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Preliminary communication

CHIRAL η^6-C_6H_6 RUTHENIUM COMPLEXES

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Summary

The complexes $[\eta^6\text{-}C_6H_6RuCl(H_2NCHRCO_2)]$ (R = H, Me) are prepared by treating $[\eta^6\text{-}C_6H_6RuCl_2]_2$ with the corresponding amino acid anion in methanol. Although the coordinated chloride is readily substituted by water in both cases, giving the species $[\eta^6\text{-}C_6H_6Ru(H_2O)(H_2NCHRCO_2)]^+$, ^1H and ^{13}C NMR spectroscopy readily distinguish between the diastereomers of the alanato complex (R = Me). Thus epimerization at the ruthenium is a relatively slow process.

One of the more interesting developments in organotransition metal chemistry in recent years is the successful resolution of a variety of pseudotetrahedral η^5-cyclopentadienyl complexes in which the centre of chirality is a metal ion [1]. As a result, a variety of mechanistic studies of reactions involving possible stereochemical changes at metal have been made feasible [1,2].

Although chiral pseudotetrahedral η^6-arenemetal complexes should also, in principle, be accessible, to date only the complexes η^6-arene $CrL_1L_2L_3$(L_n = various combinations of CO, CS and a number of tertiary phosphine donors) have actually been reported [3]. We [4] and others [5,6] have previously shown that a wide variety of derivatives of the complex $[\eta^6\text{-}C_6H_6RuCl_2]_2$ (I) can be prepared. We now find that I reacts readily with amino acid anions, such as glycinate and alanate, with substitution of one chloride ion to form pseudotetrahedral complexes in which the ruthenium ion is chiral (IIa, IIb and their corresponding enantiomers).

Treatment of a suspension of I in a minimum of methanol with an equivalent amount of potassium glycinate at room temperature resulted in the gradual disappearance of the reddish-brown crystals of I and precipitation of greenish-yellow crystals of $[\eta^6\text{-}C_6H_6RuCl(NH_2CH_2CO_2)]$ (IIa). The IR spectrum of the compound exhibits ν(CO) at 1590 cm^{-1} [7], ν(RuCl) at 282 cm^{-1} [4] (Nujol mulls): The ^1H NMR spectrum (D_2O solution, DSS* internal reference) exhibits sharp η^6-C_6H_6 resonances at δ 5.90 (strong) and 5.78 (weak) ppm, and a

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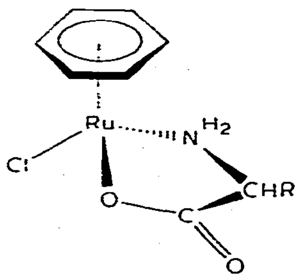
*DSS = sodium 2,2-dimethyl-2-silapentane-5-sulphonate.



(IIa) R = H
(IIb) R = Me

rather broad CH_2 resonance at $\sim\delta$ 3.1 ppm. The high-field arene resonance gains intensity at the expense of the low-field resonance in the presence of excess chloride ion, suggesting that the chloride of IIa can be substituted by water and that the benzene resonance at δ 5.90 ppm is to be attributed to the complex $[\eta^6\text{-}C_6H_6Ru(D_2O)(H_2NCH_2CO_2)]Cl$, that at δ 5.78 ppm to $[\eta^6\text{-}C_6H_6RuCl(H_2NCH_2CO_2)]$. Similar solvation reactions of I have been noted previously [4,5]. The ^{13}C NMR spectrum (D_2O solution, 5-fold excess of LiCl added to suppress aquation) exhibits singlets at 84.3 and 46.6 ppm downfield from the methyl resonance of DSS, attributable to the benzene and methylene carbon resonances, respectively. The carboxylato carbon could not be detected, presumably because T_1 is long for carbons of this type, with no protons attached, and saturation occurs readily [8]. Although no precedents appear to be available for ^{13}C chemical shifts of arenes coordinated to metals in positive oxidation states, we note that the arene ^{13}C chemical shift noted here lies almost midway between those of $\eta^6\text{-}C_6H_6Cr(CO)_3$ [9] and $(\eta^6\text{-}C_6H_6)_2Cr$ [10]. ^{13}C chemical shifts for amino acid complexes also seem scarce, but the glycinate methylene resonance is approximately 4.4 ppm downfield from the corresponding chemical shift of the free acid in neutral aqueous solution [11], consistent with bidentate coordination [12].

The yellow alanato complex, IIb, can be prepared in a similar manner from racemic alanate and has a very similar IR spectrum to that of IIa, i.e. ν(CO) 1620 cm^{-1}, ν(RuCl) 278 cm^{-1}. As well as η^6-benzene resonances in its ^1H NMR spectrum at δ 6.03 (strong) and 5.94 (medium) ppm, the former of which disappears in the presence of excess chloride ion, there are also two methyl doublets at δ 1.51 (strong) and 1.44 (medium) ppm. The doublet structures arise from spin—spin coupling (J 7.0 Hz) with the methyne proton, the resonance of which was not observed, either because it is broad or perhaps it lies under the residual HDO resonance.

The relative proportions of the two methyl doublets are not dependent on the concentration of free chloride, and thus they must be attributed to the presence of the two diastereomerically related pairs of enantiomers, *RR*, *SS* and *RS*, *SR** (Fig. 1) as has been observed for diastereomeric alanatoplatinum

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*The convention employed for specification of chirality at the metal is outlined by Stanley and Baird [13].

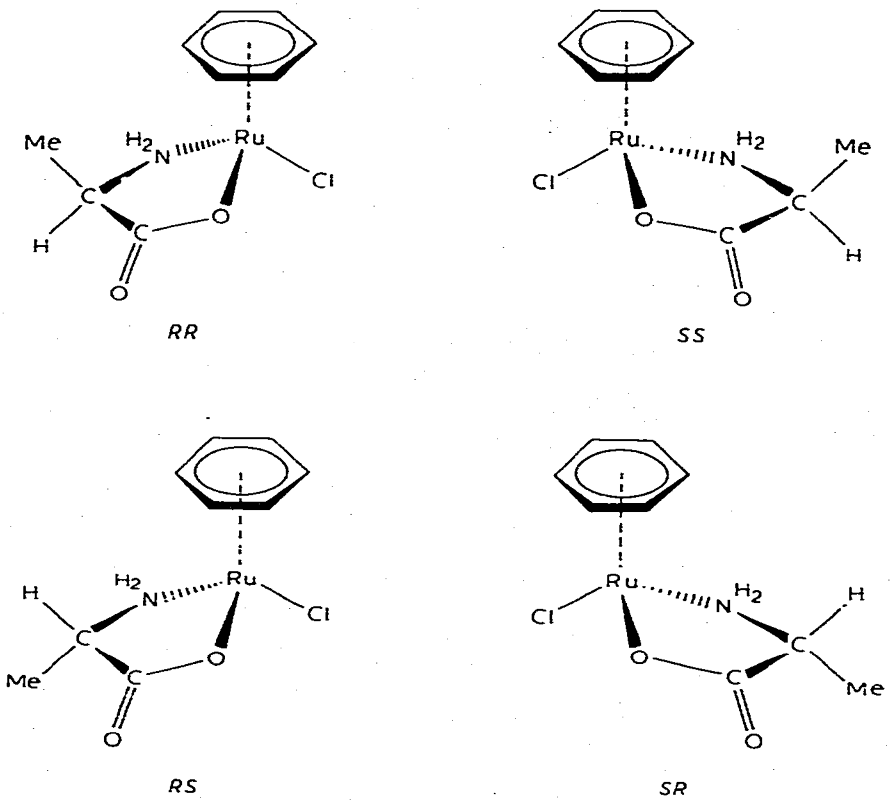

Fig. 1. Stereoisomers of η^6-$C_6H_6RuCl(H_2NCHMeCO_2)$.

complexes [14]. The ^{13}C NMR spectrum of IIb (D_2O, 5-fold excess of LiCl) is consistent with this interpretation, exhibiting two η^6-C_6H_6 carbon resonances at 84.8 (medium) ppm and 84.1 (strong) ppm, two methyne carbon resonances at 55.8 (medium) ppm and 53.5 (strong) ppm, a methyl carbon resonance at 20.6 ppm and, in this case, a carboxylato carbon resonance at 189.1 ppm. The methyne and carboxylate resonances are approximately 3.5 and 12.6 ppm downfield from the corresponding chemical shifts of the free acid in neutral aqueous solution [11], again consistent with bidentate coordination [12]. Space-filling molecular models suggest that the more stable diastereomer would be the *RS*, *SR* pair of enantiomers, in which the methyl group is pointing away from the aromatic ring. The slightly greater shielding of the methyl proton resonance of the less stable diastereomer may then be a result of ring current effects [15].

Although we have not yet succeeded in actually resolving the alanato complex, our results show that epimerization at the ruthenium is at the very least slow on the NMR time scale. Thus resolution experiments with this type of complex, employing commerically available *l*-amino acids, may well prove feasible.

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