Me) 108.6 (5) and 112.2 (5)°, ∠C(3)-N-Pd 108.8 (3)°, ∠Pd-N-C(Me) 107.5 (4) and 111.1 (4)°), and the palladium to *N*-methyl contacts are essentially identical (Pd···C(7) 2.908 (5) and Pd···C(8) 2.923 (6) Å). In marked contrast to this situation is the irregular geometry found at C(1) (Figure 3). Here there are severe distortions from tetrahedral valence angles (e g., ∠Pd-C(1)-C(5) is reduced to 97.9 (3)°), and the C(1)-C(5) bond (1.460 (8) Å) is significantly *shorter* than anticipated for a normal C_{sp^3}-C_{sp^2} single bond (1.505 Å).[8] The nature of the bonding to palladium and formulations which are consistent with these observations are discussed below.

The orientation of the aldehydic carbonyl oxygen atom above the five-membered ring (torsion angle H-C(1)-C(5)-H 31°), as opposed to a conformation with the hydrogens on C(1) and C(5) trans, probably arises from a favorable dipole-dipole interaction with the nitrogen atom, which is formally positive.

The low value of the carbonyl stretching frequency in the IR spectrum of **3a**, which implies a weakening of the C═O bond, first drew our attention to the possibility of an interaction between the aldehyde group and the palladium atom. Comparable stretching frequency values have been reported[9] for other 2-oxoalkyl derivatives of transition metals, but apparently no explanation had been advanced for this phenomenon until very recently.[10] The orientation of the aldehyde group as revealed by the x-ray investigation indicates that this in-

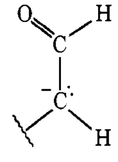
Table II

	(A) Bond Lengths, Å[a,b,c]		
C(1)-C(2)	1.523 (7)	Pd-Cl	2.335 (1)
C(1)-C(5)	1.460 (8)	Pd-Cl′	2.476 (1)
C(2)-C(3)	1.511 (7)	Pd-C(1)	2.036 (4)
C(2)-C(4)	1.535 (7)	Pd-N	2.076 (4)
C(2)-C(6)	1.529 (8)		
C(3)-N	1.512 (6)	C(1)-H(1)	1.01 (5)
C(5)-O	1.234 (8)	C(3)-H(3A)	0.97 (6)
N-C(7)	1.506 (8)	C(3)-H(3B)	1.14 (6)
N-C(8)	1.442 (8)	C(5)-H(5)	1.00 (8)
	(B) Valency Angles, deg[a]		
Cl-Pd-Cl′	87.7 (1)	C(3)-C(2)-C(4)	108.4 (4)
Cl-Pd-C(1)	92.2 (1)	C(3)-C(2)-C(6)	114.1 (5)
Cl′-Pd-N	95.6 (1)	C(4)-C(2)-C(6)	108.1 (5)
C(1)-Pd-N	84.5 (2)	C(2)-C(3)-N	112.5 (4)
Pd-Cl-Pd′	92.3 (1)	C(1)-C(5)-O	126.3 (6)
Pd-C(1)-C(2)	107.9 (3)	Pd-N-C(3)	108.8 (3)
Pd-C(1)-C(5)	97.9 (3)	Pd-N-C(7)	107.5 (4)
C(2)-C(1)-C(5)	120.0 (4)	Pd-N-C(8)	111.1 (4)
C(1)-C(2)-C(3)	107.3 (4)	C(3)-N-C(7)	108.6 (5)
C(1)-C(2)-C(4)	110.9 (4)	C(3)-N-C(8)	112.2 (5)
C(1)-C(2)-C(6)	108.1 (4)	C(7)-N-C(8)	108.5 (7)

[a] Since the methyl groups were refined as rigid bodies, all C-H distances are 1.08 Å and H-C-H angles are 109.5° in these groups. [b] The coordinates of a primed atom are obtained from the coordinates in Table I by the symmetry operation $1-x$, $1-y$, $-z$. [c] Standard deviations in parentheses.

teraction involves the palladium atom and the carbonyl carbon atom rather than the more distant oxygen or hydrogen atoms. Indeed, the magnitude of the chemical shift of the aldehydic proton is normal for an aliphatic aldehyde.

In the present case we can conceive of two ways of describing the bonding between the palladium and carbon depending on whether the ligand is envisaged as a localized carbanion (F) or as a delocalized enolate anion (G). In the former case the C(1) (Figure 3) carbanion would form a σ bond with palladium, which would in turn donate electrons to the carbonyl carbon C(5), e.g., by overlap of the metal d_{xz} (d_{yz}) orbital with the carbon end of the carbonyl π* orbital, which is favorably oriented.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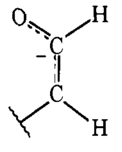
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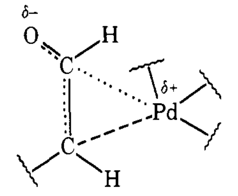


H

In the latter case bonding between the π system of the delocalized anion (G) and the palladium would be involved. The observed molecular geometry would then be explained if bonding to the palladium stabilized a hybrid with a considerable proportion of carbanion character (see H; i.e., an unsymmetrically bonded π-oxapropenyl system). A comparable type of bonding has previously been invoked for the interaction of a vinyl alcohol with platinum(II).[11] Both descriptions (F) and (G) satisfactorily explain the small Pd-C(1)-C(5) bond angle (Figure 3); the latter description more directly accounts for the observed shortening of the C(1)-C(5) bond.

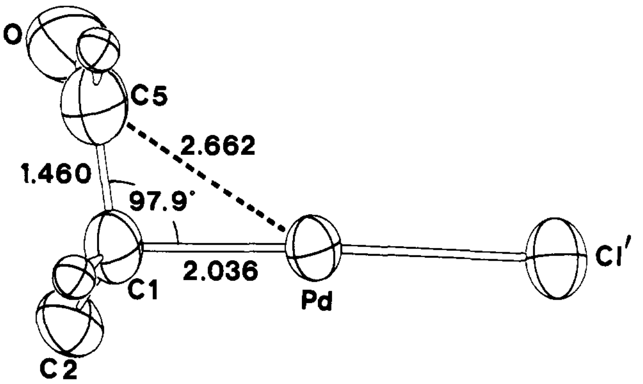
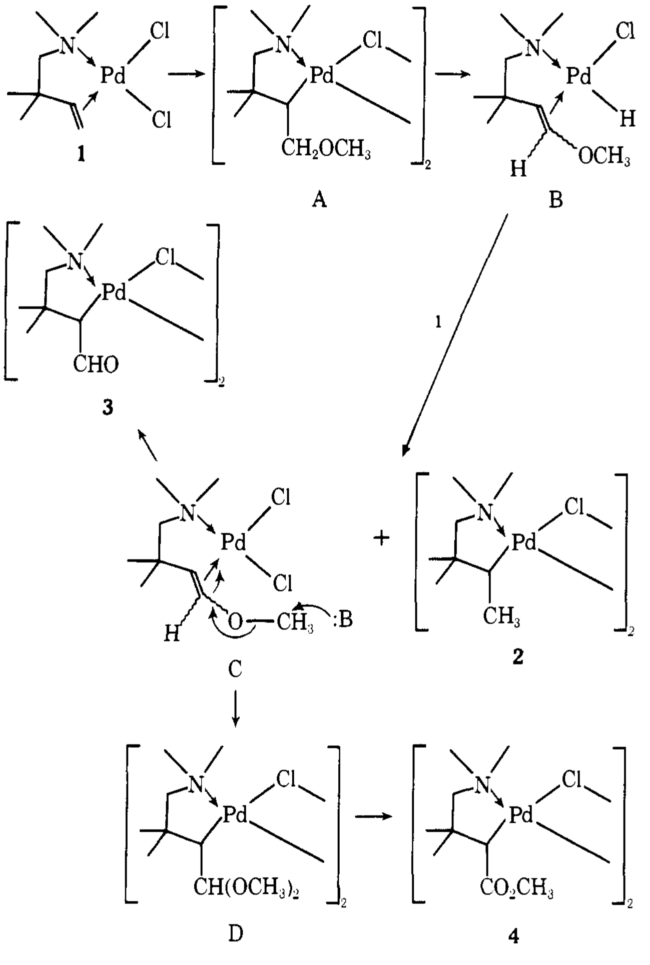


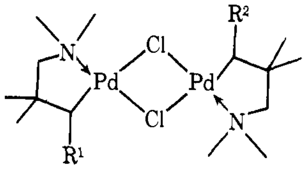
Figure 3. View normal to the C(1), C(5), Pd plane showing the geometry of the palladium-carbon bonding.

Scheme I. Proposed Routes to Products Obtained by Base-Promoted Reaction of Dichloro(2,2,*N*,*N*-tetramethyl-3-buten-1-amine)palladium with Methanol



A possible route to complexes **2**–**4**, involving initial formation of methoxypalladation product (A), is outlined in Scheme I. Transfer of hydrogen from carbon to palladium to give intermediate B from A is analogous to a step proposed for the Wacker reaction and related processes.[4] In the latter instances, further reaction involves readdition of Pd-H to the newly formed double bond to give an α-oxyalkylpalladium intermediate which undergoes irreversible decomposition to products. In the present instance, such readdition of Pd-H would result in the formation of a six-membered ring. This may be highly unfavorable if it involves a species such as B in which the coordinated double bond has to rotate so that the C=C bond axis lies in, or near, the general plane of the complex before migration of hydrogen can take place. The palladium hydride intermediate **B** may therefore prefer to decompose with deposition of palladium, or exchange H for Cl from **1**, thus yielding dimer **2** and a vinyl ether complex C. Formation of **3** might be envisaged as involving base-promoted nucleophilic attack on the ether-methyl carbon atom of C.[12] A competing methoxypalladation of C to yield D followed by a series of steps analogous to those proposed for the conversion of A to **3** could give rise to **4**.

Although we have not obtained any evidence for mixed dimers E we cannot discount their formation in the course of the reaction. One or both of the following may explain our failure to isolate them. First, the mixed dimers may be relatively unstable and decompose. Second, since it is likely that the dimers can equilibrate via monomeric species under the TLC conditions employed, one would anticipate separation of the mixture into bands containing symmetrical dimers, since the least polar dimer of all should be **2** and the most polar **3**.[13] The partial separation of two isomers of **3** on TLC would require that equilibration is relatively slow in this case.



E

$R^1, R^2 = CH_3, CO_2CH_3$ or CHO; $R^1 \neq R^2$

Experimental Section

General. NMR spectra were recorded on Varian Associates A-60A and HR-220 spectrometers for deuteriochloroform solutions with tetramethylsilane as an internal standard. Infrared spectra were measured on a Beckman IR12 spectrophotometer. Plates for thin layer chromatography (TLC) were spread with Kieselgel G (Merck) and developed with methanol-dichloromethane (1:99). The elemental analysis was performed by Mr. H. S. McKinnon, University of Guelph.

Base-Promoted Reaction of Dichloro(2,2,*N*,*N*-tetramethyl-3-buten-1-amine)palladium (1) with Methanol. (a) Triethylamine (0.376 g, 3.71 mmol) was added to the complex (**1**, 1.130 g, 3.71 mmol) in methanol (175 ml) at 0 °C. The mixture was stirred at this temperature for 2 days and the small amount of black material (Pd^0) which precipitated was filtered off. The resulting greenish yellow solution was evaporated in vacuo and the residue submitted to preparative TLC.

At least four bands could be distinguished after development. The third band showed severe tailing and it was divided into three fractions (IIIi, IIIii, IIIiii). The bands were extracted with acetone and the residues remaining after evaporation of this solvent were examined by ^1H NMR (60 MHz) and are discussed below in order of increasing polarity. The residue (37 mg) from pale yellow band I showed δ 0.66 (d, J = 7.2 Hz, $CHCH_3$). 0.95, 1.33 (both s, quaternary CCH_3), 2.22, 2.68 (both d, J = 12.4 Hz, NCH_2), and 2.77 (s, 2 NCH_3). In a spectrum at 220 MHz, the signal at δ 1.33 is split into two peaks. Band I darkened fairly rapidly when left on the plate. The extract (68 mg) from band II (yellow) showed δ 0.90, 1.63 (both s, quaternary $C-CH_3$), 2.18, 2.93 (both d, J = 12 Hz, NCH_2), 2.78 (br s, 2 NCH_3), and 3.65 (s, OCH_3); peaks at δ 1.63 and 2.78 split in 220 MHz spectrum; IR ($CDCl_3$) 1680 ($\nu_{C=O}$) and 1152 cm^{-1} (ν_{C-O}). Band II also darkened when left on the plate, although more slowly than band I. In contrast, the orange-yellow band III retained its appearance for several days on the plate. The extracts (see above) from this band (i, 527 mg; ii, 12 mg; iii, 17 mg) all showed δ 1.02, 1.60 (both s, quaternary CCH_3), 2.12, 3.66 (both d, J = 12.2 Hz, NCH_2), 2.55, 2.71 (both s, NCH_3) 3.56 (s, PdCH), and 9.40 (s, CHO). Spectra recorded at 220 MHz are shown in Figure 1. Crystallization (acetone/hexane) of the material from fraction IIIi gave orange-yellow prisms (**3a**), mp 164-166 °C dec (capillary, uncorrected): IR (Nujol) 1644 ($\nu_{C=O}$) and 2723 cm^{-1} (ν_{CHO}); IR ($CDCl_3$) 1635 ($\nu_{C=O}$) and 2730 cm^{-1} (ν_{CHO}).

Anal. Calcd for $C_{16}H_{32}Cl_2N_2O_2Pd_2$: C, 33.83; H, 5.68; N, 4.93. Found: C, 34.08; H, 5.97; N, 4.83.

The extract (184 mg) from band IV, which had barely moved away from the baseline, showed a relatively complex NMR spectrum, including resonances ascribable to ethyl groups on nitrogen coordinated to palladium.

(b) The same products in similar proportions were obtained on addition of 2,2,*N*,*N*-tetramethyl-3-buten-1-amine (0.509 g, 4.00 mmol), then triethylamine (0.405 g, 4.00 mmol) to an ice-cold solution of sodium tetrachloropalladite (1.177 g, 4.00 mmol) in methanol (120 mL), followed by stirring at 0 °C for 2 days.

(c) The experiment outlined in b was repeated under dry nitrogen using carefully dried reagents. Evaporation of the solvent in vacuo and extraction of the residue with $CDCl_3$ gave a solution, the NMR spectrum of which showed significant HC=O resonance but no peak ascribable to either acetal methyl groups or $-CH(OMe)_2$. TLC of the mixture gave the same products as in a.

(d) The experiment outlined in c was repeated on a 2-mmol scale using anhydrous potassium carbonate (0.166 g, 1.2 mmol) in place of the triethylamine. TLC of the product mixture gave the following fractions (I-VI) in order of increasing polarity (examined by NMR): I (27 mg, largely **2**), II (43 mg, mixture of **1**, **2**, and **4**), III (95 mg, largely **4**), IV (205 mg, largely **3**), V (28 mg, complex mixture), and VI (40 mg, complex mixture).

X-Ray Analysis of 3a. Crystal Data: $C_{16}H_{32}Cl_2N_2O_2Pd_2$, fw = 568.1 g, tetragonal, a = 16.535 (4). c = 7.956 (2) Å, V = 2175.2 Å^3, D_x = 1.74 g cm^{-3}, Z = 4, λ(Mo Kα) = 0.710 69 Å, μ(Mo Kα) = 17.47 cm^{-1}, $F(000)$ = 1136, space group $P4_2/n$ (C^4_{4h}, No. 86), platy crystal, 0.25 × 0.37 × 0.06 mm.

Accurate cell parameters were obtained by a least-squares refinement of the setting angles of 12 reflections measured on a Hilger and Watts Y290 computer-controlled four-circle diffractometer. Three-dimensional data were collected to a maximum Bragg angle of 25° by the θ-2θ scan technique using graphite monochromatized Mo radiation. Corrections were applied for Lorentz, polarization, and absorption factors;[15] of the 3610 independent reflections measured, 2045 had $I > 3\sigma I$ and were used in subsequent calculations. Structure solution was by the heavy atom method; refinement by full-matrix least-squares calculations with anisotropic thermal parameters for the nonhydrogen atoms and weights from the counting statistics led to R factors[16] R_1 = 0.040, R_2 = 0.054. A difference synthesis computed at this stage revealed only maxima consistent with hydrogen atom positions; these were then included in the least-squares calculations. Positional and isotropic thermal parameters were refined for the nonmethyl hydrogen atoms; the four methyl groups were treated as rigid bodies with C-H = 1.08 Å and $\angle$H—C—H = 109.5°. In the structure factor calculations, scattering factors from ref 17 were used for hydrogens, from ref 18 for all others, and anomalous dispersion corrections[19] were applied for chlorine and palladium atoms. Final R factors at convergence were R_1 = 0.034 and R_2 = 0.043. A list of observed and calculated structure factors has been deposited together with an analysis of variance and a table of thermal parameters.

Acknowledgments. We thank the National Research Council of Canada for financial support, and Professor P. M. Henry for interesting discussions. The 220 MHz ^1H NMR spectra were run at the Canadian 220-MHz NMR Centre, University of Toronto.

Supplementary Material Available: Tables of temperature factors, analysis of variance at convergence, and observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Paper in preparation.
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(3) See, e.g., P. M. Maitlis, "The Organic Chemistry of Palladium", Vol. II, Academic Press, New York, N.Y., 1971, pp 74–79.
(4) See ref 3, pp 141–142.
(5) It appears likely that the more polar isomer differs from **3a** only in having both aldehyde groups on the same side of the plane defined by the Pd_2Cl_2 ring. This isomer would be expected to be more polar than **3a**. We feel that a structure involving a cis configuration of the ligating atoms is less likely, since no complexes of this type have been reported.
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(12) Formation of **3** by hydrolysis of D by traces of water present in the reaction mixture appears unlikely under the conditions employed.
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Preparation and Characterization of Compounds Containing the Octamethylditungsten(II) Anion and Partially Chlorinated Analogues

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Abstract: Reactions of methyllithium with tungsten(IV) and tungsten(V) chlorides at temperatures at or below 0 °C in ether allow the isolation of $Li_4W_2Me_8 \cdot 4Et_2O$ (**1**) when a 1-2 molar excess of LiMe is used. When only about a 0.5 molar excess of LiMe is used, nonstoichiometric products of the type $Li_4W_2Me_{8-x}Cl_x \cdot 4Et_2O$ (**2**) are obtained. The former is red, the latter red purple, and the Et_2O in each can be replaced by THF, giving **3** and **4**. It has not yet been possible to determine the crystal structure of **1** but a sample of **4** with $x \approx 3.2$ has been shown to contain a statistically disordered $W_2Me_{8-x}Cl_x{}^{4-}$ anion with virtual D_{4h} symmetry and W-W = 2.26 Å. The $W_2Me_8{}^{4-}$ ion is presumed to be very similar. None of the compounds is thermally stable above 0 °C and the mixed methyl-chloro ones seem unstable above −20 °C. All are exceedingly reactive to air or moisture. The electronic spectra agree well with previously suggested correlations for other $M_2Me_8{}^{n-}$ ions containing Cr, Mo, and Re.

Since the discovery, in 1964, that quadruple bonds exist,[2-4] a great many compounds of rhenium,[4-8] technetium,[4,9,10] ruthenium,[4] chromium,[4] and especially molybdenum[4,11-16] have been shown to contain quadruple bonds or bonds of similar character in structurally similar circumstances, namely, in ions or molecules of the sort $L_4M \equiv ML_4$ (where L_4 may represent a mixed set of ligands) with $M_2(O_2CR)_4$ constituting a very important special case.[4] It is striking that while molybdenum is, on current data, the most prolific former of such bonds, rhenium forms them rather readily and chromium forms analogues to many, though by no means all, of the molybdenum compounds, quadruply bonded pairs of tungsten atoms had never been shown conclusively to exist. A series of compounds, $W_2(O_2CR)_4$, with R = C_6H_5, p-$CH_3C_6H_4$, C_6F_5, C_3H_7, and C_3F_7, were prepared[17] and have been reproduced many times by different workers, but never has a crystalline sample of any of them come into our hands. Hence, direct structural proof of the existence of a quadruple bond in these molecules has not been obtainable.

On the other hand, the isolation of $[MoW(O_2CCH_3)_4]I \cdot CH_3CN$ with its Mo-W bond[18] of order 3.5 and the fact that there exist as many, or more, stable compounds containing W-W triple bonds as Mo-Mo triple bonds[19-21] justified some optimism about obtaining and authenticating at least a few compounds containing W-W quadruple bonds. Also, a scattered wave Xα-SCF calculation[10] for the hypothetical $W_2Cl_8{}^{4-}$ ion gave results qualitatively and quantitatively similar to those for $Mo_2Cl_8{}^{4-}$.[22]

Efforts to prepare some quadruply bonded ditungsten species were undertaken independently and, initially, without mutual awareness, in our two laboratories. In both cases the explicit objective was the $W_2Me_8{}^{4-}$ ion, for which the analogues $Cr_2Me_8{}^{4-}$,[23] $Mo_2Me_8{}^{4-}$,[24] and $Re_2Me_8{}^{2-}$ [8] were already known and well characterized.[25] In this paper we report the successful results obtained in both laboratories. A part of this work has already been described in a preliminary note.[26]

Experimental Section

General. All syntheses and other operations were conducted in vacuum or under rigorously oxygen-free nitrogen or argon. The thermal instability of the products precluded combustion analysis and other methods were therefore used. Methyl groups were determined by hydrolysis and measurement of methane in a gas buret. Chlorine was precipitated and weighed as AgCl. Tungsten was determined gravimetrically as WO_3 (Texas) or using a plasma arc emission-absorption instrument (London). Lithium analysis was also done with the latter instrument. For further details, see below.

Starting Materials. Methyllithium was prepared by reaction of lithium metal with methyl chloride in diethyl ether. The tungsten halides were prepared, according to the suggestion of King and McCarley,[27] by reactions of WCl_6 with $W(CO)_6$. For WCl_4 a mole ratio of 2:1 was heated to reflux in chlorobenzene. The WCl_4 precipitated and was isolated by filtration, dried under vacuum, and used without further purification. WCl_5 was obtained by placing 10-20 g of WCl_6 in a glass tube, under argon, adding a slight excess over a 1:5 mole ratio of $W(CO)_6$ and connecting the tube to a mercury bubbler. The tube was then heated to 100 °C in an oil bath. The reaction was allowed to proceed 4-6 h. Unreacted $W(CO)_6$ was removed by connecting the reaction tube to the vacuum line and subliming the material into a cold trap. The remaining product was transferred to a two-compartment tube and the WCl_5 was sublimed away from small amounts of WCl_4 in vacuo at 250 °C. Elemental analyses were made

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