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The Chemical Behaviour of Biacetyl Bis (N-Methyl. N-phenyl)Osazone Coordinated to Pd^{II}

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The ligand biacetyl-bis-(N-methyl, -N-phenyl)-osazone (L) coordinated to palladium(II) to form the complex [$PdLCl_2$] undergoes hydrogen chloride elimination to give a monomer [Pd(L-H)Cl], containing a carbon-palladium covalent bond. The chemical properties of the two complexes are compared and discussed.

Introduction

In a previous paper[1], we investigated the coordination of some osazones to palladium(II). It was shown that, on using as ligands the osazones 1,2-cyclohexanedione-bis-phenylhydrazone and biacetyl-bis-phenylhydrazone which contain N-H groups, the simple adducts [$PdLCl_2$] can be prepared and characterized, and also that they undergo HCl elimination to form dimers of the type Pd(L-H)Cl_2, which are Pd^{II} complexes containing, Pd-N amido bonds.

We were therefore surprised to find, in further experiments, that the ligand biacetyl-bis-(N-methyl, N-phenyl)osazone, which does not contain an NH group, can also undergo hydrogen chloride elimination.

In this paper, we report the preparation and characterisation of the simple adduct of biacetyl-bis(N-methyl, N-phenyl) osazone $PdCl_2$ and of the product derived from it, and discuss the general chemical behaviour of these species[2].

Experimental Section

The starting palladium(II) complex trans–[Pd-$(C_6H_5CN)_2Cl_2$] was prepared accordingto the method of Karasch et al.[3] Biacetyl-bis-(N-methyl, N-phenyl) osazones (L) was prepared, according to the method reported in the literature[4], by adding a methanolic solution of N-methyl, N-phenyl -hydrazine (3.225 gr. 21,5 m.mole) to a methanolic solution of biacetyl (1.164 gr. 1.075 m.mole) in the presence of some drops of acetic acid. The resulting solution was refluxed for about 1h. On cooling, a yellow powder was obtained.

It was washed with petroleum ether and crystallized from CH_2Cl_2/hexane.

Its purity was established by T.L.C. on silica gel.

Preparation of cis–[Pd(L)(Cl)$_2$]. To a solution of L(4.48 m.mole) dissolved in 100 ml of CH_2Cl_2 1,72 gr (4.48 m.mole) of trans-[$Pd(C_5H_5CN)_2Cl_2$] dissolved in 150-ml of CH_2Cl_2 was added dropwise. The solution was stirred for about 1h. The dark ppt. obtained was filtered off, washed with CH_2Cl_2 and dried in vacum. (C calc. 45.85 found 45.75; H calc. 4.67 found 4.45; N calc. 11.88 found 12.10; Cl calc. 15.07 found 15.35).

Preparation of [Pd(L-H)Cl]. A mixture of 0.600 gr. 127 m.mole) of cis[Pd(L)Cl_2] and 200 gr. of SiO_2 (0.05 – 0,2 mm) in 150-ml of CH_2Cl_2 was stirred at room temperature for two days. After addition of 50-ml of CH_2Cl_2, the dark red mixture obtained, was passed down a silica gel column with $CHCl_3$ eluant. The dark red fraction was collected and recrystallized from CH_2Cl_2/cyclohexane. Dark red crystals of [Pd-(L-HCl] were obtained. (C calc. 49.65 found 49.50; H calc. 4.82 found 5.00; N. calc. 12.87 found 12.65; Cl calc. 8.16 found 8.30).

Reaction of cis[PdL(Cl)$_2$] with P(C_6H_5)$_3$. An excess of $P(C_6H_5)_3$ (0.042 gr) was added to 0.037 gr. of *cis*-[$PdL(Cl)_2$] in 200 ml of benzene. The mixture was stirred for 36h. It was also refluxed for 1h. The solvent was distilled off and the residue dissolved in $CHCl_3$. By chromatography on SiO_2, using $CHCl_3$ as eluant, the ligand L. and the complex trans[$Pd(Ph_3P)_2$-Cl_2] were obtained in an almost quantitative yeld.

Reaction of Pd(L-H)Cl with LiA1D$_4$ (or LiAH$_4$). Small portions of $LiA1D_4$ were added to 0.730 gr. of Pd(L-H)Cl (167 m.mole) in 10 ml of anhydrous tetrahydrofuran, under stirring, at room temperature, until the dark red colour of the suspension dissappeared. The mixture was filtered and D_2O was added to the solution.

The tetrahydrofuran solution was dried and concentred. It was then chromatographed on SiO_2 (eluant cyclohexane/ethylacetate 90/10) and the deuterated ligand (in the case of $LiA1D_4$) was obtained.

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(1) L. Caglioti, L. Cattalini, M. Ghedini, F. Gasparrini and P.A. Vigato, *J. Chem. Soc.*, Dalton 514 (1972).
(2) G. Bombieri, L. Caglioti, L. Cattalini, E. Forsellini, F. Gasparrini R. Graziani and P.A. Vigato, *Chem. Comm.*, 1415 (1971).
(3) M.S. Karasch, R.C. Seyler and F.R. Mayo. *J. Amer. Chem. Soc.*, *60*, 882 (1938).

Reaction of Pd(L-H)Cl with KCN. 0.7187 gr. of KCN in 20 ml of H_2O were added to 0.46gr. (10.66 m.mole) of Pd(L-H)Cl suspended in a mixture of 40 ml of diethyl-ether and 40 ml of CH_2Cl_2 (ratio complex/KCN = 1/10).

The suspension was refluxed for 48h, then extracted by CH_2Cl_2 and the extracts, dried over anhydrous Na_2SO_4, were chromatographed on SiO_2, eluant cyclohexane/ethyl-acetate (1/1). The principal products were N-methyl, N-phenyl-hydrazone and biacetyl-N-methyl, N-phenyl-hydrazine, identified by chromatography.

N.B. Biacetyl, N-methyl, N-phenyl hidrazine was completely changed into Biacetyl bis N-methyl, N-phenyl hydrazone by N-methyl, N-phenyl hydrazine.

Reaction of [Pd(L-H)Cl] with $(Bu_4N)Br$. An excess of Bu_4NBr was added to 0.730 gr. (1.67 m.mole) of Pd(L-H)Cl in 50 ml. of methylene chloride. The mixture was stirred for 20 h. The solvent was distilled and the residue was dissolved in acetone. From the solution Pd(L-H)Br was obtained in a quantitative yield.

Physico-chemical measurements. The infrared spectra of Nujol or hexachloro-butadiene mulls or KBr pellets of the free ligand and complexes in the range 4000–200 cm^{-1} were recorded with a Perkin-Elmer 621 spectrophotometer and in the range 400-100 cm^{-1} with a Beckmann I.R. 11. ^{1}H.n.m.r. spectra were obtained with a Jeol HL 60 with DMSO-d_6 or pyridine -d_5 as solvent and TMS as internal standard.

Molecular Weight was determined by a Hewlett-Packard 302 B Vapour Pressure Osmometer Chromatographic data were recorded with a Hewlett-Packard Research Chromatograph, on using A.P.L. column (1m. long and with celite as support). N_2 was used as carried with a 50 ml/m flow. The column was thermostated at 120°C.

Results and Discussion

The first species which has been isolated by reacting the ligand (L) with *trans*-$[Pd(C_6H_5CN)_2Cl_2)]$ is the simple adduct *cis*-$[PdLCl_2]$ complex A) which is formed according to the reaction

$$L + trans\text{—}[Pd(C_6H_5CN)_2Cl_2] \longrightarrow cis\text{—}[PdLCl_2] + 2C_6H_5CN$$

This formulation is in agreement with the analytical results as well as wit hthe I.R. and ^{1}H.n.m.r. data and the reaction corresponds exactly to those of other osazones at the same Pd^{II} substrate.

The infrared spectrum shows the two characteristic absorption bands (327, 315 cm^{-1}) corresponding to the antisymmetric and symmetric Pd-Cl stretching vibrations in a cis structure.

The ^{1}H.n.m.r. (data in Table), obtained in DMSO-d_6 indicate the equivalence of the phenyl groups as well as of the CH_3-N and CH_3-C sites in the coordinated ligand. In addition, by reacting the complex with Ph_3P(excess) in CH_2Cl_2, the complex *trans*-$[Pd(PPh_3)_2Cl_2]$ is formed and the free osazones recovered in almost quantitative yield.

On reacting the complex $[Pd(L)Cl_2]$ under the appropriate experimental condition, HCl elimination is observed and a new complex formed.

The structure of this compound (complex B) has determined by X-ray diffraction[2] and corresponds to the formulation reported in figure 2.

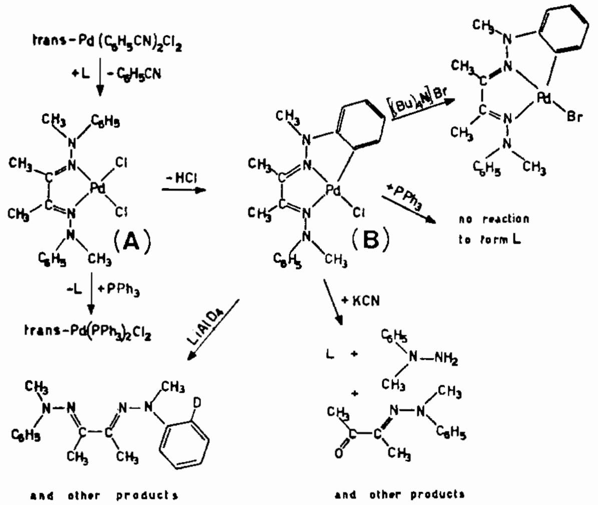

Figure 1.

This formulation is obviously in agreement with the physico chemical data relating to complex (B). The infrared spectrum shows only one absorption band in the region of the Pd-Cl stretching vibrations; this band is shifted, as expected, to 226 cm^{-1}, when the chloride is replaced, by way of metathetical exchange, (see experimental), by bromide.

The ^{1}H.n.m.r. data relating to compound B, measured both in DMSO-d_6 and pyridine-d_5, clearly indicate, (see Table), the presence of only 9 aromatic hydrogens, and the non equivalence of the methyl groups bonded to carbon atoms and of those bonded to the nitrogen atoms. The analytical data correspond to the proposed formulation (see experimental) and the molecular weight clearly indicates the presence of monomeric species (calc. 434.16 found 406).

As far as the bond lengths determined by the X-ray investigation are concerned, we can mention, as a significant feature, that the Pd-N bond *trans* to the Pd-C bond is longer (2.11 Å) than the Pd-N bond *cis* to the Pd-C bond (2.00 Å). This fact can be easily related to a ground-state trans effect of the type already observed in Pt^{II} and in gold(III) chemistry[6]. Biacetyl-bis-(N-methyl, N-phenyl) osazone reacts with trans-$[Pd(PhCN)_2Cl_2]$ to form the simple 1:1 adduct corresponding to complex A but does not undergos HCl elimination.

This strong tendency of the complexes of osazones with Pd(II), to undergo HCl elimination seems remarkable to us. In the case reported in this paper,

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(5) A.C. Cope and R.M. Sickman. *J. Amer Chem. Soc. 87*, 3272 (1965).

(6) F. Basolo and R.G. Pearson. Mechanism of Inorganic Reactions, Edit. J. Wiley and sons N.Y. pag. 351 (1967).

Table I. ^{1}H n.m.r. data of Pd^{II} complexes with biacetyl-bis-(N methyl, N-phenyl)osazone.

Complex	Aromatic	N-CH$_3$	CH$_3$-C=N	Solvent
Pd(L)Cl$_2$	6.8-7.5^m(10H)	3.32^s(6H)	2.3^s (6H)	DMSO-d$_6$
Pd(L-H)Cl	6.2-7.5^m(9H)	3.18^s(3H)	2.18^s(3H)	DMSO-d$_6$
		3.30^s(3H)	2.34^s(3H)	
Pd(L-H)Cl		3.15^s(3H)	2.10^s(3H)	py-d$_5$
		3.32^s(3H)	2.20^s(3H)	

m = multiplet; s = singlet; (xH) = number of H; standard TMS.

a Pd-C bond is formed and this is not uncommon in Pd^{II} chemistry [5]. However comparing these data with those of the previous work obtained under the some experimental conditions, it seems interesting that the formation of a Pd-N bond when this is possible, seems be preferred to the formation of a Pd-C bond. The chemical behaviour of complex B differs markedly from that of complex A and could be of interest from a number of points of view.

By reacting complex B with Ph$_3$P an unidentified product. which still contains the original osazone ligand firmly attached to the Pd atom by Pd-C bond, is obtained.

The reduction of complex B with LiAlD$_4$ in THF leads to the recovery from the reaction mixture of the free ligand, deuterated in the ortho-position of one of the phenyl groups; this also agrees with the formulation proposed above.

The reaction of complex B with KCN leads to the formation of Pd(CN)$_4^{2-}$ together with the free ligand L and other organic products such as N-methyl, N--phenyl-hydrazine and the N-methyl, N-phenyl hydrazone.

It seems resonable to assume that free ligand is formed by reaction of these two species. The second one could be of interest in providing a synthetic pathway for the production of asymmetric osazones.