

Preliminary communication

Asymmetric synthesis of complexed cyclic N,O-Acetals by use of platinum(II) complexes. Crystal structure of *trans*-[PtCl₂(C₂H₄)(2-*p*-NO₂C₆H₄CHNH(CH₂)₃O)]

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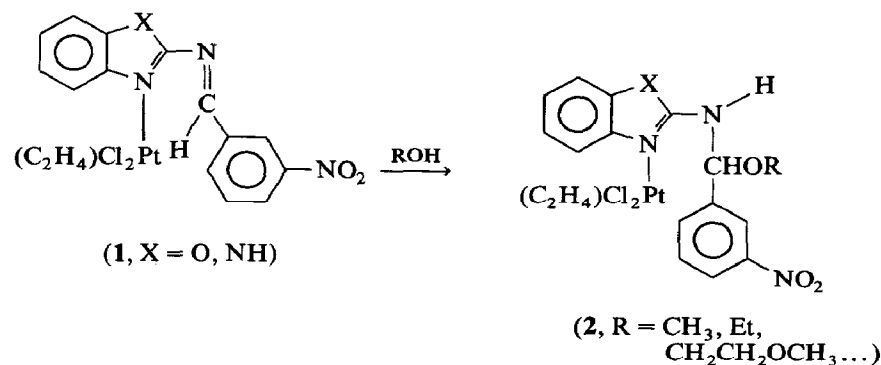
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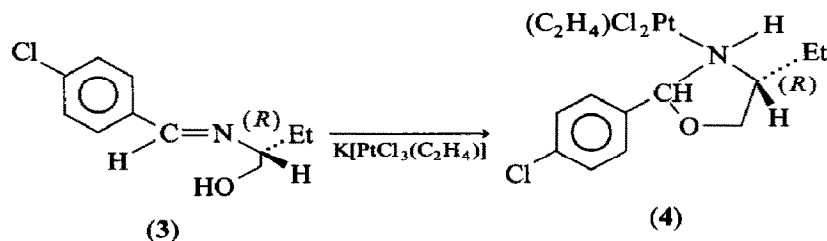
Abstract

Optically active *p*-ClC₆H₄CH=NCH(Et)CH₂OH(R) cyclizes in the presence of Zeise's salt to afford one diastereomer of the complexed oxazolidine *p*-ClC₆H₄-CHNHCH(Et)CH₂O in high chemical yield. The analogous cyclization of *p*-NO₂-C₆H₄CH=NCH₂CH₂OH affords *trans*-PtCl₂(C₂H₄)(*p*-NO₂C₆H₄CHNHCH₂CH₂O) whose crystal structure has been determined.

The synthesis of optically active substrates in high enantiomeric excess continues to attract much interest [1]. Specifically, N,O-acetals are useful precursors in the preparation of optically active secondary or tertiary benzylic amines with > 95% enantiomeric excess [2a]. However, these compounds are not always very stable, and tetrahedral α -aminoethers can be short-lived intermediates [2b]. We have recently shown that the complexes **1** react with alcohols to give α -aminoethers, **2** [3]. These

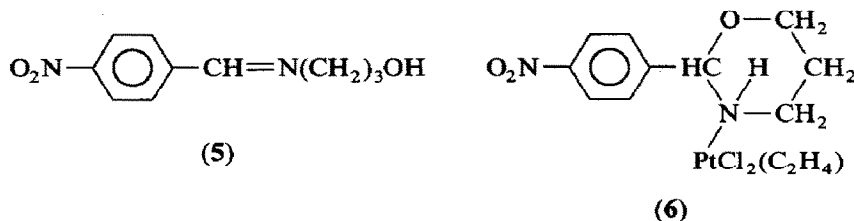


complexed ligands show surprising resistance to hydrolysis when compared with the uncoordinated compounds. As the aldimine carbon-bearing the aryl group is prochiral, we decided to look at a related reaction in which the alcohol function was part of an optically active fragment. Since the substrates **1** are rather specific, we chose to examine the metal assisted cyclisation of **3** (derived from the aldehyde and (*R*)-2-amino-1-butanol), and found that this reaction proceeds in high yield to afford a single diastereomer [**4***]. This is a rare example of a high yield



stereospecific metal-assisted ring closure. In the absence of the metal compound **3** does not cyclize, and the analogous (*S*) isomer on treatment with Zeise's salt also gives a single diastereomer. Overhauser studies are now in progress to determine the relative stereochemistry at the new chiral center. The oxazoline **4** is readily recognized in solution from the ^1H and ^{13}C NMR data. The signal from the imine proton of **3** at δ ca. 8.11 disappears and is replaced by signal at 5.85 ppm. Similarly, in the ^{13}C spectrum, the imine carbon signal at δ 160.9 is replaced by a new signal at 93.1 ppm.

To extend the potential of this cyclization chemistry we carried out the reaction with **5**, and found it to give the six-membered ring species **6**. Crystals of **6**, suitable



for diffraction studies [**5***] were grown from CH_2Cl_2 /hexane solution and an ORTEP view of the molecule is shown in Fig. 1. In agreement with indications from the IR data on the basis of the Pt-Cl stretching frequencies and symmetry considerations, the complex is seen to have a *trans* geometry, with the ethylene, two halogens and heterocyclic moiety as the four ligand components of this slightly distorted square planar Pt^{II} complex. The bond lengths and bond angles within the coordination sphere are normal for this type of complex [3,6], and some of the relevant values are shown in the caption to Fig. 1.

We have carried out a number of additional reactions and find that: (i) this type of cyclization can be accomplished with various phosphine complexes, and (ii) the reaction is most successful when there are electron-withdrawing groups on the aromatic ring, in keeping with the view that the imine carbon has an enhanced

* Reference number with asterisk indicates a note in the list of references.

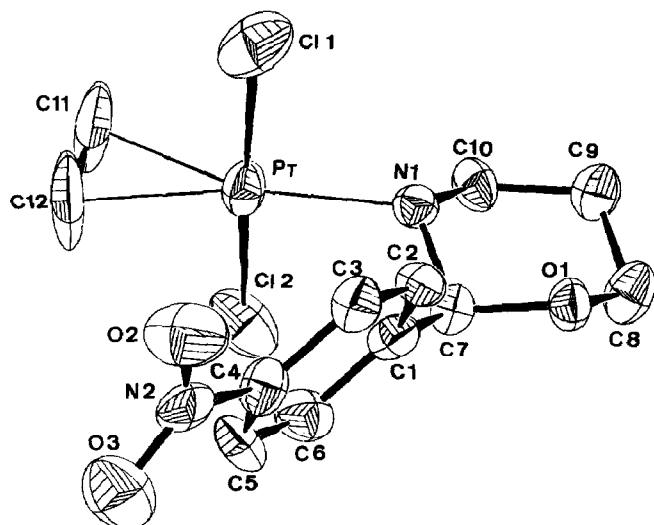


Fig. 1. An ORTEP view of **6**. Relevant bond distances (Å) and angles (°) are: Pt–Cl(1) 2.293(4), Pt–Cl(2) 2.301(3), Pt–N(1) 2.107(6), Pt–C(11) 2.19(1), Pt–C(12) 2.15(2), N(1)–C(7) 1.48(1), O(1)–C(7) 1.42(1), Cl(1)–Pt–Cl(2) 177.0(1), Cl(1)–Pt–N(1) 91.0(2), Cl(2)–Pt–N(2) 86.0(2), Cl(1)–Pt–(11) 91.3(5), Cl(2)–Pt–C(12) 93.7(6), Cl(1)–Pt–N(1)–C(7) –62.2(5), N(1)–C(7)–C(1)–C(2) 103.7(9), Cl(1)–Pt–C(11)–C(12) 87.1(8).

electrophilicity when coordinated to platinum. Reports of these and further studies will be presented separately.

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References

- 1 R. Noyori, *Chimia*, 42 (1988) 215; B. Weidmann and D. Seebach, *Angew. Chem. Int. Ed. Engl.*, 22 (1983) 31; K.B. Sharpless, S.S. Woodward and M.G. Finn, *Pure & Appl. chem.*, 55 (1983) 1823.
- 2 A. L. Neelakantan, *J. Org. Chem.*, 36 (1971) 2256; *ibid.*, 2261; (b) M. Cocivera, C.A. Fyfe, A. Effio, S.P. Vaish and H.E. Chen, *J. Am. Chem. Soc.*, 98 (1976) 1573.
- 3 A. Albinati, C. Arz and P.S. Pregosin, *Inorg. Chem.*, 27 (1988) 2015.
- 4 2-(4-Chlorophenyl)-5-ethyloxazolidine (57.4 mg, 0.27 mmol) was added to a solution of $K[PtCl_3(C_2H_4)]$ (100 mg, 0.27 mmol) in 20 ml CH_2Cl_2 and the solution was stirred for 1 h. Filtration followed by removal of the solvent under vacuum gave the crude product, which was recrystallized from CH_2Cl_2 /hexane; yield: 120 mg (89%).
- 5 The crystals are monoclinic, space group $P2_1/n$; $Z = 4$, a 12.602(2) Å, b 9.855(1) Å, c 13.786(2) Å, β 114.15(1)°; V 1562.4 Å³, ρ_{calc} 2.130 g cm⁻³. 3056 independent reflections were collected using a NONIUS CAD4 diffractometer in the range $2.4 \leq \theta \leq 26.0$ (graphite monochromated Mo- K_α radiation). Data were corrected for Lorentz and Polarization and for absorption (using ψ scans of 5 reflections at high $\chi \geq 85.0$). 2539 reflections (with $F_o \geq 2\sigma(F_o)$) were considered as observed and used in the subsequent analysis. The structure was solved by Patterson and Fourier methods and refined by block-diagonal least squares using anisotropic temperature factors to the present R factor of 0.038 (for the observed reflections). A table of atom coordinates and a complete list of bond lengths and angles will be deposited at the Cambridge Crystallographic Data Centre.
- 6 N.B. Pahor, M. Calligaris, P. Delise, L. Randaccio, L. Maresca and G. Natile, *Inorg. Chim. Acta*, 19 (1976) 45; R.A. Love, T.F. Koetzle, G.J.B. Williams, L.C. Andrews and R. Bau, *Inorg. Chem.*, 14 (1975) 2653.