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Preliminary communication

Asymmetric synthesis of complexed cyclic N,O-Acetals by use of platinum(II) complexes. Crystal structure of *trans*-$[PtCl_2(C_2H_4)(2\text{-}p\text{-}NO_2C_6H_4\overline{CHNH(CH_2)_3O})]$

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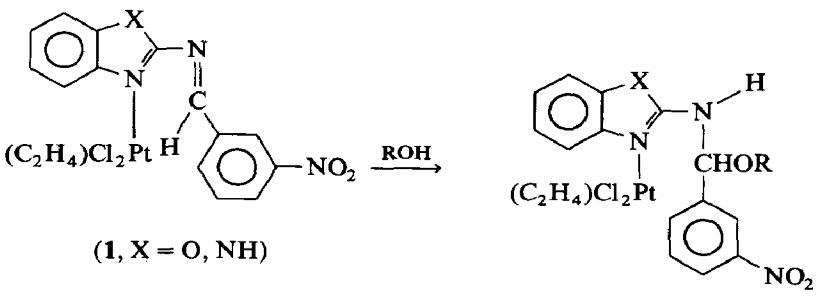
Abstract

Optically active $p\text{-}ClC_6H_4CH{=}NCH(Et)CH_2OH(R)$ cyclizes in the presence of Zeise's salt to afford one diastereomer of the complexed oxazolidine $p\text{-}ClC_6H_4\text{-}\overline{CHNHCH(Et)CH_2O})$ in high chemical yield. The analogous cyclization of $p\text{-}NO_2\text{-}C_6H_4CH{=}NCH_2CH_2OH$ affords *trans*- $PtCl_2(C_2H_4)(p\text{-}NO_2C_6H_4\overline{CHNHCH_2\text{-}CH_2O})$ 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



(**1**, X = O, NH)

(**2**, R = CH_3, Et, $CH_2CH_2OCH_3$...)

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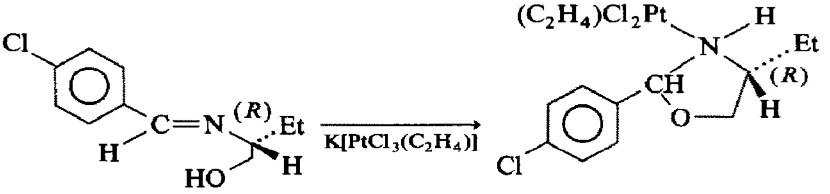
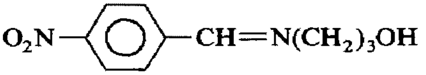
complexed ligands show surprising resistance to hydrolysis when compared with the uncoordinated compounds. As the aldimine carbon-bearing the aryl group is prochiral, we decided to look at a related reaction in which the alcohol function was part of an optically active fragment. Since the substrates **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 ^{1}H 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.



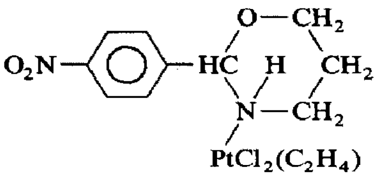
(3)

(4)

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.



(5)



(6)

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

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

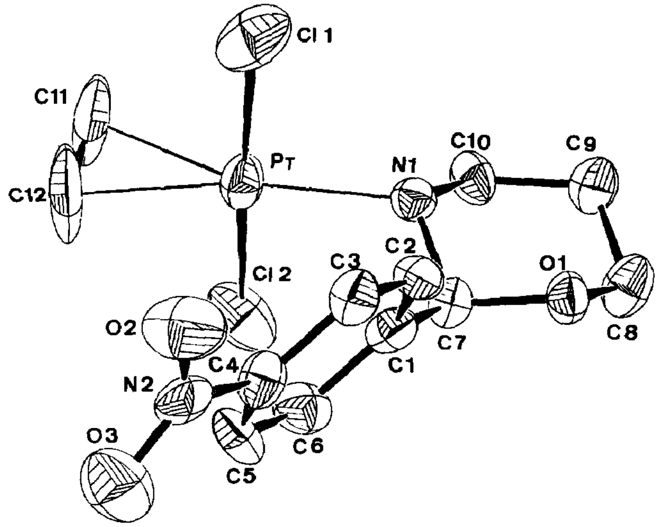

Fig. 1. An ORTEP view of **6**. Relevant bond distances (Å) and angles (°) are: Pt–Cl(1) 2.293(4), Pt–Cl(2) 2.301(3), Pt–N(1) 2.107(6), Pt–C(11) 2.19(1), Pt–C(12) 2.15(2), N(1)–C(7) 1.48(1), O(1)–C(7) 1.42 (1), Cl(1)–Pt–Cl(2) 177.0(1), Cl(1)–Pt–N(1) 91.0(2), Cl(2)–Pt–N(2) 86.0(2), Cl(1)–Pt–(11) 91.3(5), 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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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 Å^3, ρ_{calc} 2.130 g cm^{-3}. 3056 independent reflections were collected using a NONIUS CAD4 diffractometer in the range $2.4 \leqslant \theta \leqslant 26.0$ (graphite monochromated Mo-K_α radiation). Data were corrected for Lorentz and Polarization and for absorption (using ψ scans of 5 reflections at high $\chi \geqslant 85.0$). 2539 reflections (with $F_o \geqslant 2\sigma(F_o)$) 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.

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