

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

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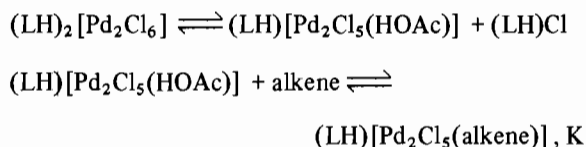
We have previously reported [1] that the dimeric chloro-bridged *ortho* palladated derivative of *N,N*-dimethylbenzylamine, the complex $[\text{PdCl}(\text{C}_6\text{H}_4\text{CH}_2\text{-NR}_2)]_2$ (**I**), where R = Me (**a**), reacts readily with LiCl in acetic acid/benzene mixture as a solvent to afford a new compound formulated as the anionic cyclopalladated monomer $[\text{PdCl}_2(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)]^- \text{Li}^+$. The assignment has been done on the basis of analytical and ^1H 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 PdCl_4^{2-} and $\text{Pd}_2\text{Cl}_6^{2-}$ in the case of **Ia** and **Ib**, respectively.

The absence of the Pd-C bond in complexes $[\text{C}_6\text{H}_5\text{CH}_2\text{NHMe}_2]_2^+[\text{PdCl}_4]^{2-}$ (**IIa**) and $[\text{C}_6\text{H}_5\text{CH}_2\text{NHEt}_2]_2^+[\text{Pd}_2\text{Cl}_6]^{2-}$ (**IIb**) was confirmed by the ^{13}C NMR study of the compounds in $[\text{}^2\text{H}_6]\text{DMSO}$ solvent. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **IIa** contains a single resonance from a quaternary carbon at δ 134.3 (C¹). Other aromatic signals are located at δ 134.9 (C², C⁶), 132.7 (C³, C⁵) and 133.4 (C⁴). The assignment was additionally verified by analysis of the ^{13}C NMR spectrum coupled with hydrogen. Aliphatic carbons resonate at δ 63.4 (CH₂N) and 45.5 (NCH₃); 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 (CH₂N) and 54.9 (NCH₃). These observations indicate that complex **IIa** does not contain a Pd-N bond. Note that in the ^1H NMR spectrum of **IIa** signals from CH₂N and NCH₃ 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 PdCl_4^{2-} and $\text{Pd}_2\text{Cl}_6^{2-}$, 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 PdCl_4^{2-} and $\text{Pd}_2\text{Cl}_6^{2-}$ 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



where LH = $\text{C}_6\text{H}_5\text{CH}_2\text{NH}^+\text{Me}_2$; alkene = H-, 4-Br-, 4-Cl-, 4-Me- and 4-MeO-C₆H₄CH=CH₂; 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).

***IIa**: *Anal.* Found: C, 41.31; H, 5.41, N, 5.36. Calc. for $\text{C}_{18}\text{H}_{28}\text{N}_2\text{Cl}_6\text{Pd}$: C, 41.51; H, 5.38; N, 5.38%.

****IIb**: *Anal.* Found: C, 35.15; H, 4.85; Cl, 28.17. Calc. for $\text{C}_{22}\text{H}_{36}\text{N}_2\text{Cl}_8\text{Pd}_2$: C, 35.02; H, 4.78; Cl, 28.26%. NMR (δ , $[\text{}^2\text{H}_6]\text{DMSO}$): ^1H : 7.44(m, Ar), 4.25(s, ArCH₂N), 3.02-(q, NCH₂Me), 1.79(t, CH₂CH₃); ^{13}C : 128.9(C², C⁶), 128.3-(q, C¹), 127.35(C⁴), 126.8(C³, C⁵), 53.1(ArCN), 44.1(NC), 6.5 (NCC).