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Preliminary communication

Diastereoisomeric (η^6-arene)ruthenium(II) chiral Schiff base complexes: crystal structure of a triphenylphosphine adduct

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Abstract

Reaction of $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}(\text{L}^\star)]$ with AgClO_4 in Me_2CO gives a perchlorate complex which on subsequent treatment with PPh_3, γ-picoline or Cl^- yields adducts showing that there can be retention as well as inversion of configuration at the metal centre. The $(R)_{\text{Ru}},(S)_{\text{C}}$ absolute configurations of the chiral centres in the triphenylphosphine adduct have been established by an X-ray diffraction study [$\text{HL}^\star$, (*S*)-α-methylbenzylsalicylaldimine]. The CD spectral study reveals that there is an inversion of configuration during formation of the PPh_3 adduct.

Current interest [1–5] in the chemistry of chiral half-sandwich transition-metal complexes is directed towards understanding the mechanistic aspects of chemo- and stereo-selective reactions that are mediated by electron-deficient pyramidal intermediates. Although chiral cyclopentadienyl complexes have been the subject of extensive studies [1–4], the chemistry of analogous arene complexes is virtually unknown [6]. In this communication we report some preliminary results obtained from a stereochemical investigation carried out with a diastereoisomeric areneruthenium(II) complex, $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}(\text{L}^\star)]$, of a chiral bidentate N,O-donor Schiff base ligand [$\text{HL}^\star$ = (*S*)-α-methylbenzylsalicylaldimine].

Syntheses relevant to this work * are depicted in Scheme 1. The reactions were carried out under dinitrogen atmosphere with a 1 : 1 molar ratio of the reactants. The precursor complex, $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}(\text{L}^\star)]$, is obtained as a mixture of two diastereoisomers (**1**, **1′**) in a 5.7 : 1 molar ratio, as indicated by the ^{1}H NMR spectrum of the mixture. This mixture reacts with AgClO_4 in acetone at 0 °C to give

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* Analytical data [C,H,N found (calc.)]: **1**, 59.7 (60.6), 5.9 (5.7), 3.0 (2.8); **2**, 53.3 (53.7), 5.2 (5.0), 3.2 (2.5); **3**, 57.6 (57.5), 5.0 (4.6), 1.7 (1.5); **4**, 57.1 (57.1), 5.7 (5.4), 4.5 (4.3). Selected ^{1}H NMR data (δ, ppm) for **1** (in CDCl_3, 200 MHz): {$\text{C(CH}_3)_2$, 0.99 (d); 1.14 (d)}; {*p*-CH_3, 2.11(s)}; **1′**: {$\text{C(CH}_3)_2$, 1.17(d); 1.22(d)}; {*p*-CH_3, 2.16(s)}; **2** (in acetone-d_6): {$\text{C(CH}_3)_2$, 1.10(d); 1.13(d)}; {*p*-CCH_3, 2.10(s)}; **3′** (in CDCl_3): {$\text{C(CH}_3)_2$, 0.85(d); 1.07(d); {*p*-CCH_3, 1.59(s)}; **3**: {$\text{C(CH}_3)_2$, 1.12(d); 1.18(d)}; {*p*-CCH_3, 1.71(s)}; **4** (in CDCl_3): {$\text{C(CH}_3)_2$, 0.82(d); 1.04(d)}; {(*p*-CH_3, 1.79(s)}; **4′**: {$\text{C(CH}_3)_2$, 1.06(t)}; {(*p*-CH_3, 1.83(s)} (s = singlet, d = doublet, t = triplet, J(H–H) = 7 Hz).

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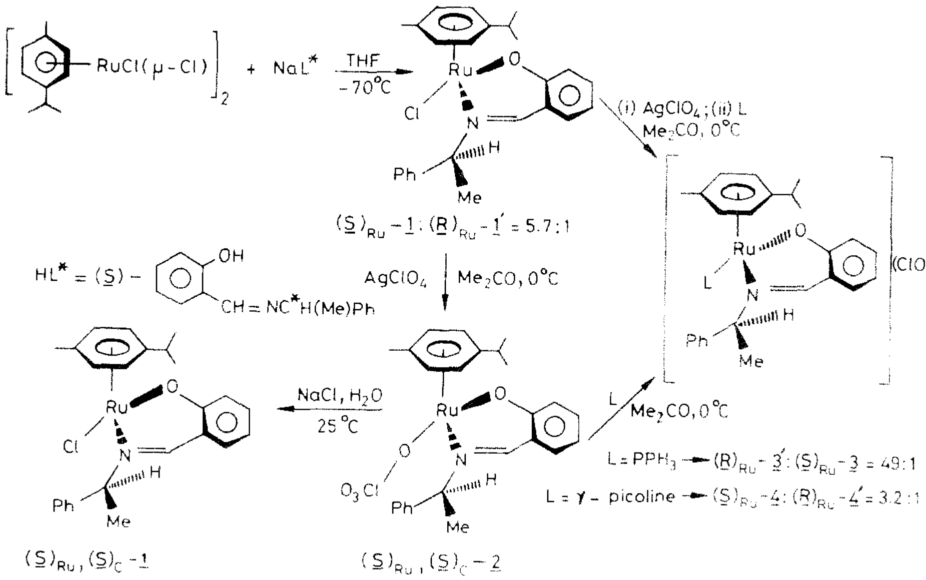

Scheme 1.

a yellow coloured solution, from which a pyrophoric (*caution*!) solid **2** was isolated in ~ 70% yield.

Reaction of PPh_3 with **2** in acetone gives essentially pure diastereoisomeric PPh_3 adduct **3′** (there is a 49 : 1 ratio of **3′** and **3**). Single crystals of **3′**, grown from $CHCl_3$–petroleum ether in presence of NH_4PF_6, belong to the noncentrosymmetric space group *P*1 with two molecules in the unit cell ** (Fig. 1). The absolute configurations of the metal centres are assigned [7] as $(R)_{Ru}$ in accord with the ligand priorities: (η^6-*p*-cymene) > PPh_3 > O[(*S*)-L*] > N[(*S*)-L*]. A comparison of the CD spectral features (Fig. 2) of **1**, **2**, γ-picoline and PPh_3 complexes reveals that there has been an inversion of configuration at the metal centre in the PPh_3 substitutions. Unlike the phosphine adduct, the γ-picoline product, isolated either from an *in situ* reaction of the precursor complex with $AgClO_4$ and γ-picoline or from a reaction of **2** with γ-picoline, is a mixture of two diastereoisomers, $(S)_{Ru},(S)_C$-**4** and $(R)_{Ru},(S)_C$-**4′**, in a 3.2 : 1 molar ratio of **4** : **4′**.

** Crystal data: $[C_{43}H_{43}NOPRu](ClO_4, PF_6)_{1/2}\cdot0.75CHCl_3$, $M = 950.8$, triclinic, space group *P*1, $a = 10.852(2)$, $b = 14.028(1)$, $c = 15.950(2)$ Å; $\alpha = 91.51(1)$, $\beta = 105.97(1)$, $\gamma = 106.11(1)^\circ$, $U = 2228(17)$ Å^3, $F(000) = 961$, $Z = 2$, $D_{calc.} = 1.41$ g cm^{-3}. Mo-K_α radiation, $\lambda = 0.7107$ Å, μ(Mo-K_α) = 5.33 cm^{-1}, transmission coeff.: 0.98–1.0. 8258 intensity data were collected at 290 K on an Enraf–Nonius CAD4 diffractometer by the ω–2θ scan method in the range $2 \leq \theta \leq 25^\circ$. Final *R* value = 0.0721, $R_w = 0.0761$ for 7283 independent reflexions $[F_o > 5\sigma(F_o)]$ with 538 parameters and $w = 1.0/[\sigma^2F + 0.005499F^2]$. Absorption correction on the data was made by the method of North et al. [9] after obtaining the complete structural model. The structure was solved by a combination of direct methods and difference Fourier techniques, and refined by full matrix least square analysis using SHELX-76 [10]. A selected number of atoms were refined anisotropically leaving the remaining non-hydrogen atoms at the isotropic stage due to CPU time constraint. The atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, UK.

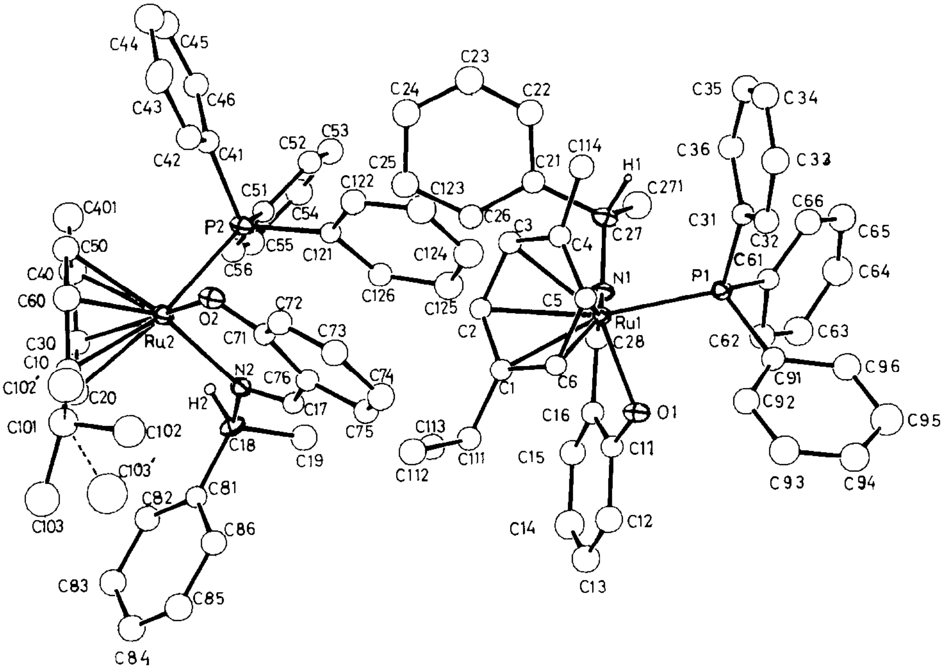

Fig. 1. The molecular structures of two [(η^6-*p*-cymene)Ru(PPh$_3$)L*]$^+$ cations in the unit cell along with the atom labelling scheme. Selected bond lengths (Å) and angles (deg): Ru(1)–C$_0^a$, 1.771; Ru(2)–C$_0^b$, 1.741; Ru(1)–P(1), 2.360(2); Ru(2)–P(2), 2.383(3); Ru(1)–O(1), 2.061(8); Ru(2)–O(2), 2.074(6); Ru(1)–N(1), 2.140(9); Ru(2)–N(2), 2.094(8); C$_0^a$–Ru(1)–O(1), 122.8; C$_0^a$–Ru(1)–N(1), 129.9; C$_0^a$–Ru(1)–P(1), 130.2; C$_0^b$–Ru(2)–P(2), 130.4; C$_0^b$–Ru(2)–O(2), 121.4; C$_0^b$–Ru(2)–N(2), 131.3; P(1)–Ru(1)–N(1), 89.6(2); P(2)–Ru(2)–N(2), 88.4(3); P(1)–Ru(1)–O(1), 82.6(2); P(2)–Ru(2)–O(2), 80.6(3); O(1)–Ru(1)–N(1), 86.0(3); O(2)–Ru(2)—N(2), 88.6(3); [C$_0^a$ and C$_0^b$ are the centroids of the *p*-cymene ring of molecules A and B].

The mechanistic aspects of the substitution reactions were investigated after the isolation of the intermediate species, **2**. The IR spectrum of **2** displays two intense bands at 1095 and 1056 cm^{-1} (compare the appearance of one band, at 1092 cm^{-1}, for **3′**), indicating the presence of a weakly coordinating perchlorate anion [8]. The ^{1}H NMR spectra of **2** in $(CD_3)_2CO$ and $CDCl_3$ do not show the presence of any coordinated ligands such as Me_2CO or H_2O in **2**. The molar conductance of 131 Ω^{-1} cm^2 mol^{-1} for **2** in acetone corresponds to a 1 : 1 electrolyte. This also indicates that there is only weak perchlorate coordination in **2** in the solid state. The participation of **2** in the substitution reactions is reflected in the isolation of a pure diastereoisomeric product $(S)_{Ru},(S)_C$-**1** from the reaction of **2** with NaCl in an aqueous medium. Organotransition-metal chiral half-sandwich complexes of weakly coordinating, anionic ligands are known [1–4] to play a role as intermediates in the substitution reactions through a 16-electron, pyramidal, chiral intermediate. Brunner has shown [2] that the pyramidal intermediates have sizable inversion barriers, and accordingly the adduct formation with donor ligands occurs with retention of configuration at the metal centre. The reactions of **1** or **2** with γ-picoline, PPh$_3$ and Cl$^-$ are of significance, since both retention and inversion of configuration are observed in these substitution reactions, which are believed to be mediated by an

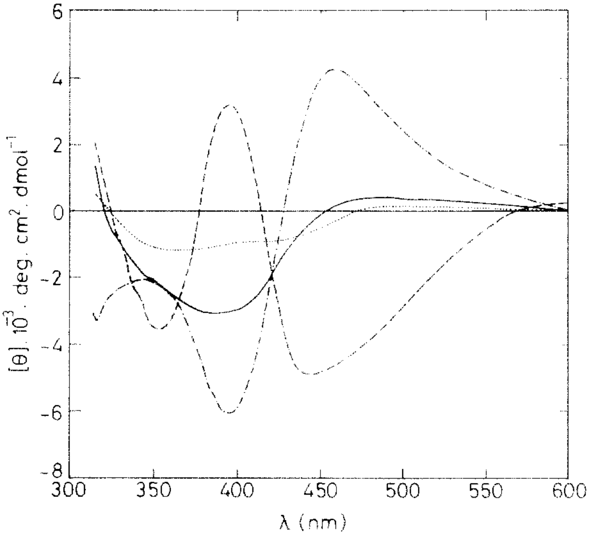

Fig. 2. CD spectra of the complexes **1** (dotted line), **2** (full line), **3′** (dashed line), and **4** (dashed-dotted line) in acetone.

electron-deficient chiral intermediate with a low energy barrier for inversion. Further studies directed towards X-ray structural characterization of **1** and **2** and the use of **2** in organic synthesis are in progress.

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