Inorganica Chimica Acta, 54 (1981) L195–L197
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Different Behaviour of Lithium Chloride towards some Cyclopalladated Complexes of N,N-dimethylbenzylamine in Acetic Acid

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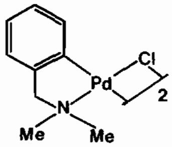
Received April 2 1981

Recently the reactions of cyclometallated compounds have become the topic of current interest [1–3]. Their importance comes not only from the synthetic utility of the compounds, but also from the variety of inorganic pathways and mechanisms, operative in the chemistry of these complexes. The reactions of di-μ-chloro-bis[N,N-dimethylbenzylamine-2C,N]dipalladium(II) (I) with different substrates may proceed, in principle, by at least three pathways, involving the Pd–C bond [4–8], chloro-bridges [9–11], or the Pd–N bond. These patterns depend both on the nature of the attacking substrate and on the nature of the ligands in the coordination sphere of palladium(II). However, only minor attention has been drawn to the latter problem. It is known that I and its monomeric derivative II possess almost the same reactivity towards methyl vinyl ketone [4], but complex I is much more reactive than II towards styrene [5]. In the present paper we wish to report an illustrative example, reflecting the influence of ligands on reactions of LiCl with I and II in acetic acid to give the monomeric anionic complex III and the neutral dimer IV respectively.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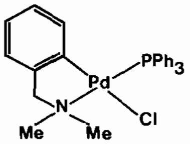
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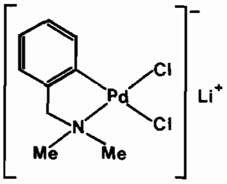
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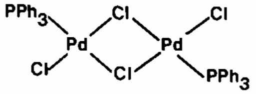
IV

Results and Discussion

In the course of our study of salt effects on the kinetics of styrene insertion into Pd–C bond of I [12] we have observed that addition of LiCl to the solution of I in HOAc causes rapid loss of the absorption band at 340 nm and the appearance of a new band at 450 nm. These spectral changes indicate the conversion of the initial complex II to some other material. To isolate this new compound the solution of LiCl (~4-fold molar excess with respect to I) in HOAc was added to the solution of I in benzene and the resulting mixture was thermostatted at 70 °C for 90 min. The brown precipitate formed was isolated and on the basis of analytical data, IR and ^{1}H NMR measurements it is assumed to be the monomeric anionic complex lithium *cis*-dichloro[N,N-dimethylbenzylamine-2C,N]palladate(II) (III). The *cis* assignment of chloro ligands in III is supported by two ν(Pd–Cl) absorptions at 320 and 290 cm^{-1}*. The ^{1}H NMR spectrum of III shows two sharp singlets assignable to N–CH$_2$ and N–CH$_3$ protons at 4.30 and 2.75 ppm (δ) respectively. The downfield shift of these signals compared with those of free N,N-dimethylbenzylamine strongly suggests that nitrogen is coordinated to the metal [3]. Complex III is stable in HOAc solvent in the presence of excess of LiCl; its absorption spectrum remains unchanged after a prolonged (24 hr) heating of the solution at 70 °C.

To our knowledge III is the first example of an anionic N,N-dimethylbenzylamine complex of the type. It has been reported earlier [13] that V can

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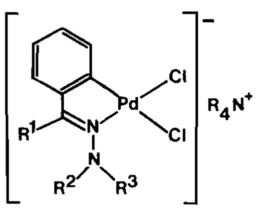
*Analysis of far IR spectral data was based on refs. [6, 9] and the literature cited therein.



V

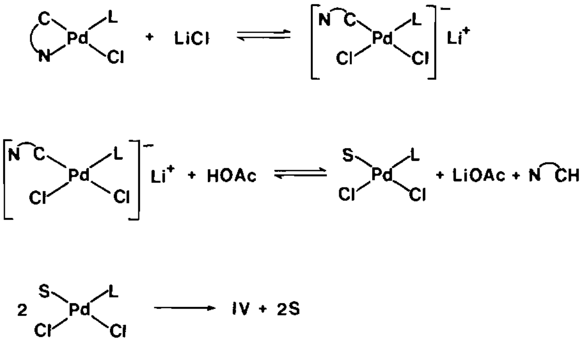
R^1= Ph; R^2= H, Me, Ph; R^3=H,Me

be obtained from the respective chloro-bridged dimer and $R_4N^+Cl^-$ in CH_2Cl_2. However, complex I was found to be completely inert under the latter conditions. Only addition of HOAc to this system promotes monomerization of I. Thus, HOAc turns to be an important ingredient in this bridge-splitting process.

We have found that the acetato-analog of I, di-μ-acetato-bis[N,N-dimethylbenzylamine-2C,N] dipalladium(II) (VI) also reacts with LiCl under the same conditions as I to form III. The identity of products, obtained from I and VI, was confirmed on the basis of their electronic and IR spectra.

The behaviour of the monomeric complex chloro-(N,N-dimethylbenzylamine-2C,N)(triphenylphosphine)palladium(II) (II), differs markedly from that of complex I in this system. Heating of the solution of II in HOAc–C_6H_6 (1:1) mixture in the presence of an equimolar quantity of LiCl for 10 min at 80 °C results in precipitation of an orange-red material. The ^1H NMR spectrum of the compound shows the signals of aromatic protons only. Its far IR spectrum reveals the strong band at 357 cm^{-1}, assigned to *trans* ν(Cl–Pd–Cl), and two weaker bands at 332 and 257 cm^{-1}, involving bridging Pd–Cl bonds in the binuclear Pd_2Cl_2 unit*. These findings together with analytical data support structure IV for this orange-red material, obtained from II. The reaction of IV with PPh_3 in MeOH to form the well-characterized *trans*-$Pd(PPh_3)_2Cl_2$ gives additional evidence to the structure proposed. Besides, IV was synthesized independently according to ref. [14]. The spectral (UV–VIS and IR) characteristics of both compounds were identical within experimental error, indicative of the identity of the substances.

Consider some aspects of the interaction of I (III) and II with LiCl. Bridge-splitting reaction of I to give III is not, of course, unique. Depolymerization of dimers $Li_2Pd_2Cl_6$ in the presence of LiCl in HOAc solution was studied by Henry [15]. We wish to point out that isolation of III in high yield (85%), when LiCl was in excess with respect to I, implies that under these conditions the primary product of interaction between I and LiCl, complex III, does not react further with LiCl. This is confirmed also by independent experiments. Contrary to the monomeric compound III, the other monomeric compound II undergoes protonolysis, resulting in dissociation of N,N-dimethylbenzylamine ligand. It seems reasonable that the dramatic change in reactivity of II towards LiCl compared with that of I or III is due to the presence of the phosphine ligand in the coordination sphere of the former. The strong *trans*-effect of this ligand [16] could weaken the Pd–N bond significantly, providing substitution of N donor atom for chloride with dechelation of N,N-dimethylbenzylamine ligand. Then, the Pd–C bond, being no more stabilized by chelation, could be cleaved by an HOAc molecule. So, the probable mechanism of this reaction can be represented as follows. Here S = a solvent molecule, N͡CH = N,N-dimethylbenzylamine, and L = PPh_3. Obviously, there is no such weakening of the Pd–N bond in complexes I or II; so, the Pd–N bond cannot be ruptured by chloride, chelation is retained and no protonolysis occurs.



Scheme

Experimental

The UV–VIS spectra were recorded on a Hitachi-356 spectrophotometer. The IR spectra were recorded on a Pye Unicam SP 2000 spectrophotometer in KBr pellets (4000–400 cm^{-1}) or in polyethylene discs (400–200 cm^{-1}). The ^1H NMR spectra were obtained on a Tesla (100 MHz) spectrometer using deuteriodimethylsulphoxide as the solvent with TMS as internal standard.

Cyclopalladated compounds I [5] and II [9] were prepared by published methods. Complex IV was independently obtained according to ref. [15].

The Reaction of Complex I with LiCl

To a solution of I (0.34 g, 0.61 mmol) in 20 ml of benzene was added a solution of LiCl (0.08 g, 1.96 mmol) in 20 ml of HOAc. The mixture was thermostatted at 70 °C for 90 min. The precipitated brown

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*Analysis of far IR spectral data was based on refs. 6 and 9 and the literature cited therein.

complex III was filtered off, washed with cold HOAc and C_6H_6, and dried *in vacuo*. Yield 85%. The UV–VIS spectrum of III (HOAc):λ(max) = 450 nm, ϵ(max) = 158 M^{-1} cm^{-1}; IR: 320 and 290 cm^{-1} (*cis*-$PdCl_2$); ^1H NMR (δ, p.p.m.): 7.36–7.56 (m, 4 aromatic protons), 4.30 (s, 2 methylene protons), 2.75 (s, 6 methyl protons). M.p. 91–93 °C. *Anal.*: Found: C, 33.37; H, 4.24; N, 4.11%. Calcd. for $C_9H_{12}NPdCl_2Li$: C, 33.92; H, 3.77; N, 4.40%. Complex III is soluble in water, acetone, HOAc, and DMSO, but insoluble in benzene and chloroform.

The Reaction of Complex II with LiCl

A solution of II (0.543 g, 1.01 mmol) and LiCl (0.042 g, 1.01 mmol) in HOAc was thermostatted at 80 °C for 10 min. The precipitated orange-red complex IV was filtered off, washed with HOAc and dried over NaOH. Yield 86%. The UV–VIS spectrum of IV (EtOH): λ(max) = 276 nm, ϵ(max) = 683 M^{-1} cm^{-1}; IR: 357 cm^{-1} (*trans*-$PdCl_2$), 332 and 257 cm^{-1} (two bridging Pd–Cl); ^1H NMR (δ, ppm) 7.89–8.16 (m, aromatic protons). M.p. 240–255 °C dec., lit. 250 °C dec. [17]. *Anal.*: Found: C, 51.36; H, 3.66; P, 7.06; N, 0.00%. Calcd. for $C_{18}H_{15}PPdCl_2$: C, 49.20; H, 3.41; P, 7.06%. The UV–VIS and IR spectra of IV were consistent with those of an authentic sample.

The Reaction of Complex IV with PPh_3

The suspended IV (0.05 g, 0.057 mmol) in methanol solution of PPh_3 (0.034 g, 0.13 mmol) was refluxed for 90 min. The yellow complex *trans*-$Pd(PPh_3)_2Cl_2$ formed was isolated in 72% yield. M.p. dec. 248–268 °C, lit. 250–270 °C dec. [17]. The IR spectrum of the compound was identical with that reported in [17].

Acknowledgements

We wish to thank Dr. A. N. Kurskii for recording IR spectra and Dr. V. A. Polyakov for recording NMR spectra.

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