essentially of olefin-to-metal donation. Whether this be valid or not, it is interesting that the $C_6H_6Cr(CO)_3$, $(CH_3)_6C_6Cr(CO)_3$, $dienCr(CO)_3$, and $(TMCOT)Cr(CO)_3$ molecules are so similar in respect to the Cr–CO bond lengths.

(7) Finally, it is appropriate to compare the $(TMCOT)Cr(CO)_3$ structure with the structures of the two closely related compounds $(COT)Mo(CO)_3$[16] and (cycloocta-1,3,5-triene)$Cr(CO)_3$.[27] The $(COT)Mo(CO)_3$ molecule is more symmetrical than $(TMCOT)Cr(CO)_3$, possessing rigorous, crystallographic mirror symmetry. Aside from this, it is structually very similar. The dihedral angle between the two planes formed by the ring is 130°, compared to 119° in $(TMCOT)Cr(CO)_3$. This and some other differences may be a consequence of changing Cr for Mo, but a detailed analysis is elusive. It is interesting that, in all three compounds, the pattern of OC–metal–CO bond angles is the same, one angle being about 80° while the other two are 91–94°.

---

[27] V. S. Armstrong and C. K. Prout, *J. Chem. Soc.*, 3770 (1962).

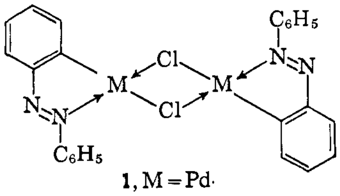
Electrophilic Aromatic Substitution Reactions by Platinum(II) and Palladium(II) Chlorides on N,N-Dimethylbenzylamines

Arthur C. Cope[1a] **and Edwin C. Friedrich**[1b]

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received May 26, 1967*

Abstract: Potassium tetrachloroplatinate(II) and lithium tetrachloropalladate(II) react readily with N,N-dimethylbenzylamine to give di-μ-chloro-bis(N,N-dimethylbenzylamine-2-C,N)diplatinum(II) and -dipalladium(II), respectively. These stable crystalline complexes possess both *ortho*-attached covalent metal–carbon bonding and coordinate metal–nitrogen bonding to the benzylamine. Similar bond formation by palladium(II) is observed in its complexes with the *p*-methoxy and 3,5-dimethoxy derivatives of N,N-dimethylbenzylamine. However, no palladium–carbon bonds are present in the palladium(II) chloride complexes obtained from *p*-nitro-N,N-dimethylbenzylamine and the N,N-dimethyl-2-phenyl-1-ethyl- and 3-phenyl-1-propylamines or from benzylamine and various secondary benzylamines.

The observation by Cope and Siekman[2] that azobenzene reacts with platinum(II) chlorides and palladium(II) chlorides to give complexes **1** and **2** having carbon-to-metal σ bonds has led us to search for similar reactions with other aromatic systems. This work was carried out in an attempt to obtain information concerning the structural requirements for aromatic substitution by platinum and palladium and whether the substitution reaction is confined to azobenzene and its derivatives. The systems investigated were limited to benzylamines and other classes of aromatic compounds containing groups which could coordinate to the metal and form structures similar to **1** and **2** if *ortho* substitution into the ring takes place.



1, M = Pd
2, M = Pt

Results and Discussion

The reactions of both the simple unsubstituted benzylamine and the secondary benzylamine, N-methylbenzylamine, with potassium tetrachloroplatinate(II) in aqueous methanol solvent did not meet with any success. Only intractable black products were obtained. Reaction of these amines with lithium tetrachloropalladate(II) in methanol did give good yields of crystalline complexes. Analyses, however, showed that these (**3** and **4**) were of the usual dichlorobis(amine)palladium(II) type[3] in which the two amines are coordinated through nitrogen to the metal, and no metal–carbon σ bonding is involved. Attempts to facilitate the aromatic substitution by palladium with the secondary benzylamines by changing the substituent on nitrogen from methyl to benzyl or phenyl, or by reaction with the highly activated N-phenyl-3,5-dimethoxybenzylamine, were unsuccessful. Again only the usual dichlorobis(amine)palladium(II) type complexes **5**, **6**, and **7** were obtained.

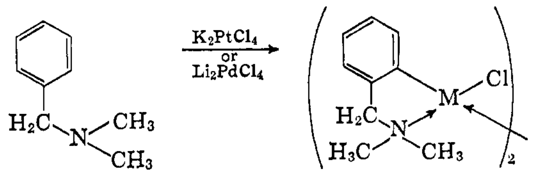
In contrast to the results obtained with the primary and secondary benzylamines, N,N-dimethylbenzylamine was found to react smoothly with the platinum(II) and palladium(II) chlorides to give crystalline products whose elemental analyses suggested that the desired di-μ-chloro-bis(N,N-dimethylbenzylamine-2-C,N)diplatinum(II) and -dipalladium(II) complexes had been formed. These materials have structures **8** and **9** similar to the type found by Cope and Siekman[2] with azobenzene. Thus, when a solution of N,N-dimethylbenzylamine and a half-molar quantity of potassium tetrachloroplatinate(II) in aqueous methanol was allowed to stand at room temperature for 45 hr, a dark brown pre-

---

[1] (a) Deceased; (b) Department of Chemistry, University of California, Davis, Calif. 95616.

[2] A. C. Cope and R. W. Siekman, *J. Am. Chem. Soc.*, **87**, 3272 (1965).

[3] E. Pietsch, Ed., "Gmelins Handbuch der Anorganischen Chemie–Palladium," Vol. 65, 8th ed, Verlag Chemie, GMBH, Weinheim/Bergstrasse, 1942, p 391.



8, M = Pt
9, M = Pd

cipitate was formed. This precipitate, after purification, gave a 28% yield of di-μ-chloro-bis(N,N-dimethylbenzylamine-2-C,N)diplatinum(II) (**8**) as white needles. Correspondingly, the reaction of 2 moles of N,N-dimethylbenzylamine with lithium tetrachloropalladate(II) in methanol solution for 20 hr at room temperature gave a 95% yield of di-μ-chloro-bis(N,N-dimethylbenzylamine-2-C,N)dipalladium(II) (**9**) as a yellow crystalline solid. Both of these complexes are stable to heat and storage and are readily soluble in benzene and chloroform. A competition experiment between azobenzene and N,N-dimethylbenzylamine with lithium tetrachloropalladate(II) showed that the benzylamine–palladium complex **9** is formed at a much faster rate. None of the complex **1** from azobenzene was observed.

When N,N-dimethylbenzylamine was allowed to react with an equimolar quantity of lithium tetrachloropalladate(II), only a 35% yield of the complex **9** was isolated. Also, there was obtained a small quantity of a red crystalline product which upon analysis was shown to be dichlorobis(N,N-dimethylbenzylamine hydrochloride)palladium(II). The yield of **9** could be increased either, as mentioned previously, by using an excess of the benzylamine or by adding another weak base such as tri-*n*-butylamine to neutralize the hydrogen chloride formed in the reaction. Complex **9** was also prepared in good yield by an inhomogeneous reaction of the benzylamine with a half-molar quantity of palladium(II) dichloride in methanol solution. These results are summarized in Table I.

Table I. Platinum and Palladium Complexes of N,N-Dimethylbenzylamine

Reagent[a]	Mole ratio amine: reagent	Reaction time, hr	Isolated yield, %	Mp, °C
K_2PtCl_4	2:1	45	28	225–227 dec
Li_2PdCl_4	2:1	20	96	185–187 dec
Li_2PdCl_4	1:1	16	35	184–186 dec
Li_2PdCl_4[b]	1:1	1	78	183–185 dec
$PdCl_2$	2:1	4	68	183–185 dec

[a] Run in methanol or methanol–water solution at room temperature. [b] In the presence of 2 moles of tri-*n*-butylamine.

The reactions of the *p*-methoxy- and 3,5-dimethoxy-N,N-dimethylbenzylamines with lithium tetrachloropalladate(II) gave good yields of the di-μ-chloro-bis(amine)dipalladium(II) complexes **10** and **11** of the same type as was obtained from N,N-dimethylbenzylamine. On the other hand, the reaction of *p*-nitro-N,N-dimethylbenzylamine with lithium tetrachloropalladate(II) gave a product **12** whose analysis indicated that it has a dichlorobis(amine)palladium(II) structure of the same type as was obtained from benzylamine and the various secondary benzylamines. The failure for aromatic substitution to take place with the deactivated *p*-nitro-N,N-dimethylbenzylamine indicates that palladium(II) must only be a weak electrophile.

Substitution of an aromatic hydrogen *ortho* to the methylene substituent by palladium in the N,N-benzylamine complexes was demonstrated by lithium aluminum deuteride reduction of the palladium–N,N-dimethyl-*p*-methoxybenzylamine complex (**10**). The N,N-dimethyl-*p*-methoxybenzylamine reduction product[4] was examined by mass spectrometry and found to contain 90% of d_1 species and 10% of d_0 species. Also, the nmr spectrum of this material integrated for only one proton at the 7.27-ppm position for the aromatic protons *ortho* to the methylene substituent.

Confirmation for the *ortho* substitution was obtained by examination of the nmr spectra of the palladium complexes, especially those (**10** and **11**) derived from the *p*-methoxy- and 3,5-dimethoxybenzylamines. Their spectra showed conclusively that one aromatic ring proton *ortho* to the methylene groups was missing in each of the complexes. The nmr spectrum of the platinum–N,N-dimethylbenzylamine complex (**8**) also provided evidence that in these materials nitrogen is coordinated through its unshared pair of electrons to the metal. The methyl proton and methylene proton signals in the spectrum of this complex were observed as triplets due to coupling with the Pt^{195} (spin $^1/_2$) isotope. A summary of the nmr spectral data is given in Table II.

To determine whether formation of the five-membered ring structure is essential for aromatic substitution by palladium, the reactions of lithium tetrachloropalladate(II) with the N,N-dimethyl-2-phenyl-1-ethyl- and 3-phenyl-1-propylamines were examined. If substitution by palladium occurred into the *ortho* positions of these materials, products containing six- and seven-membered rings would be formed. The products **13** and **14** obtained from these reactions, however, which were quite unstable and difficult to handle, were shown by analyses to be dichlorobis(amine)palladium(II) complexes in which no palladium–carbon bonds had been formed.

As a logical extension of the study of the reactions of the N,N-dimethylbenzylamine with lithium tetrachloropalladate(II), the commercially available N,N-dimethyl-1-naphthylamine was investigated. This material was found to give rapid formation of a palladium(II) complex **15** whose analysis indicated that it also must be of the same carbon-to-palladium σ-bonded type as was obtained with the N,N-dimethylbenzylamines. It is felt that in this complex the palladium must have undergone electrophilic substitution at the 8 position on the naphthalene ring *via* a five-ring transition state similar to that encountered with the N,N-dimethylbenzylamine. This, however, has not yet been definitely established. Competition experiments for lithium tetrachloropalladate(II) with the N,N-dimethyl-1-naphthylamine indicated that it reacts much slower than N,N-dimethylbenzylamine, but at least ten times faster than azobenzene.

In summary, the following conclusions may be made. The aromatic substitution reactions by platinum(II) and palladium(II) chlorides discovered by Cope and Siekman[2] are not limited to the azobenzene system and,

---

(4) 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); J. K. Stille and R. A. Morgan, *ibid.*, **88**, 5135 (1966).

Table II. Nmr Spectral Data[a-c]

							Aromatic		
Compound	CH_3N-	-CH_2N-		-CH_2Ph	Other -CH_2-	CH_3O-	*o*- to CH_2		*m*- or *p*- to CH_2
N,N-Dimethylbenzylamine	2.22 (s)		3.39 (s)					7.27 (s)	
Pt complex **8**	3.00 (t)[d]		3.89 (t)[e]					7.00 (bs)	
Pd complex **9**	2.83 (s)		3.92 (s)					6.92 (m)	
p-Methoxy-N,N-dimethylbenzylamine	2.22 (s)		3.39 (s)			3.79 (s)	7.27 (d)[f]		6.97 (d)[f]
Pd complex **10**	2.83 (s)		3.89 (s)			3.77 (s)	6.80 (d)[f,g]		6.78 (bs)[g] 6.62 (q)[g,h]
3,5-Dimethoxy-N,N-dimethylbenzylamine	2.25 (s)		3.37 (s)			3.79 (s)	6.53 (d)[i]		6.39 (t)[g,i]
Pd complex **11**	2.70 (s)		3.95 (s)			3.73[j]	6.20 (d)[g,i]	or reversed	6.03 (d)[g,i]
N,N-Dimethyl-2-phenyl-1-ethylamine	2.29 (s)		2.72 (m)					7.33 (s)	
Pd complex **13**	2.62 (s)	3.72 (m)		2.75 (m)				7.33 (s)	
N,N-Dimethyl-3-phenyl-1-propylamine	2.25 (s)	2.70 (m)		2.20 (m)	1.79 (m)			7.33 (s)	
Pd complex **14**	2.55 (s)		2.67 (m)					7.34 (s)	

[a] Run in $CDCl_3$ solvent. [b] Reported in ppm (δ) downfield from internal TMS. [c] s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad. [d] $J_{Pt^{195},H} = 48$ cps. [e] $J_{Pt^{195},H} = 55$ cps. [f] $J_{o,m} = 8.0$ cps. [g] Area = 1. [h] $J_{o,m} = 8.0$ cps, $J_{m,m} = 2.5$ cps. [i] $J_{o,p} = 2.0$ cps. [j] Doublet, 1.5-cps separation.

in fact, are even more facile with N,N-dimethylbenzylamine and N,N-dimethyl-1-naphthylamine. The reaction of the palladium(II) chlorides with N,N-dimethylbenzylamine probably occurs by an initial rapid coordination of the nitrogen to the metal. This process is then followed by attack of the metal at an *ortho* position on the ring. Apparently, the favorable entropy factors for electrophilic attack by the coordinated palladium *via* a five-membered ring transition state are necessary to facilitate the aromatic substitution. No products containing palladium–carbon bonds were obtained from the deactivated *p*-nitro-N,N-dimethylbenzylamine, or from the N,N-dimethyl-2-phenylethyl- and 3-phenylpropylamines which would have to react *via* six- and seven-membered ring transition states. Similar conclusions may be drawn by analogy for the reaction of potassium tetrachloroplatinate(II) with N,N-dimethylbenzylamine. The reasons for the differences observed in the reactions of the platinum(II) and palladium(II) chlorides with the tertiary N,N-dimethylbenzylamine and with the primary and secondary benzylamines are not entirely clear. In the complex formation the initial step must involve coordination of the metal to nitrogen followed by attack on the ring. Since one would expect for steric reasons that the primary and secondary amines should coordinate more strongly to the metal than do the tertiary amines, this stronger coordination may decrease the electrophilic character of the metal sufficiently to prevent later attack upon the phenyl ring. Also, if the initial metal–amine complex involves 2 moles of amine, the energy required to displace the second mole of amine during the ring substitution step may be so great in the case of the strongly coordinated primary and secondary amines as to prevent the substitution from taking place. Further work is continuing on this question as well as on the reactions and synthetic utility of the N,N-dimethylbenzylamine– and N,N-dimethyl-1-naphthylamine–palladium complexes.

Experimental Section

Melting points and boiling points are uncorrected. Ultraviolet and visible spectra were recorded on a Cary Model 21 spectrophotometer. Nuclear magnetic resonance spectra were determined on a Varian Associates Model A-60 instrument in deuteriochloroform solvent. Chemical shift values are reported in parts per million (δ) downfield from internal TMS. Molecular weights were obtained with a Mecrolab Model 301-A osmometer. Microanalyses were performed by Dr. S. N. Nagy and associates or by the Scandanavian Microanalytical Laboratory, Herlev, Denmark.

Materials. Potassium tetrachloroplatinate(II) was obtained from Englehard Industries, Inc. Palladium dichloride was Fisher dry purified grade. Benzylamine, N-methylbenzylamine, dibenzylamine, N,N-dimethylbenzylamine, N-phenylbenzylamine, and N,N-dimethyl-1-naphthylamine were Eastman White Label quality. Lithium aluminum deuteride was obtained from Metal Hydrides, Inc. Lithium chloride was Mallinckrodt Analytical Reagent quality. These materials were all used without further purification.

Lithium Tetrachloropalladate(II). A mixture of 30.0 g (0.17 mole) of palladium(II) dichloride and 14.4 g (0.34 mole) of lithium chloride in 100 ml of distilled water was heated and stirred until solution was complete. The resulting dark red solution was cooled and filtered, and most of the water was removed on a rotary vacuum evaporator. Removal of more of the water by heating on a steam bath at 1 mm gave a red-purple solid. The solid was broken into small pieces and dried to constant weight by heating in an Abderhalden at 1 mm over refluxing water (42.6 g, 96% yield). This material, which is very soluble in water or with slight warming in methanol, was used without further purification. It is highly hygroscopic and also corrosive to metal utensils when wet.

Attempted Reaction of N-Methylbenzylamine with Potassium Tetrachloroplatinate(II). To a solution of 1.0 g (0.0024 mole) of potassium tetrachloroplatinate(II) in 30 ml of water and 5 ml of methanol was added 0.29 g (0.0024 mole) of N-methylbenzylamine. The resulting clear, deep red solution was then allowed to stand at room temperature. After 3 days, the black solid which had separated was filtered and washed well with methanol (0.40 g). This black solid was insoluble in all the usual solvents, including boiling acetone and boiling chloroform, and therefore was not investigated further.

Dichlorobis(benzylamine)palladium(II) (3). The reaction of 0.50 g (0.0047 mole) of benzylamine and 0.60 g (0.0024 mole) of lithium tetrachloropalladate(II) in 40 ml of methanol at room temperature gave an immediate yellow precipitate. After standing for 4 hr the precipitate was filtered and washed well with methanol (0.70 g, 76% yield). Recrystallization from 100 ml of boiling methanol gave 0.40 g (44% yield) of long yellow needles, mp 180–182° dec. The nmr spectrum of this material showed a multiplet at 3.22 ppm (area 4) for the methylene protons and a singlet at 7.33 ppm (area 10) for the aromatic ring protons.

Anal. Calcd for $C_{14}H_{18}N_2PdCl_2$: C, 42.92; H, 4.60; N, 7.15; Pd, 27.18; Cl, 18.14. Found: C, 42.91; H, 4.68; N, 7.09; Pd, 27.21; Cl, 18.15.

Dichlorobis(N-methylbenzylamine)palladium(II) (4). A solution of 0.50 g (0.0041 mole) of N-methylbenzylamine in 20 ml of methanol was mixed with a solution of 0.53 g (0.0021 mole) of lithium tetrachloropalladate(II) in 20 ml of methanol. A precipitate formed immediately which after standing for 4 hr at room temperature was filtered and washed well with methanol (0.80 g, 93% yield). Recrystallization from 100 ml of boiling methanol gave 0.35 g (41% yield) of **4** as fine yellow needles, mp 208–209° dec. The nmr spectrum of this complex possessed multiplets at 2.45 ppm (area 6) and 3.45 ppm (area 4) for the N-methyl and methylene protons, respectively, and a singlet at 7.39 ppm (area 10) for the aromatic ring protons.

Anal. Calcd for $C_{16}H_{22}N_2PdCl_2$: C, 45.78; H, 5.25; N, 6.68; Pd, 25.37; Cl, 16.93. Found: C, 45.72; H, 5.28; N, 6.40; Pd, 25.37; Cl, 16.87.

Dichlorobis(dibenzylamine)palladium(II) (5). A solution of 0.75 g (0.0038 mole) of dibenzylamine and 0.50 g (0.0019 mole) of lithium tetrachloropalladate(II) in 40 ml of methanol was allowed to stand at room temperature for 4 hr. The precipitate which formed (0.92 g, 86% yield) was filtered, dissolved in 30 ml of boiling benzene, diluted with 20 ml of *n*-hexane, and cooled to obtain 0.75 g (70% yield) of **5** as dull orange crystals, mp 196–197° dec. The nmr spectrum of this material showed a multiplet at 3.50 ppm (area 8) for the methylene protons and a singlet at 7.33 ppm (area 20) for the aromatic protons.

Anal. Calcd for $C_{28}H_{30}N_2PdCl_2$: C, 58.80; H, 5.25; N, 4.90; Pd, 18.62; Cl, 12.43. Found: C, 58.71; H, 5.26; N, 4.83; Pd, 18.54; Cl, 12.38.

Dichlorobis(N-phenylbenzylamine)palladium(II) (6). To a solution of 1.30 g (0.0050 mole) of lithium tetrachloropalladate(II) in 20 ml of methanol was added 0.92 g (0.0050 mole) of N-phenylbenzylamine in 20 ml of methanol. After standing at room temperature for 21 hr, the solution was filtered to obtain 1.30 g (95% yield) of **6** as a dark yellow microcrystalline solid, mp 185–187° dec.

Anal. Calcd for $C_{26}H_{26}N_2PdCl_2$: C, 57.42; H, 4.78; N, 5.15; Pd, 19.58; Cl, 13.07. Found: C, 57.14; H, 4.85; N, 5.16; Pd, 19.66; Cl, 13.05.

Dichlorobis(N-phenyl-3,5-dimethoxybenzylamine)palladium(II) (7). The reaction of 0.30 g (0.0012 mole) of N-phenyl-3,5-dimethoxybenzylamine (mp 68–69°)[5] and 0.32 g (0.0012 mole) of lithium tetrachloropalladate(II) in 40 ml of methanol resulted in immediate formation of an orange crystalline complex. After standing at room temperature for 18 hr the complex was filtered (0.38 g, 95% yield) and recrystallized from 20 ml of boiling 80:20 benzene–hexane (0.25 g, 63% yield), mp 178–180° dec. The nmr spectrum of this complex showed a multiplet at 3.92 ppm (area 4) for the methylene protons, a singlet at 3.62 ppm (area 12) for the methoxy protons, a triplet at 6.32 ppm (area 2), a doublet at 6.45 ppm (area 4), and a broadened singlet at 7.29 ppm (area 10) for the aromatic ring protons.

Anal. Calcd for $C_{30}H_{34}N_2O_4PdCl_2$: C, 54.27; H, 5.13; N, 4.22; Pd, 16.04; Cl, 10.70. Found: C, 54.32; H, 5.13; N, 4.16; Pd, 15.85; Cl, 10.69.

Di-μ-chloro-bis(N,N-dimethylbenzylamine-2-C,N)diplatinum(II) (8). To a solution of 4.15 g (0.01 mole) of potassium tetrachloroplatinate(II) in 50 ml of water was added a solution of 2.70 g (0.02 mole) of N,N-dimethylbenzylamine in 20 ml of methanol. The initially clear red solution, after 45 hr at room temperature, had become colorless and precipitated 3.15 g of brown solids. These solids were extracted with 200 ml of boiling benzene and filtered to remove 1.60 g of brown insoluble material, and the benzene was removed on a rotary vacuum evaporator. Chromatography of the resulting brown residue through a short silicic acid column with chloroform gave 1.0 g (28% yield) of **8** as pale yellow crystals. These crystals were dissolved in 100 ml of boiling benzene, diluted with 150 ml of *n*-hexane, and cooled to obtain 0.85 g of dull white needles, mp 225–227° dec.

Anal. Calcd for $C_{18}H_{24}N_2Pt_2Cl_2$: C, 29.63; H, 3.29; N, 3.84; Pt, 53.50; Cl, 9.74. Found: C, 29.99; H, 3.28; N, 3.69; Pt, 53.30; Cl, 10.01.

Di-μ-chloro-bis(N,N-dimethylbenzylamine-2-C,N)dipalladium(II) (9) from Lithium Tetrachloropalladate(II). A solution of 0.50 g (0.0037 mole) of N,N-dimethylbenzylamine in 20 ml of methanol was mixed with a solution of 0.50 g (0.0019 mole) of lithium tetrachloropalladate(II) in 20 ml of methanol. The initially clear red mixture very quickly became lighter in color and after about 1 min at room temperature began to precipitate a yellow solid. After standing for 20 hr, the yellow product was filtered (0.50 g, 96% yield). Recrystallization from 50 ml of boiling 50:50 benzene–*n*-hexane gave 0.45 g of **9** as yellow crystals, mp 185–187° dec; $\lambda_{\max}^{\mathrm{CH_2Cl_2}}$ 340 mμ (ε 2520).

Anal. Calcd for $C_{18}H_{24}N_2Pd_2Cl_2$: C, 39.14; H, 4.35; N, 5.07; Pd, 38.56; Cl, 12.87; mol wt, 552. Found: C, 39.47; H, 4.42; N, 4.77; Pd, 38.24; Cl, 12.79; mol wt (osmometer), 495.

In a similar run using equimolar quantities of amine (0.50 g, 0.0037 mole) and lithium tetrachloropalladate(II) (0.97 g, 0.0037 mole), after 16 hr there was obtained 0.80 g of a mixture of red and yellow crystals. The yellow portion of the product, which was soluble in 20 ml of hot benzene, was filtered from the red material. The filtrate was diluted with 25 ml of *n*-hexane and cooled to obtain 0.35 g (35% yield) of **9**, mp 184–186° dec. The benzene-insoluble red plates weighed 0.25 g, mp 208–210° dec, and were shown by analysis to be dichlorobis-(N,N-dimethylbenzylamine hydrochloride)palladium(II).

Anal. Calcd for $C_{18}H_{28}N_2PdCl_4$: C, 41.51; H, 5.38; N, 5.38; Pd, 20.45; Cl, 27.29. Found: C, 41.22; H, 5.40; N, 5.45; Pd, 20.60; Cl, 27.40.

In a further run in the presence of 1.38 g (0.0075 mole) of tri-*n*-butylamine, the reaction of 0.50 g (0.0037 mole) of N,N-dimethylbenzylamine with 0.97 g (0.0037 mole) of lithium tetrachloropalladate(II) in 40 ml of methanol at room temperature for 1 hr gave 0.80 g (78% yield) of crude **9**. Recrystallization from boiling benzene–*n*-hexane gave 0.75 g of beautiful bright yellow crystals, mp 183–185° dec.

Di-μ-chloro-bis(N,N-dimethylbenzylamine-2-C,N)dipalladium(II) (9) from Palladium(II) Dichloride. A heterogeneous mixture of 5.40 g (0.04 mole) of N,N-dimethylbenzylamine and 3.5 g (0.02 mole) of palladium(II) dichloride in 200 ml of methanol was stirred at room temperature. After 4 hr, all of the palladium dichloride had dissolved and was replaced by a yellow-brown crystalline solid. This was recrystallized from boiling benzene–*n*-hexane to obtain 3.75 g (68% yield) of **9**, mp 183–185° dec.

Competition between N,N-Dimethylbenzylamine and Azobenzene for Lithium Tetrachloropalladate(II). The reaction of 1.35 g (0.01 mole) of N,N-dimethylbenzylamine and 1.82 g (0.01 mole) of azobenzene with 1.32 g (0.005 mole) of lithium tetrachloropalladate(II) in 40 ml of methanol for 10 hr at room temperature gave 1.23 g of greenish yellow crystals, mp 183–185° dec. The nmr spectrum of this material showed that it consisted entirely of the benzylamine–palladium complex (**9**).

Di-μ-chloro-bis(N,N-dimethyl-*p*-methoxybenzylamine-2-C,N)dipalladium(II) (10). A solution of 1.25 g (0.007 mole) of N,N-dimethyl-*p*-methoxybenzylamine[6] (bp 67–69° (0.1 mm), $n^{25}\mathrm{D}$ 1.5104) and 2.0 g (0.0076 mole) of lithium tetrachloropalladate(II) in 20 ml of methanol was allowed to stand at room temperature for 22 hr. The solvent was then removed on a rotary vacuum evaporator, and the resulting red-yellow residue was extracted with 50 ml of boiling benzene. The benzene solution was filtered, diluted with 70 ml of *n*-hexane, and cooled to obtain 1.15 g (50% yield) of **10** as yellow crystals. An analytical sample was prepared by recrystallization from boiling benzene, mp 184–185° dec; $\lambda_{\max}^{\mathrm{CH_2Cl_2}}$ 343 mμ (ε 2960).

Anal. Calcd for $C_{20}H_{28}N_2O_2Pd_2Cl_2$: C, 39.23; H, 4.58; N, 4.58; Pd, 34.78; Cl, 11.61. Found: C, 39.39; H, 4.76; N, 4.33; Pd, 34.52; Cl, 11.73.

A portion of the benzene-insoluble dichlorobis(amine hydrochloride)palladium(II) product was recrystallized from hot water, mp 146–148° dec.

Anal. Calcd for $C_{20}H_{32}N_2O_2PdCl_4$: C, 41.35; H, 5.51; N, 4.82; Pd, 18.33; Cl, 24.47. Found: C, 41.42; H, 5.63; N, 5.30; Pd, 17.96; Cl, 24.67.

Di-μ-chloro-bis(N,N-dimethyl-3,5-dimethoxybenzylamine-2-C,N)dipalladium(II) (11). The reaction of 0.98 g (0.005 mole) of N,N-dimethyl-3,5-dimethoxybenzylamine (bp 96–97° (0.5 mm), $n^{25}\mathrm{D}$ 1.5184) with 0.66 g (0.0025 mole) of lithium tetrachloropalladate(II) in 100 ml of methanol at room temperature for 12 hr gave 0.95 g of orange plates. These were dissolved in 50 ml of boiling benzene, filtered to remove 0.25 g of insoluble material, diluted with 60 ml of *n*-hexane, and cooled to obtain 0.55 g (66% yield) of **11**, mp 138–140° dec.

Anal. Calcd for $C_{22}H_{32}N_2O_4Pd_2Cl_2$: C, 39.30; H, 4.76; N, 4.17; Pd, 31.68. Found: C, 39.72; H, 4.77; N, 3.77; Pd, 31.70.

---

[5] Y. Asahina and T. Matsuzaki, *J. Pharm. Soc. Japan*, **509**, 527 (1924).

[6] M. Tiffeneau, *Bull. Soc. Chim. France*, **9**, 827 (1911).

Dichlorobis(N,N-dimethyl-*p*-nitrobenzylamine)palladium(II) (12). Reaction of 1.80 g (0.01 mole) of N,N-dimethyl-*p*-nitrobenzylamine[7] (bp 92–94° (0.1 mm), n^{25}D 1.5395) with 1.31 g (0.005 mole) of lithium tetrachloropalladate(II) in 200 ml of methanol for 1 hr at room temperature gave 2.2 g (82% yield) of **12** as yellow crystals. An analytical sample was prepared by recrystallization from toluene, mp 127–128° dec.

Anal. Calcd for $C_{18}H_{24}N_4O_4PdCl_2$: C, 40.19; H, 4.47; N, 10.42; Pd, 19.85; Cl, 13.21. Found: C, 40.28; H, 4.57; N, 9.91; Pd, 19.83; Cl, 13.48.

Lithium Aluminum Deuteride Reduction of Di-μ-chloro-bis(N,N-dimethyl-*p*-methoxybenzylamine-2-C,N)dipalladium(II) (10). To a stirred slurry of 0.50 g (0.012 mole) of lithium aluminum deuteride in 100 ml of ether was added in small portions 1.50 g (0.0024 mole) of complex **10**. After stirring at room temperature for 1 hr, the resulting black slurry was worked up by the careful addition of 3 ml of >99.7% deuterium oxide followed by anhydrous sodium sulfate. The ether solution was filtered through anhydrous sodium sulfate and the solids were washed well with ether. Removal of the ether solvent by distillation through a short Vigreux column gave an oil which was distilled at 0.1 mm (bath 70°) under nitrogen through a microdistillation apparatus (0.63 g, 80% yield, n^{25}D 1.5113). The nmr spectrum of this distilled material showed the expected singlets at 2.22 ppm (area 6), 3.39 (2), and 3.79 (3) for the N-methyl, methylene, and methoxy protons, respectively, of N,N-dimethyl-*p*-methoxybenzylamine. In the aromatic region, the signal at 6.97 ppm, which was a doublet ($J_{o,m}$ = 8.0 cps) in the undeuterated material, was found as a multiplet (area 2.0). The signal at 7.27 ppm for the aromatic protons *ortho* to the methylene group, which was a doublet (area 2) in the undeuterated material, was found to be a doublet ($J_{o,m}$ = 8.0 cps, area 1.1) in the redution product.

Dichlorobis(N,N-dimethyl-2-phenyl-1-ethylamine)palladium(II) (13). The reaction of 1.49 g (0.01 mole) of N,N-dimethyl-2-phenyl-1-ethylamine[8] (bp 65–66° (3.0 mm), n^{25}D 1.5009) with 1.31 g (0.005 mole) of lithium tetrachloropalladate(II) in 40 ml of methanol for 20 hr at room temperature gave a slight palladium mirror and 1.50 g (64% yield) of **13** as a reddish orange crystalline precipitate, mp 93–94°.

Anal. Calcd for $C_{20}H_{30}N_2PdCl_2$: C, 50.48; H, 6.31; N, 5.89; Pd, 22.38; Cl, 14.93. Found: C, 50.28; H, 6.49; N, 6.22; Pd, 23.04; Cl, 15.23.

Dichlorobis(N,N-dimethyl-3-phenyl-1-propylamine)palladium(II) (14). The reaction of 1.63 g (0.01 mole) of N,N-dimethyl-3-phenyl-1-propylamine[9] (bp 74–75° (2.0 mm), n^{25}D 1.4971) with 1.30 g (0.005 mole) of lithium tetrachloropalladate(II) in 35 ml of methanol for 14 hr at room temperature gave a red solution containing a small amount of a black precipitate. Removal of the solvent on a rotary vacuum evaporator gave an orange crystalline residue which was extracted into 100 ml of boiling *n*-hexane, filtered, and cooled to obtain 1.50 g (60% yield) of **14**, mp 83–85°.

Anal. Calcd for $C_{22}H_{34}N_2PdCl_2$: C, 52.44; H, 6.75; N, 5.56; Pd, 21.14; Cl, 14.10. Found: C, 52.70; H, 6.79; N, 5.76; Pd, 21.21; Cl, 14.35.

Di-μ-chloro-bis(N,N-dimethyl-1-naphthylamine-8-C,N)dipalladium(II) (15). To a solution of 1.30 g (0.0076 mole) of N,N-dimethyl-1-naphthylamine in 150 ml of methanol was added 1.0 g (0.0038 mole) of lithium tetrachloropalladate(II) in 50 ml of methanol. After about 3 min of standing at room temperature, a yellow crystalline precipitate began to form. After 3 hr of standing, the product was filtered and washed well with methanol (1.15 g, 49% yield). This was extracted with 60 ml of boiling benzene, filtered, diluted with 60 ml of *n*-hexane, and cooled to obtain 0.50 g (21% yield) of **15**, mp >300° (blackens at 220°). The nmr spectrum of this material possessed a singlet at 3.55 ppm (area 12) for the N-methyl protons and a multiplet at 7.59 ppm (area 12) for the aromatic ring protons.

Anal. Calcd for $C_{24}H_{24}N_2Pd_2Cl_2$: C, 46.17; H, 3.85; N, 4.49; Pd, 34.11; Cl, 11.38. Found: C, 46.53; H, 3.91; N, 4.33; Pd, 34.30; Cl, 11.59.

Competition between N,N-Dimethylbenzylamine and N,N-Dimethyl-*p*-methoxybenzylamine for Lithium Tetrachloropalladate(II). The reaction of 1.65 g (0.01 mole) of N,N-dimethyl-*p*-methoxybenzylamine and 1.35 g (0.01 mole) of N,N-dimethylbenzylamine with 1.32 g (0.005 mole) of lithium tetrachloropalladate(II) in 40 ml of methanol at room temperature for 10 hr gave 1.30 g of yellow precipitate. Examination of this material by nmr methods showed that it consisted of approximately a 50:50 mixture of the palladium complexes **9** and **10** of the two amines.

Competition between N,N-Dimethyl-1-naphthylamine and N,N-Dimethyl-*p*-methoxybenzylamine for Lithium Tetrachloropalladate(II). A solution containing 0.85 g (0.005 mole) of N,N-dimethyl-1-naphthylamine, 0.82 g (0.005 mole) of N,N-dimethyl-*p*-methoxybenzylamine, and 0.66 g (0.0025 mole) of lithium tetrachloropalladate(II) in 300 ml of methanol was allowed to stand for 3 hr at room temperature. The 0.65 g of yellow crystals which was obtained was examined by nmr and found to consist entirely of the palladium complex **15** of the N,N-dimethyl-*p*-methoxybenzylamine.

Competition between N,N-Dimethyl-1-naphthylamine and Azobenzene for Lithium Tetrachloropalladate(II). The reaction of 0.85 g (0.005 mole) of N,N-dimethyl-1-naphthylamine and 0.91 g (0.005 mole) of azobenzene with 0.66 g (0.0025 mole) of lithium tetrachloropalladate(II) in 250 ml of methanol for 3 hr at room temperature gave 0.55 g of a mixture of red and yellow crystals. The nmr spectrum of this mixture showed that it consisted of at least 90% of the palladium complex **15** of N,N-dimethyl-1-naphthylamine.

Acknowledgment. The authors wish to thank Dr. Robert W. Siekman for his assistance in obtaining the mass spectra.

---

[7] G. M. Bennett and G. H. Willis, *J. Chem. Soc.*, 264 (1929).

[8] E. C. Horning, Ed., "Organic Synthesis," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, pp 723–725.

[9] M. Tiffeneau and K. Fuhner, *Bull. Soc. Chim. France*, **15**, 173 (1914).