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# Optically active pseudoctahedral rhodium(III), iridium(III), and ruthenium(II) complexes with $\alpha$-amino acidato ligands. Crystal structures of $R_{\mathrm{Ir}}S_{\mathrm{C}}S_{\mathrm{N}}$- and $S_{\mathrm{Ir}}S_{\mathrm{C}}S_{\mathrm{N}}$-$[(C_5Me_5)Ir(pro)Cl] \cdot \frac{1}{2}H_2O$ (Hpro = L-Proline)

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## Abstract

The synthesis and characterization of optically active amino acidato complexes of the types $[(C_5Me_5)M(aa)Cl]$, $[(p\text{-cymene})Ru(aa)Cl]$, $[(C_5Me_5)M(aa)(PPh_3)]BF_4$, and $[(p\text{-cymene})Ru(aa)(PPh_3)]BF_4$ (M = Rh, Ir; Haa = L-alanine, L-proline), in which the metal is a chiral centre, are reported. The cationic species were prepared via the solvato-complexes $[(C_5Me_5)M(aa)(MeOH)]^+$ and $[(p\text{-cymene})Ru(aa)(MeOH)]^+$, which epimerize rapidly on the $^1H$ NMR time scale. The crystal structure of the complex $[(C_5Me_5)Ir(pro)Cl]$ is reported; the asymmetric unit contains two independent molecules differing in the configuration at the metal.

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Organometallic compounds containing a chiral metal centre have attracted considerable interest in recent years because they offer the possibility of highly enantioselective catalytic or stoichiometric transformations [1–4]. As ligands amino acids are of interest because of their biological importance and the variety of metal coordination modes they can display [5].

We have shown that acetylacetonate complexes react with ligands containing acidic protons by displacement of acetylacetone and coordination of the resulting anionic ligands [6–9]. We report here the use of this reaction in the preparation of amino acidato complexes of rhodium(III), iridium(III) and ruthenium(II) with chiral metal centres. The related ruthenium complexes $[(C_6H_6)Ru(aa)Cl]$ (Haa = glycine, adenine) were reported by Dersnah and Baird [10]. Very recently Sheldrick and

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Heeb have reported the synthesis and structural characterization of $\eta^6$-benzene-ruthenium(II) complexes of $\alpha$-amino acids [11,12].

The acetylacetonate complexes $[(C_5Me_5)M(acac)Cl]$ (M = Rh, Ir) [13] reacted in methanol with stoichiometric amounts of the $\alpha$-amino acids L-alanine (Hala) and L-proline (Hpro) to give the neutral complexes $[(C_5Me_5)M(aa)Cl]$ [M = Rh, aa = ala (I), pro (II); M = Ir, aa = ala (III), pro (IV)] in almost quantitative yield. The related *p*-cymene-ruthenium complexes [(*p*-cymene)Ru(aa)Cl] [aa = ala (V), pro (VI)] can be similarly prepared starting from [(*p*-cymene)Ru(acac)Cl] [14] and the corresponding amino acid *.

The spectroscopic data are consistent with the usual coordination of the $\alpha$-amino acidato anions through the carboxy oxygen and the amino group forming five-membered rings [5,15].

The alaninato complexes were prepared as 50/50 (I, III) and 68/32 (V) mixtures of diastereomers as indicated by the $^1$H NMR spectra of the crude reaction mixtures. The room-temperature $^1$H NMR spectra, in $CDCl_3$, of crude reaction mixtures of the prolinato compounds II, IV and VI show the presence of only two diastereomers in 95/5, 95/5 and 90/10 ratios, respectively. The spectra remain essentially unchanged down to $-60\,^\circ$C. Work-up of the reaction mixtures gave analytically pure powders with identical diastereomer ratios. Epimerization does not occur for these chloride complexes, the diastereomeric composition remaining unchanged during three days in $CDCl_3$ solution at room temperature.

Monocrystals of the iridium prolinato complex $[(C_5Me_5)Ir(pro)Cl]$ (IV) were grown by slow diffusion of acetone into a chloroform solution of the compound. Its structure was determined by an X-ray diffraction study **. The most striking feature of the structure was the presence of two independent molecules in the asymmetric unit, differing in the configuration at the metal: $R_{Ir}S_CS_N$ for molecule A and $S_{Ir}S_CS_N$ for molecule B ***. A perspective view and the numbering scheme for each molecule are presented in Fig. 1. The coordination around the iridium is pseudoctahedral. An $\eta^5$-$C_5Me_5$ group occupies three *fac* coordination positions. One chlorine atom and the prolinato anion coordinated through one oxygen and the nitrogen atom complete the coordination sphere of the metal. The structural parameters are very similar for both independent molecules. The five-membered

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* Satisfactory elemental analyses have been found for all reported complexes.

** Crystal data for IV: $C_{15}H_{23}ClNO_2Ir\cdot\frac{1}{2}H_2O$, $M = 486.03$, orthorhombic, space group $P2_12_12_1$, *a* 9.8131(7), *b* 15.7813(15), $\sigma$ 21.5385(14) Å, *V* 3335.5(5) Å$^3$, $Z = 8$, $D_c$ 1.94 g cm$^{-3}$, F(000) = 1880. $\lambda$ 0.71069 Å, $\mu$(Mo-$K_\alpha$) 81.41 cm$^{-1}$. The intensities of 6680 reflections were collected on a Siemens AED-2 diffractometer ($3 \leqslant 2\theta \leqslant 50\,^\circ$) using the $\overline{\omega}/2\theta$ scan mode and Mo-$K_\alpha$ radiation (graphite monochromator), 5516 reflections with $F_o > 5.0\ \sigma(F_o)$ were used in the refinement. Absorption correction was made based on DIFABS program (minimum–maximum correction factors 0.869–1.216). The structure was solved by Patterson methods; full matrix least-squares refinement of atomic positional and thermal parameters (anisotropic for non-hydrogen atom, except solvent) was carried out. Hydrogens were included in the last cycles of refinement in calculated positions and refined riding on their heavy atoms with two common thermal parameters. Final *R* and $R_w$ values were 0.033 and 0.034. The atomic coordinates and a complete list of bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre.

*** The descriptors *R* and *S* for the metal atom are assigned according to Baird and Sloan's proposals [16,17]. The absolute configuration was determined by refining both enantiomers of each independent molecule. The lower *R* and $R_w$ values were associated with the previously known *S* configuration of the asymmetric carbon atom of L-proline.

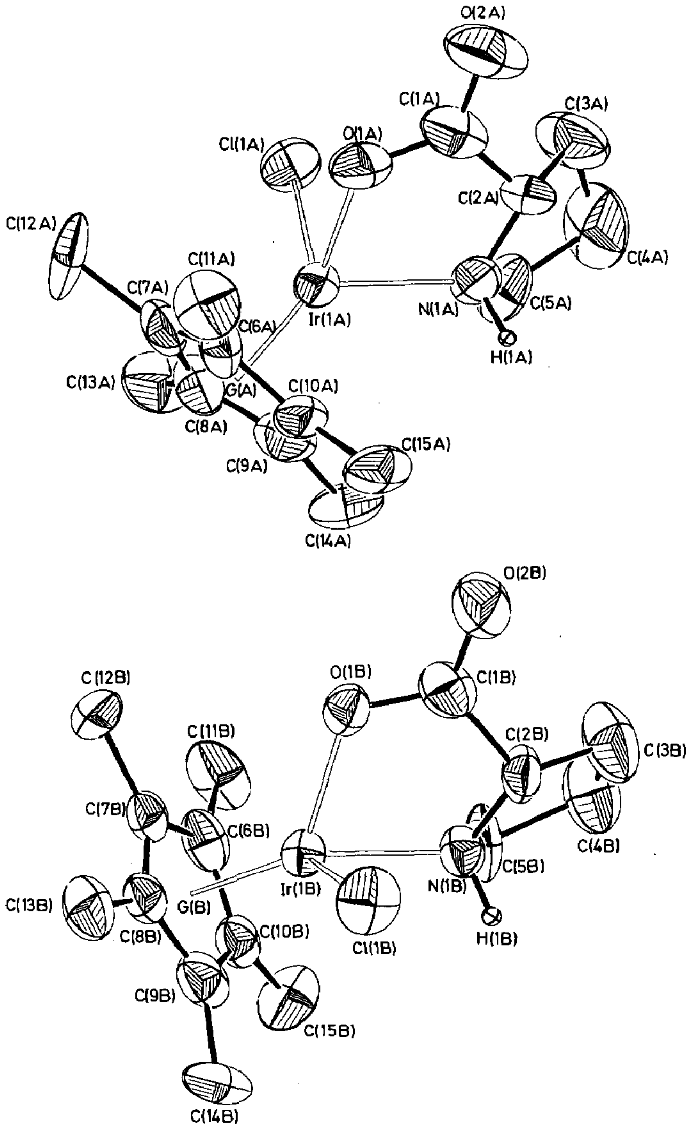

Fig. 1. Ortep of the two independent molecules of complex IV. Selected bond distances and bond angles: Molecule A, Ir(1A)–Cl(1A), 2.409(3); Ir(1A)–O(1A), 2.093(6); Ir(1A)–N(1A), 2.140(8); Ir(1A)–G(A), 1.766(5) Å. Cl(1A)–Ir(1A)–O(1A), 83.2(2), Cl(1A)–Ir(1A)–N(1A), 88.5(2); N(1A)–Ir(1A)–O(1A), 79.1(3)°. Molecule B, Ir(1B)–Cl(1B), 2.421(2); Ir(1B)–O(1B), 2.078(6); Ir(1B)–N(1B), 2.132(7); Ir(1B)–G(B), 1.770(4) Å. Cl(1B)–Ir(1B)–O(1B), 86.6(2); Cl(1B)–Ir(1B)–N(1B), 84.4(2); N(1B)–Ir(1B)–O(1B), 77.3(3)°.

chelate ring deviates significantly from planarity. The iridium atom is 0.2889(4) (molecule A) and 0.5818(3) Å (molecule B) out of the plane defined by the O(1)–C(1)–C(2)–N(1) group. The bond distances within the prolinato ligand are not significantly different from those in the free L-proline [18].

Although the chloride complexes I–VI are non-conducting in chloroform or acetone ($\Lambda_M < 2.0\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$) they conduct moderately in methanol ($\Lambda_M$

Table 1

Diastereomeric compositions of the cationic complexes VII–XII

| Complex | Crude reaction mixture | Isolated |
|---|---|---|
| $[(C_5Me_5)Rh(ala)(PPh_3)]BF_4$ (VII) | 95/5 | 95/5 |
| $[(C_5Me_5)Rh(pro)(PPh_3)]BF_4$ (VIII) | 66/34 | 62/38 |
| $[(C_5Me_5)Ir(ala)(PPh_3)]BF_4$ (IX) [a] | 77/23–37/63 | 81/18–20/80 |
| $[(C_5Me_5)Ir(pro)(PPh_3)]BF_4$ (X) | 72/28 | 65/35 |
| [(*p*-cymene)Ru(ala)($PPH_3$)]$BF_4$ (XI) | 64/36 | 64/36 |
| [(*p*-cymene)Ru(pro)($PPh_3$)]$BF_4$ (XII) | 90/10 | 100/0 |

[a] The diastereomeric composition strongly changes from one preparation to another.

from 3.4 to 16 $\Omega^{-1}$ cm$^2$ mol$^{-1}$) and appreciably in water ($\Lambda_M > 58.9$ $\Omega^{-1}$ cm$^2$ mol$^{-1}$). The NMR spectra in $D_2O$ of the chloride ruthenium complexes V and VI show four sharp resonances at 2.20, 2.22, 2.25 and 2.27 ppm and 2.20, 2.22, 2.26 and 2.28 ppm *, respectively, for the methyl protons of the *p*-cymene ligand (Me-$C_6H_4$-Pr$^i$). In the presence of LiCl in both cases only the signals at 2.20 and 2.22 remain, in 68/32 (complex V) and 90/10 (complex VI) intensity ratios. The conductivity behaviour and the NMR spectra data can be accounted for by assuming the reversible ionization of the chloride ligand [10,12]. Consequently, the addition of $AgBF_4$ to complexes I–VI in methanol leads to the precipitation of AgCl and to the in situ formation of the corresponding solvato-complexes $[(C_5Me_5)M(aa)(MeOH)]^+$ and [(*p*-cymene)Ru(aa)(MeOH)]$^+$. In all cases, their room-temperature $^1$H NMR spectra, in $CD_3OD$, contain only one set of signals. At −90 °C, broadening of all signals was observed. No limiting low temperature spectra were achieved before the solution froze. These data suggest that epimerization at the metal atom takes place and that this process is fast on the $^1$H NMR time scale. Epimerization probably proceeds by dissociation of the weakly coordinated solvent molecule.

Addition of stoichiometric amounts of $PPh_3$ to methanolic solutions of the above-mentioned solvato-complexes affords new cationic compounds of formulae $[(C_5Me_5)M(aa)(PPh_3)]BF_4$ [M = Rh, aa = ala (VII), pro (VIII); M = Ir, aa = ala (IX), pro (X)] and [(*p*-cymene)Ru(aa)($PPh_3$)]$BF_4$ [aa = ala (XI), pro (XII)]. (IR and NMR data support the proposed formulations.) The diastereomeric formation ratios were deduced from the $^{31}$P NMR data of the crude reaction mixtures, and are listed in Table 1. Work-up of the crude products gave the diastereomeric isolated compositions, also listed in Table 1. From these data, it seems that formation of the cationic complexes VII–XII is largely stereospecific. The metal centre is not labile, the diastereomeric composition remaining unchanged after three days in $CDCl_3$ solution at room temperature.

Further work in progress is aimed at isolation of the pure diastereomeric species, establishing their configuration, and studying their reactivity and catalytic activity.

*Note added in proof.* After this manuscript was submitted, a paper describing an alternative route to the L-proline $[(C_5Me_5)M(pro)Cl]$ (M = Rh, Ir) complexes and

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* Sodium 2,2-dimethyl-2-silapentane-5-sulphonate was used as external reference.

the crystal structure of the iridium derivative appeared: R. Krämer, K. Polborn, H. Wanjek, I. Zahn and W. Beck, Chem. Ber., 123 (1990) 767.

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