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σ-Bonded Arylpalladium(II) Complex: Bis-[*N*,*N*-dimethylbenzylamine-2-*C*,*N*]-palladium

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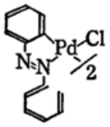
Recently the preparations of σ-bonded arylpalladium complexes have been investigated by several workers.[1-4] For example, Calvin and Coates[1] have prepared palladium complexes of the type of $Ar_2Pd(PEt_3)_2$ which were stabilized by π-bonding phosphine donors. Cope and Sieman[2] have found palladium(II) halides to react with azobenzenes to give the chloro-2-(phenylazo)-phenylpalladium dimer (1) as a surprisingly stable product. Furthermore, *N*,*N*-dimethylbenzylamine,[3] α-*N*,*N*-dimethylaminonaphthalene,[3] and 2-phenylpyridine[4] reacted with palladium chloride to form similar σ-bonded aryl derivatives of palladium. Recent observations[5] that *o*-lithio-*N*,*N*-dimethylbenzylamine reacts with chromium(III) chloride or cobalt(II) chloride to give complexes with carbon-to-metal σ-bonds have led us to examine a similar reaction between dibenzonitrile-dichloropalladium and *o*-lithio-*N*,*N*-dimethylbenzylamine.



(1)

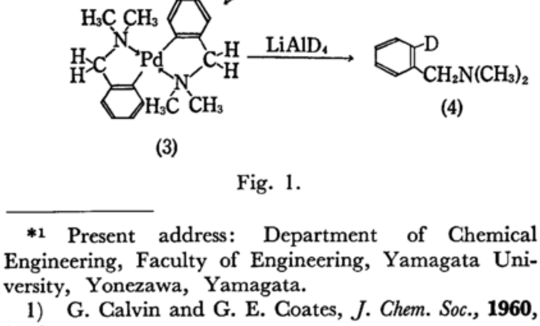


Fig. 1.

Experimental[6]

Materials. *N*,*N*-Dimethylbenzylamine was obtained commercially, while dibenzonitrile-dichloropalladium was prepared by a literature method.[7] The NMR spectra were recorded with a Hitachi H-60 instrument in deuterochloroform, using tetramethylsilane as the internal standard; the peak positions were expressed in terms of τ values. The mass spectra were obtained on a Hitachi RMU-6 mass spectrophotometer. The molecular weight was determined in benzene using a Hitachi vapor-pressure osmometer.

Bis-[*N*,*N*-dimethylbenzylamine-2-*C*,*N*]-palladium(II) (3). A mixture of *N*,*N*-dimethylbenzylamine (2.70 g, 0.02 mol), *n*-butyl lithium in ether (28 m*l* containing 0.024 mol), and ether (60 m*l*) was stirred in a nitrogen atmosphere for 24 hr. The resulting mixture of *o*-lithio-*N*,*N*-dimethylbenzylamine was cooled in an ice-salt bath and then reacted with dibenzonitrile-dichloropalladium(II) (3.83 g, 0.01 mol) under a stream of nitrogen. After stirring for 6 hr at room temperature, the mixture was treated with water (50 m*l*) and extracted with methylene chloride. The extract was washed with water, dried over anhydrous magnesium sulfate, and concentrated on a rotary evaporator. The resultant red oil was triturated with petroleum ether; the yellow crystals were filtered off and recrystallized from benzene. The yield was 0.46 g (12%); mp 209—210°C (dec.). Infrared spectrum (KBr pellet): 3020, 1590, 1465, 1440, 1000, 844 and 750 cm^{-1}. NMR spectrum: 7.52 (singlet, N-CH_3), 7.04 (doublet, J=10 cps, benzylic

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1) G. Calvin and G. E. Coates, *J. Chem. Soc.*, **1960**, 2008.

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

3) A. C. Cope and E. C. Friedrich, *ibid.*, **90**, 909 (1968).

4) A. Kasahara, This Bulletin, **41**, 1272 (1968).

5) a) G. Bähr and H. Zohm, *Angew. Chem.*, **75**, 94 (1963). b) A. C. Cope and R. W. Gourly, *J. Organometal. Chem.*, **8**, 527 (1967).

6) The melting points are uncorrected.

7) M. S. Kharasch, R. C. Seyler and F. R. Mayo, *J. Am. Chem. Soc.*, **60**, 882 (1938).

protons), 6.56 (singlet, N-CH_3), 6.20 (doublet, J=10 cps, benzylic protons) and 2.88—2.17 τ (multiplet, aromatic protons).

Found: C, 57.81; H, 6.62; N, 7.57%; mol wt, 368. Calcd for $C_{18}H_{24}N_2Pd$: C, 57.68; H, 6.45; N, 7.46%; mol wt, 374.8.

Reduction of Complex. General Procedure. The complex (0.2 g) to be reduced was slowly added to a stirred mixture containing 0.1 g of lithium aluminum hydride or deuteride in 30 m*l* of absolute tetrahydrofuran. The resulting black mixture was stirred at room temperature for 30 min; then water or deuterium oxide was added with cooling. The mixture was made acid with dilute hydrochloric acid, and the tetrahydrofuran was removed by evaporation under reduced pressure. After having been made alkaline with sodium carbonate, the mixture was extracted with ether. The ether solution was dried ($MgSO_4$) and concentrated by evaporation, and the product was isolated by preparative gas chromatography.

Reduction of 3 with Lithium Aluminum Hydride. This gave *N,N*-dimethylbenzylamine. The treatment of the product with methyl iodide gave the methodide as white crystals: mp 177—178°C.

Reduction of 3 with Lithium Aluminum Deuteride. This gave *N,N*-dimethyl-benzylamine-d_1. Methiodide derivative was made in the usual manner; mp 177—178°C. The mass spectrometric analysis showed that the product consisted of 92% d_1 and 8% d_0 species.

Results and Discussion

The *o*-metalation of *N,N*-dimethylbenzylamine with *n*-butyl lithium has previously been reported by Jones and his co-workers.[8] We reacted *o*-lithioamine (**2**) with dibenzonitrile-dichloropalladium in ether to give a yellow crystalline complex (**3**). The structure of **3** was assigned as follows. The elemental analysis is satisfactory, and the molecular weight measurement agrees with the assigned structure. In the infrared spectrum of **3**, the characteristic C–H out-of-plane deformation modes of a mono-substituted benzene at 770—730 and 690 cm^{-1} are absent; they are replaced by one at 750 cm^{-1} which can be assigned to a C–H deformation mode of an *ortho*-disubstituted benzene.[9] The lithium aluminum hydride reduction of **3** gave *N,N*-dimethylbenzylamine, whose mass spectrum and methiodide were identical with those of an authentic sample. On the other hand, the lithium aluminum deuteride reduction of **3** gave *N,N*-dimethylbenzylamine-d_1 (**4**). The gas-chromatographic analysis of **4** showed it to have the same retention time as an authentic sample of non-deuterated *N,N*-dimethylbenzylamine. The location of the deuterium in the *ortho*-position of the aromatic ring and, therefore the site of the carbon-to-palladium σ-bond, were indicated by the infrared spectrum of **4**, in which the characteristic absorption of an *ortho*-substituted benzene at 738 cm^{-1} was observed. Furthermore, the NMR spectrum of **3** is consistent with the proposed structure. We think that the complex **3** probably has a tetrahedral structure because the two *N*-methyl protons in the *N,N*-dimethylamino group are non-equivalent and appear as two singlets, at 7.52 and 656 τ. Moreover, the two protons in each pair of benzylic protons are also non-equivalent and appear as two doublets, at 7.04 and 6.20 τ. If the complex (**3**) were square-planar, a simple singlet pattern for the *N*-methyl protons of the *N,N*-dimethylamino group and also for the benzylic protons would be expected.

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[8] E. N. Jones, M. E. Zinn and C. R. Hauser, *J. Org. Chem.*, **28**, 663 (1963).

[9] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y. (1958).