Metal-catalysed Ring Opening. Reactions of 2-Amino-thiazole and -thiazoline with Palladium(II) and Platinum(II)

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Summary $[PtCl_4]^{2-}$ and $[Pd_2Cl_6]^{2-}$ ions condense in basic media with an amino-substituted thiazoline or thiazole to give complexes in which ring opening has been induced by C–S bond cleavage.

To date there have been few reports of the selective cleavage in basic media of sulphur–carbon bonds in sulphur-containing heterocycles by reaction with a transition metal ion.[1] We describe here the synthesis of complexes of Pt^{II} and Pd^{II} with 2-amino-thiazoline (NH_2th) and -thiazole (NH_2tz) where the ligands undergo an intramolecular rearrangement.

The amine α-substituent (pK_a 4·6) has a basicity weakened by the presence of the cyclic nitrogen (pK_a 3·5). At low pH, the ring nitrogen is the first to be deprotonated, followed by the amine at higher pH. The ligands thus presumably bind only through N(3) in acidic media, whereas in basic media co-ordination through the amine N(α) will be preferred.

In the presence of $[PtCl_4]^{2-}$ or $[Pd_2Cl_6]^{2-}$ and a base (1M OH^-) green $[(ML'Cl_2)_2]$ (M = Pt or Pd), or orange-brown, $[PdL'_2Cl_2]$, complexes (*ca.* 60% yield) were obtained from NH_2th and NH_2tz where L′ indicates the cleaved ligands ($SHCH_2CH_2NHCN$ or SHCHCHNHCN). Dimeric complexes were always obtained with platinum, the ligand being co-ordinated both through N(α) and N(3) and bridging two Pt atoms, whereas in the palladium complexes the ligands were either N(α) mono- or N(α),N(3)-bridged di-co-ordinated.

The occurrence of ring cleavage is supported by the i.r. data for the products; the 4000—400 cm^{-1} region showed new strong absorption bands at 2200—2100 cm^{-1}, this range being characteristic of a nitrile or carbodi-imide vibration.

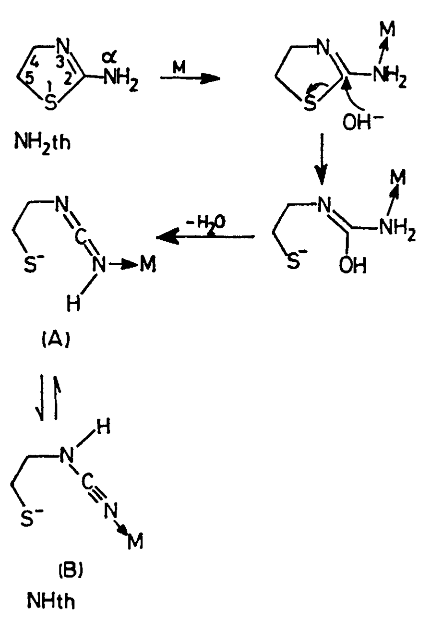
Whether mono- or bridged di-co-ordination occurs is clear from comparison of the ν(N–H) frequencies; the N–H stretching vibration is at 3195 cm^{-1} in the $[\{ML'Cl_2\}_2]$ complexes while it is shifted to 3295 cm^{-1} in the analogous $[PdL'_2Cl_2]$ compounds, where one of the nitrogen atoms is not co-ordinated.

Further supporting evidence for ring opening is provided by the ^1H n.m.r. spectra [$(CD_3)_2SO$; Me_4Si; Bruker WH-90]. $[Pd(NHth)_2Cl_2]$ for instance, shows signals at δ 1·00 (t, SH) and 3·10 br (CH_2). An SH resonance was not observed in the initial cyclic ligand NH_2th, since sulphur is included in the heterocycle, whereas the CH_2 resonances of the cleaved ligand NHth are considerably shielded in comparison with the initial form NH_2th (δ 3·80 br) because of the disappearance of the cyclic conformation.

In the case of NH_2th, the cleaved ligand was displaced from the metal complex by reaction (1). The products were recrystallised and identified by i.r. and ^1H n.m.r. spectroscopy. $[PdCl_2(PEt_3)]$ shows signals at δ 1·2 (1:4:6:4:1 quintet, Me) and 1·9 (m, CH_2), which confirms the *trans*-configuration of this complex and thus of $[Pd(NHth)_2Cl_2]$.[2] In its free state NHth is in the nitrile form [$\nu(C{\equiv}N^1)$ 2295, $\nu(C{-}N^3)$ 1260 cm^{-1}].

$$trans\text{-}[Pd(NHth)_2Cl_2] + 2PEt_3 \xrightarrow{CH_2\,Cl_2} trans\text{-}[Pd(PEt_3)_2Cl_2] + 2NHth \qquad (1)$$

In ethanolic KOH, ring opening of the thiazoline appears to be induced by the combined presence of OH^- and metal ions (Scheme). We presume the process is initiated by initial co-ordination of the amine, since the solution is basic, followed by nucleophilic attack of OH^- on C(2) and concerted cleavage of the C–S bond.[3] The final α-elimination of H_2O has been proposed since this is the only path leading to a carbodi-imide (A) or nitrile (B) function. A similar loss of water, in the α-position to nitrogen bound to a metal, has been recently observed by Evans *et al.*[4] with a hexa-ammine Ru^{III} salt. The resultant cyanamide (or carbodi-imide) appears furthermore to be stabilised by its co-ordination to the metal[4,5] (when alone in basic media, it is readily hydrolysed).



SCHEME

The presence of Pt or Pd appeared to be necessary, since no C–S bond cleavage was observed for NH_2th or NH_2tz alone in basic media. Similar heterocyclic C–S cleavages have indeed been observed in thiazoles,[6] but they were performed under more drastic conditions (Na–liq. NH_3).

In work with analogous α-mercapto or α-methyl substituted ligands, we observed no cleavage reaction.[7] It thus appears necessary to have a primary amine as the α-substituent to induce the ring opening.

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