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Chiral Iridium(III) α-Amino Acidato Complexes (R_{Ir},S_N,S_C)- and (S_{Ir},S_N,S_C)-[(η^5-C_5Me_5)Ir(L-prolinate)(C≡C-CMe_3)]

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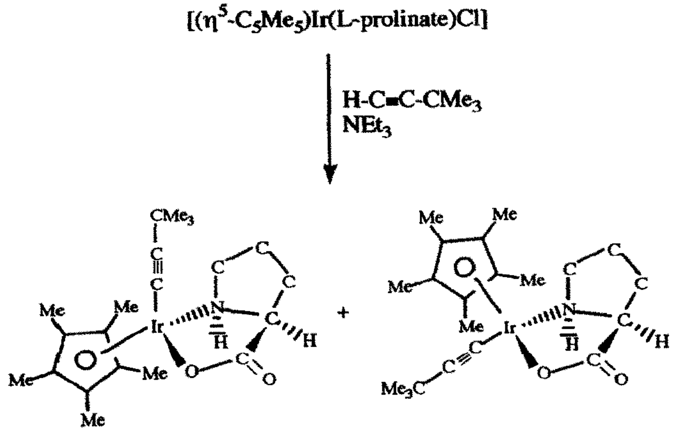
Abstract: Diastereomers (S_{Ir},S_N,S_C)- and (R_{Ir},S_N,S_C)-[(η^5-C_5Me_5)Ir(L-prolinate)(C≡C-CMe_3)] have been prepared and the structure of the later determined by X-ray diffraction methods.

We have recently reported the synthesis and characterization of optically active amino acidato complexes of the types [(η^5-C_5Me_5)M(aa)Cl] and [(η^5-C_5Me_5)M(aa)(PPh_3)]BF_4 (aa=L-amino acidate, M=Rh, Ir) in which the metal is a chiral centre.[1] In view of the synthetic potential (*e.g.* asymmetric synthesis and catalysis) of chiral organotransition metal templates[2-5] we are interested in the synthesis of these types of complexes in homochiral form. Here we report the successful preparation of the pseudoctahedral complex [(η^5-C_5Me_5)Ir(L-prolinate)(C≡C-CMe_3)] (2) and the crystal structure of its thermodynamically more stable diastereomer (R_{Ir},S_N,S_C)-[(η^5-C_5Me_5)Ir(L-prolinate)(C≡C-CMe_3)] (2a).[6]

Complex [(η^5-C_5Me_5)Ir(L-prolinate)Cl] (1) (molar ratio R_{Ir},S_N,S_C/S_{Ir},S_N,S_C = 95/5)[1] reacts in methanol with stoichiometric amounts of NEt_3 and H-C≡C-CMe_3 to give a mixture of the two diastereomers (R_{Ir},S_N,S_C)- and (S_{Ir},S_N,S_C)-[(η^5-C_5Me_5)Ir(L-prolinate)(C≡C-CMe_3)] (**2a**) and (**2a'**), respectively (Scheme 1). The more insoluble complex **2a'** $[\alpha]_{589}$ -4 (*c* 0.4, $CHCl_3$) was isolated by precipitation with diethyl ether (yield 50 %). Next, a methanolic solution of **2a'** was kept at room temperature. Epimerization occurred over course of 24 h to give pure the thermodynamically more stable **2a** diastereomer $[\alpha]_{589}$ +31 (*c* 0.4, $CHCl_3$). Complexes **2a** and **2a'** have been characterized by analytical and spectroscopic means. In particular, both diastereomers present the same $\nu(C\equiv C)$ vibration at *ca.* 2115 cm^{-1} (nujol) and differ significantly in their ^1H NMR data.[7] As expected, for epimers that differ in the configuration at metal,[2,3] the complexes **2a** and **2a'** exhibit circular dichroism spectra that are roughly mirror images above 300 nm (Figure 1).

Scheme 1



(R_{Ir},S_N,S_C)-**2a** (S_{Ir},S_N,S_C)-**2a'**

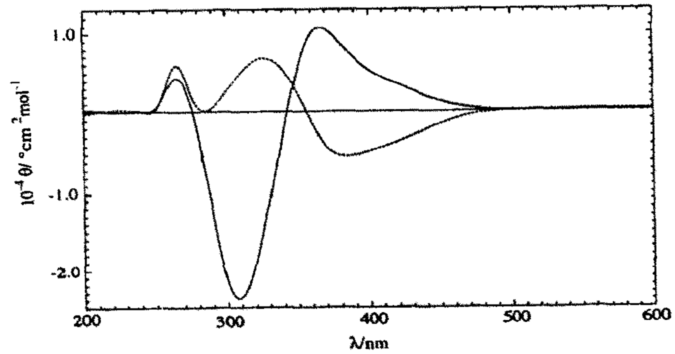


Figure 1. CD spectra of complexes **2a** (full line) and **2a'** (dashed line) in chloroform.

Single crystals of complex (R_{Ir},S_N,S_C)-**2a** were grown by slow diffusion of hexane into a chloroform solution and its structure was determined by an X-ray diffraction study[8] (Figure 2). The coordination around the iridium is pseudoctahedral. An η^5-C_5Me_5 group occupies three *fac* coordination positions. One *tert*-butylacetylide group and the prolinate anion coordinated through one oxygen and the nitrogen atom complete the coordination sphere of the metal that displays an R absolute configuration. Structural parameters of C_5Me_5 and prolinate anions are similar to those found[1] in the related complex **1**. It is crystallographically well documented that in chelate N,O prolinate complexes the nitrogen atom adopts the same absolute configuration as the asymmetric carbon.[1,9] This experimental fact, most probably due to steric reasons, permit us to assign to the less stable diastereomer **2a'** the S_{Ir},S_N,S_C configuration.

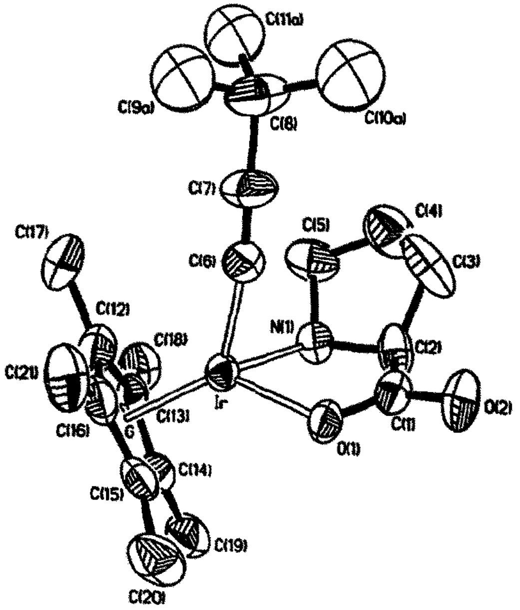


Figure 2. Molecular structure of complex (R_{Ir},S_N,S_C)-**2a**. Selected bond distances (Å) and angles (°) are as follows: Ir-O(1) 2.105(5), Ir-N(1) 2.135(6), Ir-C(6) 2.012(8), Ir-G(centroid η^5-C_5Me_5) 1.813(3), C(6)-C(7) 1.204(13), C(7)-C(8) 1.486(14); O(1)-Ir-N(1) 78.3(2), O(1)-Ir-C(6) 85.6(3), O(1)-Ir-G 131.8(2), N(1)-Ir-C(6) 87.8(3), N(1)-Ir-G 131.6(2), C(6)-Ir-G 125.2(3), Ir-C(6)-C(7) 172.0(8), C(6)-C(7)-C(8) 179.0(10).

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7. ^{1}H NMR (δ, $CDCl_3$) **2a**: 1.70 (15H, s, C_5Me_5), 1.16 (9H, s, CMe_3), 4.21 (1H, m, N*H*), 4.10 (1H, m, C**H*), 3.41, 2.79 (2H, m, NCH_2), 2.26-1.80 (4H, m, CH_2-CH_2). **2a'**: 1.69 (15H, s, C_5Me_5), 1.17 (9H, s, CMe_3), 5.24 (1H, m, N*H*), 3.86, 3.22, 2.44, 2.13, 1.94 (7H, m, CH_2-CH_2-CH_2-C**H*).
8. Crystal data: (R_{Ir},S_N,S_C)-**2a**, $C_{21}H_{32}IrNO_2$, M = 522.71, orthorhombic, space group $P2_12_12_1$, a = 9.5178(10), b = 12.3851(16), c = 18.5850(17) Å, U = 2190.8(4) Å^3, Z = 4, D_c = 1.585 g cm^{-3}, $F(000)$= 1032, μ(Mo K_α) = 60.83 cm^{-1}, λ = 0.71069 Å. An orange prismatic block, 0.612 x 0.621 x 0.618 mm, was used to collect intensities for 4633 reflections with $3 \leq 2\theta \leq 52°$ in a Siemens-Stoe diffractometer. An empirical absorption correction was applied. 4031 unique reflections with $F_o \leq 4.0\ \sigma(F_o)$ were used in the refinement. The structure was solved by Patterson, and ΔF synthesis. The *tert*-butyl group was observed disordered in two positions (atoms C(9), C(10) and C(11)). All non-disordered non-hydrogen atoms were anisotropically refined. The quirality of the molecule has been checked using Rogers method (η = 1.03(3)). Final agreement factors were R = 0.0345 and R_W = 0.0375. Full details of the crystal structure analysis have been deposited at the Cambridge Crystallographic Data Centre.
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