The Formation of Carbon to Metal σ Complexes between Palladium(II) Chloride and Allylic Amines

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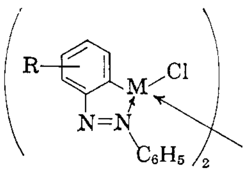
Abstract: Palladium(II) chloride or lithium chloropalladate(II) reacts with N,N-dimethylallylamine in methanol to give di-μ-chloro-bis(2-methoxy-3-N,N-dimethylaminopropyl)dipalladium(II) in 97% yield. These same reagents react with N,N-dimethyl-2-methylallylamine in methanol, ethanol, or ethylene glycol to give, respectively, di-μ-chloro-bis(2-methoxy-2-methyl-3-N,N-dimethylaminopropyl)dipalladium(II) (90%), di-μ-chloro-bis(2-ethoxy-2-methyl-3,N,N-dimethylaminopropyl)dipalladium(II) (92%), and di-μ-chloro-bis(2-β-hydroxyethoxy-2-methyl-3-N,N-dimethylaminopropyl)dipalladium(II) in 92% yield.

The observation[2] that azobenzenes and N,N-dimethylbenzylamines react with palladium(II) halides and platinum(II) halides in alcoholic solutions to give complexes I and II having carbon–metal σ bonds has led to our examination of several similar reactions between palladium(II) and isolated double bonds. The reactions of diolefin complexes of palladium(II) and platinum(II) with alcohols have been examined previously.[3] Potassium chloroplatinate(II) and sodium chloropalladate(II) react with dicyclopentadiene, 1,5-cyclooctadiene, and dipentene in methanol, yielding complexes containing methoxy groups. For example, the following transformation takes place with sodium chloropalladate(II) and 1,5-cyclooctadiene.



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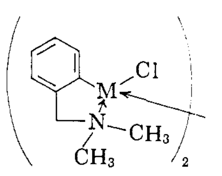
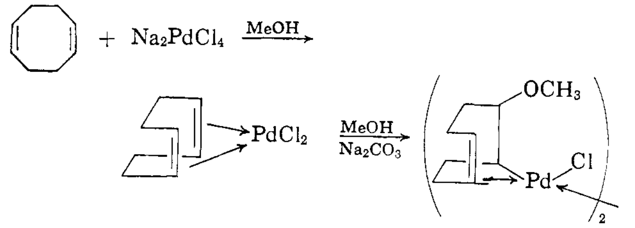


II

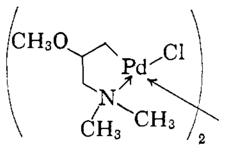
M = Pd, Pt
R = Br, NO$_2$, CH$_3$



Stille and co-workers[4] have reinvestigated the platinum(II) and palladium(II) complexes obtained with dicyclopentadiene in methanol and have established their structures to be those proposed by Chatt.[3] In addition, Tsuji and Takahashi[5] reported that 1,5-cyclooctadienepalladium(II) chloride reacts with diethyl malonate to give a product in which a dicarboethoxymethyl group is attached to the cyclooctenyl ring.

We have found that in alcoholic media tertiary allylic amines undergo a similar electrophilic substitution by palladium(II) chloride or lithium chloropalladate(II). Thus, N,N-dimethylallylamine reacts in methanol with lithium chloropalladate(II), or more slowly with palladium(II) chloride, to give di-μ-chloro-bis(2-methoxy-3-N,N-dimethylaminopropyl)dipalladium(III) in 97% yield. Similarly, N,N-dimethyl-2-methylallylamine reacts with either lithium chloropalladate(II) or with palladium(II) chloride in methanol at room temperature to give di-μ-chloro-bis(2-methoxy-2-methyl-3-N,N-dimethylaminopropyl)dipalladium (IV) in 90% yield. In ethanol solvent the product is di-μ-chloro-bis(2-ethoxy-2-methyl-3-N,N-dimethylaminopropyl)dipalladium(V) in 92% yield, and in ethylene glycol the product is di-μ-chloro-bis(2-β-hydroxyethoxy-2-methyl-3-N,N-dimethylaminopropyl)dipalladium(VI) in 92% yield.

$$CH_2{=}CHCH_2N(CH_3)_2 + Li_2PdCl_4 \xrightarrow{MeOH}$$



III

The structure of complex III was established by the following data. The nuclear magnetic resonance spectrum of compound III (Figure 1) is in agreement with the proposed structure. The singlet at 2.75 ppm corresponds to the N-methyl groups and the singlet at 3.27 ppm corresponds to the methoxyl. Lithium aluminum hydride reduction of compound III gives N,N-dimethyl-2-methoxypropylamine(IIIa), whose mass spectrum, picrate and methiodide derivatives are identical with

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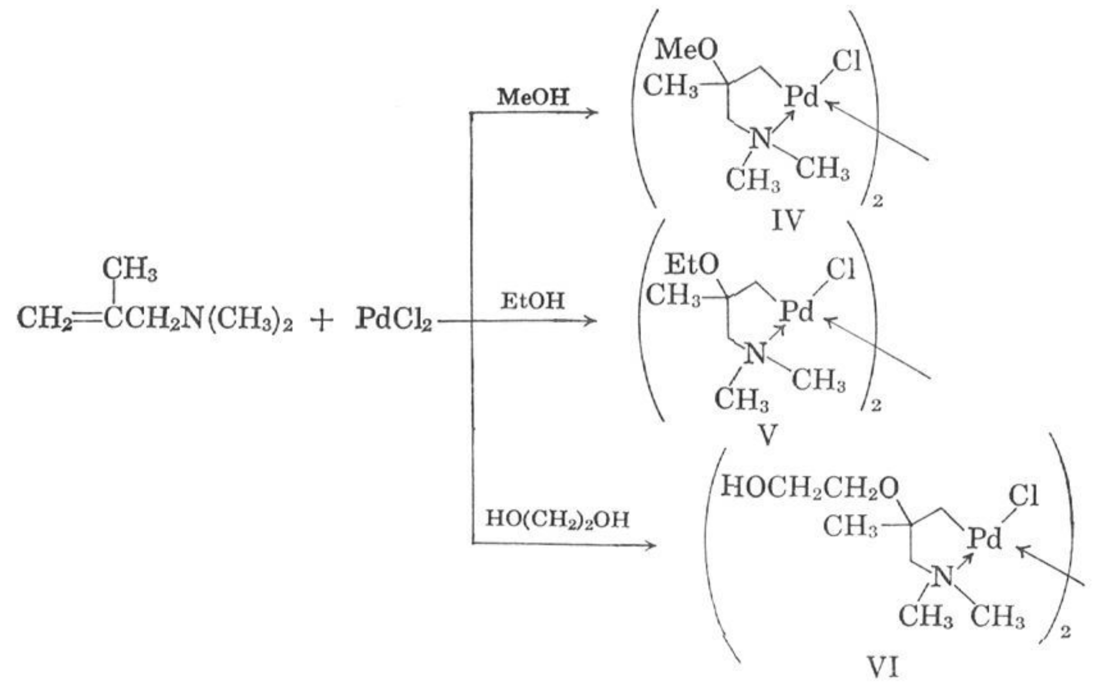
(1) (a) Deceased June 4, 1966. (b) Author to whom inquiries should be addressed: The Catholic University of America, Washington, D. C.

(2) (a) A. C. Cope and R. W. Siekman, *J. Am. Chem. Soc.*, 87, 3272 (1965). (b) To be published.

(3) See, for example, J. Chatt, L. M. Vallerino, and L. M. Venanzi, *J. Chem. Soc.*, 2496, 3413 (1957).

(4) J. K. Stille, *J. Am. Chem. Soc.*, 87, 3282 (1965).

(5) J. Tsuji and H. Takahashi, *ibid.*, 87, 3275 (1965).



IV

V

VI

those of an authentic sample.[6] Lithium aluminum deuteride reduction of compound III gives N,N-dimethyl-2-methoxypropylamine-d_1 (IIIb). The position of the deuterium, and therefore the site of the carbon to palladium σ bond, was established by a comparison of the mass spectrum of IIIb with the undeuterated IIIa. Compound IIIa gives peaks at m/e 117 (22%, parent ion), 102 (3%, loss of methyl), 86 (16%, loss of methoxyl), and 58 (100%, loss of methoxyethyl). The mass spectrum of compound IIIb shows peaks at m/e 118 (11%, parent ion), 102 (2%, loss of deuteriomethyl), 87 (9%, loss of methoxy), and 58 (100%, loss of methoxyethyl-d_1). The apparent molecular weight of this complex is 490, as measured by osmometry. Evidence that the methoxy group present in the molecule was not methanol of crystallization was obtained by recrystallization from ethanol. The product of this treatment was identical (by nmr) with the starting complex.

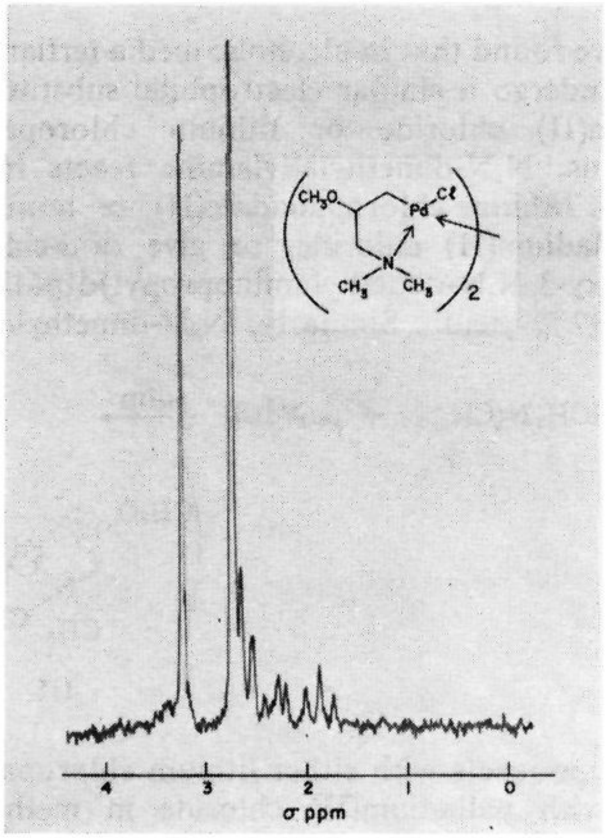


Figure 1. Proton nmr spectrum of di-μ-chloro-bis(2-methoxy-3-N,N-dimethylaminopropyl)dipalladium(II).

The structure of complex IV was confirmed using similar techniques. Lithium aluminum hydride reduction of compound IV gives N,N-dimethyl-2-methoxy-2-methylpropylamine (IVa), and lithium aluminum deuteride reduction gives N,N-dimethyl-2-methoxy-2-methylpropylamine-d_1 (IVb). The position of deuterium incorporation, and thus the carbon to palladium bond, was again determined by comparison of the mass spectra of the deuterated and undeuterated amines.

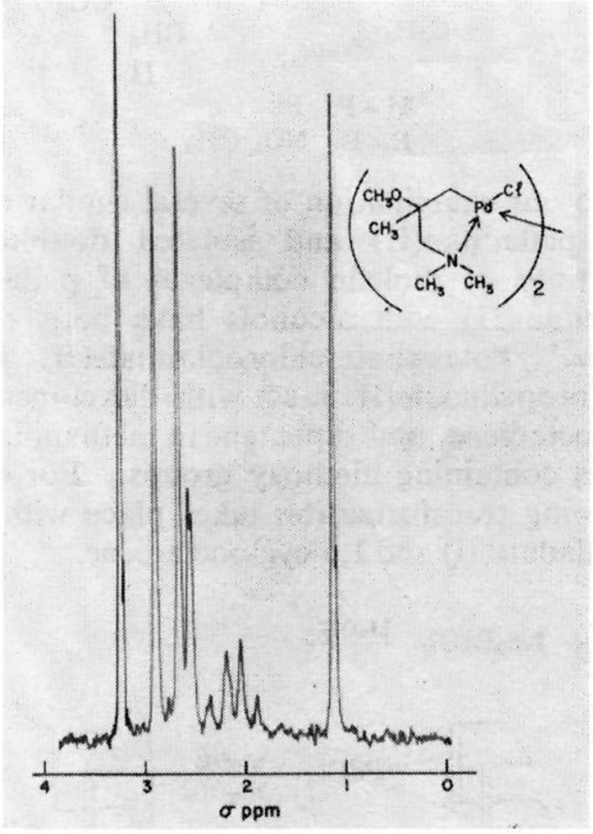


Figure 2. Proton nmr spectrum of di-μ-chloro-bis(2-methoxy-2-methyl-3-N,N-dimethylaminopropyl)dipalladium(II).

While the above evidence establishes that a σ bond has been formed between the metal and the terminal methylene group of the allyl moiety, it provides no indication of the fate of the nitrogen and its unshared pair of electrons. The fact that both a palladium–carbon σ bond and a palladium–nitrogen coordinate bond exist in these complexes was demonstrated clearly by the nmr spectrum of IV (Figure 2). The peaks at 2.75 and 2.98 ppm in this spectrum are as-

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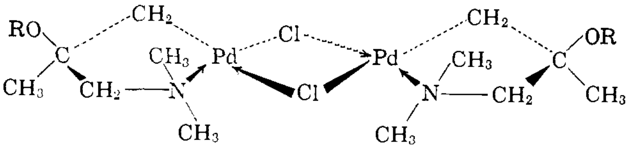
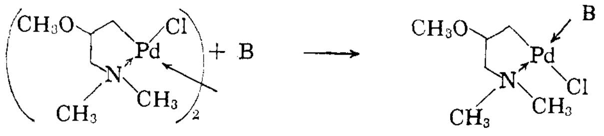
[6] For examples of similar metal hydride reductions of carbon–metal bonds see F. G. Bordwell and M. L. Douglas, *J. Am. Chem. Soc.*, **88**, 993 (1966); T. G. Traylor and A. W. Baker, *ibid.*, **85**, 2746 (1963); T. G. Traylor, *Chem. Ind.* (London), 1223 (1959).

signed to the N-methyl groups. The nonequivalence of these N-methyl groups is most easily explained in terms of a cyclic system in which nitrogen is coordinated to the metal sufficiently strongly to prevent inversion.



The strength of this coordinate bond is demonstrated by the observation that the nmr spectrum remains essentially unchanged at temperatures greater than 100°. If the nitrogen–metal bond were weak, a coalescence of the N-methyl peaks at high temperatures would be observed. Compound III also shows nonequivalent N-methyl peaks in aromatic solvents, although not in chloroform.

Complex III reacts with aniline in refluxing benzene–heptane solution to give 2-methoxy-3-N,N-dimethylaminopropylpalladium(II) chloride aniline(VII) in 86% yield. That cleavage of the chlorine bridge had taken place was evidenced by the apparent molecular weight of VII (352). Similarly, III reacts with triphenylphosphine in refluxing benzene–heptane solution to give 2-methoxy-3-N,N-dimethylaminopropylpalladium(II) chloride triphenylphosphine(VIII) in 76% yield. The chlorine bridges of complexes IV, V, and VI are cleaved in a similar manner by both aniline and triphenylphosphine.



VII, :B = $C_6H_5NH_2$
VIII, :B = $(C_6H_5)_3P$:

Experimental Section[7]

Lithium chloropalladate(II) was prepared in 98% yield by the method of Gutbier and Krell.[8] **N,N-Dimethyl-2-methylallylamine** was prepared according to the method of Cope, *et al.*[9]

Di-μ-chloro-bis(2-methoxy-3-N,N-dimethylaminopropyl)dipalladium(III) from Lithium Chloropalladate(II). To a solution of 0.85 g of N,N-dimethylallylamine (0.01 mole) in 15 ml of methanol was added a solution containing 1.31 g of lithium chloropalladate(II) (0.005 mole) in 20 ml of methanol. On mixing, a yellow precipitate immediately appeared but redissolved after a few seconds to give a clear yellow solution. The product crystallized from solution at −20°, and was isolated by filtration (1.20 g, 97% yield). Recrystallization from methanol gave 1.0 g of yellow crystals, mp 124–126° dec; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 243 mμ (ε 14,738) and 343 mμ (ε 2403). The nmr spectrum showed peaks at 2.75 ppm (singlet, 6 H, $(CH_3)_2N$) and 3.27 ppm (singlet, 3 H, CH_3O). Other more complicated peaks appeared at 1.89 (multiplet), 2.29 (multiplet), 2.63 (doublet), and 3.45 ppm (multiplet).

Anal. Calcd for $C_{12}H_{28}N_2O_2Pd_2Cl_2$: C, 27.92; H, 5.43; N, 5.43; Pd, 41.26; Cl, 13.77; mol wt, 516. Found: C, 28.01; H, 5.36; N, 5.32; Pd, 41.44; Cl, 13.70; mol wt (osmometer), 492.

Preparation of III from Palladium(II) Chloride. A mixture of 0.94 g of palladium(II) chloride (0.005 mole) was stirred in 100 ml of methanol for 10 hr. To the resulting heterogeneous mixture was added 0.85 g of N,N-dimethylallylamine (0.01 mole). The immediate yellow precipitate went back into solution after a few seconds, and filtration with Super-Cel gave a yellow solution. This solution was evaporated *in vacuo* (15 mm) to dryness and its volume brought up to 15 ml with methanol. Cooling (−20°) for several days gave III (0.239 g, 19% yield). Recrystallization from methanol gave 0.19 g of bright yellow crystals, mp 123–124°.

2-Methoxy-3-N,N-dimethylaminopropylpalladium(II) Chloride Aniline(VII). A mixture of 0.10 g of III (0.00019 mole) and 0.04 g of aniline (0.00043 mole) in 15 ml of heptane was brought to reflux and benzene added until dissolution of the then white solid occurred. Cooling (−20°) and filtration gave VII (0.114 g, 86% yield). Recrystallization from benzene–heptane gave 0.051 g of white crystals, mp 117–119°.

Anal. Calcd for $C_{12}H_{21}N_2OPdCl$: C, 41.03; H, 5.98; N, 7.98; Pd, 30.39; Cl, 10.11; mol wt, 351. Found: C, 41.39; H, 6.10; N, 7.90; Pd, 30.45; Cl, 9.98; mol wt (cryoscopic in nitrobenzene), 352.

2-Methoxy-3-N,N-dimethylaminopropylpalladium(II) Chloride Triphenylphosphine(VIII). Benzene was added to a mixture of 0.10 g of III (0.00019 mole) and 0.10 g of triphenylphosphine (0.00038 mole) in 15 ml of refluxing heptane until a clear solution resulted. Cooling (−20°) and filtration gave VIII (0.149 g, 76% yield). Recrystallization from benzene–heptane gave 0.137 g of light tan solid, mp 154–157° dec.

Anal. Calcd for $C_{24}H_{29}NOPPdCl$: C, 55.36; H, 5.57; N, 2.69; Pd, 20.51; Cl, 6.82; mol wt, 520. Found: C, 55.75; H, 5.76; N, 2.68; Pd, 21.05; Cl, 6.79; mol wt (cryoscopic in benzene), 524.

Di-μ-chloro-bis(2-methoxy-2-methyl-3-N,N-dimethylaminopropyl)-dipalladium(IV) from Lithium Chloropalladate(II). A solution containing 1.00 g of lithium chloropalladate(II) (0.0038 mole) in 5 ml of methanol was added to 0.739 g of N,N-dimethyl-2-methylallylamine (0.0074 mole) in 5 ml of methanol. The immediately formed greenish precipitate of IV (0.931 g, 90% yield) was collected by filtration after 2 days of cooling at −20°. Recrystallization from chloroform–pentane gave 0.658 g of yellow crystals, mp 128–130° dec; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 242 mμ (ε 13,952) and 340 mμ (ε 2338). The nmr showed peaks (in ppm) at 1.17 (singlet, 3 H), 2.20 (quartet, 2 H, J = 10.0 cps), 2.63 (doublet, 2 H, J = 2.5 cps), 2.75 (singlet, 3 H), 2.98 (singlet, 3 H), and 3.35 (singlet, 3 H).

Anal. Calcd for $C_{14}H_{32}N_2O_2Pd_2Cl_2$: C, 30.86; H, 5.88; N, 5.14; Pd, 39.23; Cl, 13.04; mol wt, 542. Found: C, 30.58; H, 5.69; N, 4.93; Pd, 39.59; Cl, 13.06; mol wt (cryoscopic in benzene), 554.

The Preparation of IV from Palladium(II) Chloride. A mixture 0.94 g of palladium(II) chloride (0.005 mole) and 1.50 g of N,N-dimethyl-2-methylallylamine (0.15 mole) was shaken in 15 ml of methanol for 4 hr. Filtration of the dark solution with Super-Cel gave a clear yellow solution. After cooling for 2 days at −20° the resultant solid was separated by filtration, washed with methanol and hexane, and dried to give IV (1.21 g, 88% yield). Recrystallization from benzene–heptane gave 0.854 g of yellow crystals, mp 129–131° dec.

2-Methoxy-2-methyl-3-N,N-dimethylaminopropylpalladium(II) Chloride Aniline(IX). A mixture of 0.10 g of IV (0.00018 mole) and 0.04 g of aniline (0.00043 mole) in 15 ml of heptane was heated to reflux and benzene added until a clear solution resulted. Cooling to room temperature and filtration gave IX (0.116 g, 92% yield). Recrystallization from benzene–heptane gave 0.103 g of white crystals, mp 128–130° dec.

Anal. Calcd for $C_{13}H_{23}N_2OPdCl$: C, 42.74; H, 6.30; N, 7.67; Pd, 29.23; Cl, 9.73. Found: C, 42.70; H, 6.57; N, 7.87; Pd, 29.15; Cl, 9.85.

2-Methoxy-2-methyl-3-N,N-dimethylaminopropylpalladium(II) Chloride Triphenylphosphine(X). A benzene solution (10 ml) containing 0.10 g of IV (0.00018 mole) and 0.10 g of triphenylphosphine (0.00038 mole) was heated to reflux. After cooling, the benzene was removed by evaporation and the resulting solid dissolved in 10 ml of hot heptane. Cooling and filtration gave X (0.166 g, 86% yield). Recrystallization from heptane gave 0.145 g of white crystals, mp 141–143°.

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(7) Melting and boiling points are uncorrected. Ultraviolet and visible spectra were recorded on a Cary Model 21 spectrophotometer. Chemical shifts are reported with respect to *external* tetramethylsilane in deuteriochloroform, and were measured using a Varian A-60 spectrophotometer. Mass spectra were obtained on a Hitachi-Perkin-Elmer Model RMU-6D mass spectrophotometer. Molecular weights were determined with a Microlab Model 301-A osmometer. Microanalyses were performed by Dr. S. N. Nagy and associates or by the Scandanavian Microanalytical Laboratory, Herlev, Denmark. An F & M Model 720 vapor phase chromatograph was used for preparative gas chromatography.

(8) A. Gutbier and A. Krell, *Ber.*, **38**, 2385 (1905).

(9) A. C. Cope, T. T. Foster, and P. H. Towle, *J. Am. Chem. Soc.*, **71**, 3932 (1949).

Anal. Calcd for $C_{25}H_{31}NOPPdCl$: C, 56.18; H, 5.81; N, 2.62; Pd, 19.98; Cl, 6.65; mol wt, 533. Found: C, 56.24; H, 5.83; N, 2.58; Pd, 19.85; Cl, 6.54; mol wt (cryoscopic in benzene), 540.

Di-μ-chloro-bis(2-ethoxy-2-methyl-3-N,N-dimethylaminopropyl)-dipalladium (V) from Lithium Chloropalladate(II). A solution of 1.31 g of lithium chloropalladate(II) (0.005 mole) in 5 ml of absolute ethanol was added to 1.50 g of N,N-dimethyl-2-methylallylamine (0.015 mole) in 10 ml of absolute ethanol. The immediate yellow precipitate was collected by filtration after 2 days of cooling (−20°) to give V (1.27 g, 89% yield). Recrystallization from chloroform–ethanol gave 1.11 g of yellow crystals, mp 127–130° dec; $\lambda_{max}^{CHCl_3}$ 242 mμ (ε 13,916) and 340 mμ (ε 2294). The nmr showed peaks (in ppm) at 1.17 (singlet, 3 H), 1.30 (triplet, 3 H, *J* = 7.0 cps), 2.18 (quartet, 2 H, *J* = 10.0 cps), 2.62 (doublet, 2 H, *J* = 2.0 cps), 2.75 (singlet, 3 H), 3.03 (singlet, 3 H), and 3.57 (multiplet, 2 H, *J* = 7.0 cps).

Anal. Calcd for $C_{12}H_{36}N_2O_2Pd_2Cl_2$: C, 33.54; H, 6.29; N, 4.89; Pd, 37.28; Cl, 12.41; mol wt, 572. Found: C, 33.61; H, 6.02; N, 4.97; Pd, 38.66; Cl, 12.99; mol wt (cryoscopic in benzene), 595.

The Preparation of V from Palladium(II) Chloride. A mixture of 0.94 g of palladium(II) chloride (0.005 mole) and 1.50 g of N,N-dimethyl-2-methylallylamine (0.015 mole) was shaken in 10 ml of absolute ethanol for 3 days. Separation of the thick yellow precipitate by filtration gave V (1.30 g, 92% yield). Recrystallization from benzene–heptane gave 1.24 g of yellow crystals, mp 128–130°.

2-Ethoxy-2-methyl-3-N,N-dimethylaminopropylpalladium(II) Chloride Aniline (XI). A solution of 0.10 g of V (0.00018 mole) in 5 ml of benzene was added to 0.050 g of aniline (0.00053 mole) in 15 ml of heptane. Heating to reflux and adding benzene gave a clear solution. Cooling and separating by filtration gave white crystals of XI (0.125 g, 94% yield), mp 106–109° dec.

Anal. Calcd for $C_{14}H_{25}NOPdCl$: C, 44.30; H, 6.59; N, 7.38; Pd, 28.14; Cl, 9.36. Found: C, 44.48; H, 6.68; N, 7.39; Pd, 27.73; Cl, 9.50.

2-Ethoxy-2-methyl-3-N,N-dimethylaminopropylpalladium(II) Chloride Triphenylphosphine (XII). Benzene was added to a mixture of 0.10 g of V (0.00018 mole) and 0.09 g of triphenylphosphine (0.00035 mole) in 10 ml of refluxing heptane until a clear solution resulted. Cooling (−20°) and separating by filtration gave XII (0.173 g, 90% yield). Recrystallization from benzene–heptane gave 0.155 g of white needles, mp 164–166° dec.

Anal. Calcd for $C_{26}H_{33}NOPPdCl$: C, 56.91; H, 6.02; N, 2.55; Pd, 19.46; Cl, 6.48. Found: C, 56.89; H, 6.07; N, 2.60; Pd, 19.80; Cl, 6.52.

Di-μ-chloro-bis(2-β-hydroxyethoxy-2-methyl-3-N,N-dimethylaminopropyl)dipalladium (VI) from Lithium Chloropalladate(II). To a solution of 1.31 g of lithium chloropalladate(II) (0.005 mole) in 10 ml of ethylene glycol was added 1.50 g of N,N-dimethyl-2-methylallylamine (0.015 mole). After a few minutes the brown solution turned yellow and upon warming (50°) a green solid precipitated. The mixture was cooled at −20° for several hours, and the product was separated by filtration, washed with ether, and dried to give VI (1.39 g, 92% yield). Recrystallization from benzene–heptane gave 1.00 g of yellow crystals, mp 110–112° dec; $\lambda_{max}^{CHCl_3}$ 242 mμ (ε 14,157) and 341 mμ (ε 3025). The nmr showed peaks (in ppm) at 1.20 (singlet, 3 H), 2.22 (multiplet, 2 H, *J* = 10.0 cps), 2.70 (doublet, 2 H, *J* = 1.5 cps), 2.78 (singlet, 3 H), 3.05 (singlet, 3 H), and 3.83 (unresolved multiplet, 5 H). This complex was hygroscopic, and an acceptable analysis was not obtained.

2-β-Hydroxyethoxy-2-methyl-3-N,N-dimethylaminopropylpalladium(II) Chloride Aniline (XIII). Heptane was added to a refluxing solution of 0.10 g of VI (0.00017 mole) and 0.05 g of aniline (0.00053 mole) until the solution became cloudy. After several days light brown crystals of XIII (0.75 g, 57% yield) were isolated by filtration, mp 116–119° dec.

Anal. Calcd for $C_{14}H_{25}N_2O_2PdCl$: C, 42.54; H, 6.33; N, 7.09; Pd, 26.99; Cl, 8.99. Found: C, 42.48; H, 6.41; N, 7.10; Pd, 26.99; Cl, 9.24.

N,N-Dimethyl-2-methoxypropylamine (IIIa) was prepared by the procedure of Goldfarb.[10] Distillation of the product mixture gave 3.6 g (35%) of IIIa, bp 84–86°, $n^{31}D$ 1.5959, and 3.2 g (32%) of the isomer incorrectly described by Goldfarb as IIIa, N,N-dimethyl-1-methyl-2-methoxyethylamine (IIIc), bp 111–115°, $n^{31}D$ 1.4041; methoiodide, mp 156° (lit.[10] bp 113–116°; methiodide, mp 155.5–156°]. A picrate of IIIc was prepared in the usual manner giving yellow needles, mp 131–135°. The nmr spectrum showed peaks (in ppm) at 1.38 (doublet, 3 H, *J* = 6.0 cps), 2.93 (doublet, 6 H, *J* = 4.0 cps), 3.30 (singlet, 3 H), 3.62 and 3.65 (overlapping singlet and doublet, 3 H), and 8.92 (singlet, 2 H).

A picrate derivative of IIIa was prepared giving yellow needles from benzene–heptane, mp 109–112°. The nmr spectrum (in ppm) of this compound showed peaks at 1.20 (doublet, 3 H, *J* = 6.0 cps), 3.00 (broadened singlet, 6 H), 3.23 (singlet overlapping multiplet, 5 H), 3.83 (multiplet, 1 H, *J* = 6.0 cps), and 8.93 (singlet, 2 H).

Anal. Calcd for $C_{12}H_{18}N_4O_8$: C, 41.62; H, 5.20; N, 16.18. Found: C, 41.98; H, 5.42; N, 15.91.

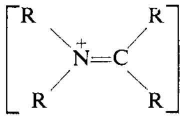
Treatment of IIIa obtained above with methyl iodide gave the methiodide as white plates from chloroform–ethyl acetate, mp 119–121°.

Differentiation between the isomers IIIa and IIIc was made by their mass spectra, given in Table I.

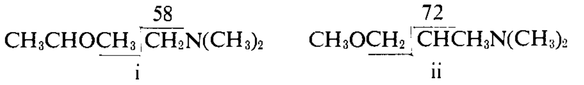
Table I

m/e fragment	% abundance IIIa	% abundance IIIc
117	7.5	3.7
102	0.9	1.3
86	4.8	2.1
73	1.0	5.1
72	1.7	100.0
71	2.4	4.6
70	1.0	4.1
59	7.2	0.9
58	100.0	7.9
56	1.6	5.4
55	0.3	1.0

Primary fragmentation of amines takes place to give fragments of the type[11]



The spectrum of IIIa corresponds, therefore, to i, whereas the spectrum of IIIc corresponds to ii.



$$\underset{\mathrm{i}}{\mathrm{CH_3CHO\underline{CH_3}}\,\overset{58}{\overline{\mathrm{CH_2}}}\mathrm{N(CH_3)_2}} \qquad \underset{\mathrm{ii}}{\mathrm{CH_3O\underline{CH_2}}\,\overset{72}{\overline{\mathrm{CH}}}\mathrm{CH_3N(CH_3)_2}}$$

Reduction of Complexes. General Procedure. The complex (0.050 g) to be reduced was slowly added to stirred mixture containing 0.050 g of lithium aluminum hydride or deuteride in 2 ml of cold absolute ether. The resulting black mixture was allowed to stir at room temperature for 30 min, then water or deuterium oxide was added with cooling. Sodium sulfate was added and the ether layer separated. The aqueous layer was washed twice with ether, and the combined ether extracts were dried (Na_2SO_4). The ether solution was concentrated by evaporation and the product isolated by preparative gas chromatography using an 8-ft, 20% silicone rubber on Firebrick preparative column at 120° and a flow rate of 60 cc of helium/min.

Reduction of III with lithium aluminum hydride gave N,N-dimethyl-2-methoxypropylamine (IIIa) (retention time 6.4 min). The mass spectrum showed peaks at *m/e* 117, 102, 86, 71, 59, and 58 (100%). A picrate derivative was made in the usual manner. Recrystallization from benzene–heptane gave flat yellow needles, mp 110–112°, mmp 111–112°.

Anal. Calcd for $C_{12}H_{18}N_4O_8$: C, 41.62; H, 5.20; N, 16.18. Found: C, 41.45; H, 5.48; N, 16.06.

Treatment of IIIa with methyl iodide gave the methiodide as white platelets from chloroform–ethyl acetate, mp 118–120°, mmp 117–119°.

The Reduction of III with lithium aluminum deuteride gave N,N-dimethyl-2-methoxypropylamine-d_1 (IIIb) (retention time 6.4 min). The mass spectrum showed peaks at *m/e* 118, 102, 87, 71, 60, and

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58 (100%). A calculation of the deuterium content showed 10% d_0, 89% d_1, and 1% d_2. A picrate derivative was prepared and recrystallized from benzene–heptane giving yellow needles, mp 110–111°.

Anal. Calcd for $C_{12}H_{17}DN_4O_8$: C, 41.50; H, 4.90; N, 16.14. Found: C, 41.43; H, 5.11; N, 15.84.

The reduction of IV with lithium aluminum hydride gave N,N-dimethyl-2-methoxy-2-methylpropylamine (IVa) (retention time 8.0 min). The nmr spectrum of IVa showed peaks (in ppm) at 1.13 (singlet, 6 H), 2.23 (singlet, 2 H), 2.28 (singlet, 6 H), and 3.15 (singlet, 3 H). The mass spectrum showed peaks at *m/e* 131, 116, 100, 85, 73, and 58 (100%).

Anal. Calcd for $C_7H_{17}NO$: C, 64.12; H, 12.98; N, 10.68. Found: C, 64.01; H, 13.18; N, 10.84.

The reduction of IV with lithium aluminum deuteride gave N,N-dimethyl-2-methoxy-2-methylpropylamine-d_1 (IVb) (retention time 8.0 min). The mass spectrum showed peaks at *m/e* 132, 117, 116, 101, 86, 85, 74, and 58 (100%). A calculation of the deuterium content showed 5% d_0 and 95% d_1.

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Geminal Organometallic Compounds. I. The Synthesis and Structure of 1,1-Diborohexane[1]

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Abstract: The hydroboration of 1-hexyne with diborane in a 3:1 ratio results in the formation of a polymeric dihydroborated product. Oxidation of this material with alkaline hydrogen peroxide produces 80% 1-hexanol and only 10–12% 1,2-hexanediol. This points to an initial rapid hydrolysis of the dihydroboration intermediate. Examination of the products from deuterioboration of 1-hexyne, followed by alkaline hydrogen peroxide oxidation, revealed that the 1-hexanol originates from a 1,1-diboron compound. Confirmatory evidence for the predominant formation of the geminal diboron derivative was obtained by its oxidation to hexanoic acid when treated with *m*-chloroperbenzoic acid. The results indicate that the dihydroboration of 1-hexyne proceeds with addition of approximately 80% of the boron atoms at the terminal carbon. The use of either 2,3-dimethyl-2-butylborane or dicyclohexylborane as the hydroborating agent gives the 1,1-diboro derivatives in a 90–96% yield.

Until recently the chemistry of geminal dimetallic compounds has received little attention.[2] The discovery of the hydroalumination and hydroboration reactions has opened a new route for the preparation of difunctional organometallic compounds.[3,4] Thus hydroboration of dibutyl ethyleneboronate with diborane yielded the tetrabutyl ethane-1,1-diboronate as the major product.[5]

In a previous paper we had proposed that dihydroboration of 1-alkynes with diborane proceeds to give predominantly the 1,1-diboro derivative, with only 10–12% of the 1,2-diboro compound.[6] Recently, however, it was claimed that dihydroboration of 1-hexyne in tetrahydrofuran produces 30% of the 1,2-diboro derivative.[7]

In view of the increasing interest in these difunctional boron compounds as useful intermediates in synthetic work it was necessary to resolve this discrepancy. Accordingly we have made a detailed study of the dihydroboration of 1-alkynes in order to definitely establish the structure of the dihydroboration product, and to develop improved procedures for converting terminal acetylenes to 1,1-diboroalkanes.

Results and Discussion

The dihydroboration of 1-hexyne with diborane results in the formation of a highly branched, polymeric product. Since it was anticipated that the reaction product would contain the two boron atoms either on adjacent carbons or on the same carbon, oxidation with alkaline hydrogen peroxide should lead either to 1,2-hexanediol or *n*-hexaldehyde, respectively. Unexpectedly, however, oxidation of the dihydroborated 1-hexyne gave, along with these, 1-hexanol as the major product. The formation of 1-hexanol from the dihydroboration intermediate can be rationalized in terms of a rapid hydrolysis of one boron–carbon bond of either the 1,1- or the 1,2-diboron compound prior to the oxidation step.

Preliminary experiments indicated that the relative ratios of the oxidation products were strongly dependent on the hydrolysis conditions. Consequently, we examined the effect of base on the dihydroborated 1-hexyne as a function of temperature and time. 1-Hexyne (25 mmoles) was hydroborated at 0° with a solution of borane in tetrahydrofuran (18.3 mmoles of BH_3). The resulting deep yellow solution was then maintained for 1 hr at 0° before diluting with 7.5 ml of 3 *N* sodium hydroxide. Measurement of the hydrogen evolved revealed that the hydroboration did

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