Interaction of Lithium Chloride with Dimeric Chloro-bridged Cyclopalladated Complexes of *N,N*-Dimethylbenzylamines in Acetic Acid. A Correction

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We have previously reported [1] that the dimeric chloro-bridged *ortho* palladated derivative of *N,N*-dimethylbenzylamine, the complex $[\mathrm{PdCl(C_6H_4CH_2NR_2)}]_2$ (**I**), where R = Me (**a**), reacts readily with LiCl in acetic acid/benzene mixture as a solvent to afford a new compound formulated as the anionic cyclopalladated monomer $[\mathrm{PdCl_2(C_6H_4CH_2NMe_2)}]^-\mathrm{Li}^+$. The assignment has been done on the basis of analytical and ^{1}H NMR spectral data. Further work has, however, revealed that the formulation is incorrect. Under the reaction conditions complex **Ia**, as well as its ethyl substituted analogue (R = Et (**b**)), reacts with a cleavage of both palladium–carbon and palladium–nitrogen bonds to give *N,N*-dimethylbenzylammonium salts, where anions are $\mathrm{PdCl_4}^{2-}$ and $\mathrm{Pd_2Cl_6}^{2-}$ in the case of **Ia** and **Ib**, respectively.

The absence of the Pd–C bond in complexes $[\mathrm{C_6H_5CH_2NHMe_2}]_2{}^+[\mathrm{PdCl_4}]^{2-}$ (**IIa**) and $[\mathrm{C_6H_5CH_2NHEt_2}]_2{}^+[\mathrm{Pd_2Cl_6}]^{2-}$ (**IIb**) was confirmed by the ^{13}C NMR study of the compounds in [^{2}H$_6$]DMSO solvent. The ^{13}C[^{1}H] NMR spectrum of **IIa** contains a single resonance from a quaternary carbon at δ 134.3 (C^1). Other aromatic signals are located at δ 134.9 (C^2, C^6), 132.7 (C^3, C^5) and 133.4 (C^4). The assignment was additionally verified by analysis of the ^{13}C NMR spectrum coupled with hydrogen. Aliphatic carbons resonate at δ 63.4 ($\mathrm{CH_2N}$) and 45.5 ($\mathrm{NCH_3}$); these signals are shifted upfield compared with free *N,N*-dimethylbenzylamine (δ 67.5 and 48.7, respectively, in the same solvent). An opposite trend is seen in the case of **Ia**. Aliphatic carbons experience a downfield drift and are observed at δ 76.0 ($\mathrm{CH_2N}$) and 54.9 ($\mathrm{NCH_3}$). These observations indicate that complex **IIa** does not contain a Pd–N bond. Note that in the ^{1}H NMR spectrum of **IIa** signals from $\mathrm{CH_2N}$ and $\mathrm{NCH_3}$ protons are strongly shifted downfield compared with those of the free ligand [1].

N,N-dialkylbenzylammonium ions crystallize under the reaction conditions with counter ions $\mathrm{PdCl_4}^{2-}$ and $\mathrm{Pd_2Cl_6}^{2-}$, or a mixture of both. The latter accounts for a variable elemental composition of the reaction product obtained from **Ia**. Only when LiCl was taken in a 2000% molar excess over **Ia**, the composition of the product corresponded exactly to **IIa**[*]. Analytical data, presented in ref. 1, characterized a compound which was actually a mixture of $\mathrm{PdCl_4}^{2-}$ and $\mathrm{Pd_2Cl_6}^{2-}$ salts.

Ethyl substituted compound **Ib** reacted in a similar way to produce **IIb**[**]. Brown crystalline products **IIa,b** are stable as solids, but undergo *ortho* metallation when dissolved in methanol with regeneration of **Ia,b**.

In the light of these results we can now specify a complexation mode between **IIa** and *para*-substituted styrenes in acetic acid solvent, which was thought to involve the anionic monomer. It is clear now that the reversible interaction described in ref. 2 should be written as

$$\mathrm{(LH)_2[Pd_2Cl_6]} \rightleftharpoons \mathrm{(LH)[Pd_2Cl_5(HOAc)]} + \mathrm{(LH)Cl}$$

$$\mathrm{(LH)[Pd_2Cl_5(HOAc)]} + \text{alkene} \rightleftharpoons \mathrm{(LH)[Pd_2Cl_5(alkene)]},\ K$$

where LH = $\mathrm{C_6H_5CH_2NH^+Me_2}$; alkene = H–, 4-Br–, 4-Cl–, 4-Me– and 4-MeO–$\mathrm{C_6H_4CH{=}CH_2}$; K (303 K) = 50, 21, 23, 98 and 234 M^{-1} in a given styrene series, respectively.

References

1 A. D. Ryabov, I. K. Sakodinskaya, V. M. Titov and A. K. Yatsimirsky, *Inorg. Chim. Acta, 54,* L195 (1981).

2 A. D. Ryabov, I. K. Sakodinskaya and A. K. Yatsimirsky, *J. Chem. Soc., Perkin Trans., 2,* 1511 (1983).

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[*] **IIa:** *Anal.* Found: C, 41.31; H, 5.41, N, 5.36. Calc. for $\mathrm{C_{18}H_{28}N_2Cl_6Pd}$: C, 41.51; H, 5.38; N, 5.38%.

[**] **IIb:** *Anal.* Found: C, 35 15; H, 4.85; Cl, 28 17. Calc. for $\mathrm{C_{22}H_{36}N_2Cl_8Pd_2}$: C, 35.02; H, 4.78; Cl, 28.26%. NMR (δ, [^{2}H$_6$]DMSO): ^{1}H: 7.44(m, Ar), 4.25(s, $\mathrm{ArCH_2N}$), 3.02(q, $\mathrm{NCH_2Me}$), 1.79(t, $\mathrm{CH_2CH_3}$); ^{13}C: 128.9(C^2, C^6), 128.3(q, C^1), 127.35(C^4), 126.8(C^3, C^5), 53.1(ArCN), 44.1(NC), 6.5 (NC$\underline{\mathrm{C}}$).

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