Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Organometallic Chemistry 691 (2006) 2270–2276
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Iridium(III) hydrido amino acid compounds: Chiral complexes and a helical extended lattice

Christopher P. Roy, Lisa A. Huff, Nick A. Barker, Michael A.G. Berg, Joseph S. Merola *

Department of Chemistry, Virginia Polytechnic Institute and State University, 107 Davidson Hall, Mail Stop 0212, Blacksburg, VA 24061-0212, United States

Received 2 October 2005; received in revised form 14 November 2005; accepted 14 November 2005
Available online 22 December 2005

Abstract

[Ir(COD)(PMe_3)$_3$]Cl, **1**, reacts with amino acids in water to yield cationic hydride amino acid complexes, [Ir(aa)(H)(PMe_3)$_3$]Cl, **2**. In general, complexes **2** display octahedral geometry with a meridional arrangement of the PMe_3 ligands, with the amino acid chelating through O and N and with hydride *trans* to N. Disubstituted amino acids on the other hand favor the formation of octahedral complexes with a facial arrangement of PMe_3 ligands. The crystal structure of the valine complex, **2c**, was obtained and, in addition to confirming the structure of the complex, showed a helical extended lattice structure due to intermolecular N–H–O bonding.

Keywords: Iridium; Amino acid complex; Hydride; Helical lattice

1. Introduction

Metals play an important role in biological systems. It is well known that the first row transition elements are involved in a variety of biochemical reaction pathways, but second and third row transition metals are rarely found in bioinorganic systems in nature. In fact, the heavier metallic elements are traditionally known for their toxic effect on many organisms. Interest in the interaction of platinum metals with biological molecules began with the discovery that certain platinum complexes exhibit anticancer activity [1]. A wide variety of Pt-amino acid complexes have been made as a result of this work [2–6]. Ruthenium amino acid complexes have also been studied as potential antitumor compounds [7]. Amino acid complexes of other transition metals may be of interest for new therapies.

Research involving the interaction of amino acids and transition metals has also found non-biological uses. Ruthenium and osmium complexes have been studied as catalysts in hydrolysis [8–11]. A series of complexes of the type [RuCl(aa)(H)(PPh_3)$_2$] were prepared by Saito et al. [12] and were studied for use as homogeneous catalysts [13–15].

It is surprising that so many studies on platinum and ruthenium with amino acids have been performed while almost none exist with the remaining platinum metals. Beck and co-workers have published a long series of papers on "Metal Complexes with Biological Ligands" with many of the later papers dealing with various modes of complexation of amino acids to many different metals, including iridium [16,17]. A DNA binding complex of amino acids with pentamethylcyclopentadienyl fragments has also been reported [18]. To our knowledge, the complexes characterized in this study are the first examples of iridium amino acid hydride complexes.

Our interest in Ir(III) amino acid complexes was initially based on their potential use as asymmetric catalysts. It was our goal to develop water soluble catalysts that can be used for hydrogenation as well as other organic transformations. We have previously demonstrated that [Ir(COD)(PMe_3)$_3$]Cl (**1**) will undergo oxidative addition reactions with a number of bonds including H–H [19], B–H [20], C–H [21,22], N–H [23], and O–H [24]. Preliminary studies

* Corresponding author. Tel.: +1 540 231 4510; fax: +1 540 231 3255.
E-mail address: jmerola@vt.edu (J.S. Merola).

0022-328X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2005.11.028

of the oxidative addition of amino acids to the complex **1** have focused on the possible binding modes of the amino acid to the iridium center.

2. Experimental

2.1. General methods

All reactions were performed in an inert atmosphere of purified nitrogen. Standard glassware and Schlenk line techniques were used. All amino acids were used as received without further purification. $[Ir(COD)(PMe_3)_3]Cl$ (**1**) was synthesized by a known procedure [25]. All other chemicals were reagent grade and used without further purification. The proton and carbon NMR spectra were obtained on a Bruker WP270SY or WP200SY instrument. The ^{31}P NMR spectra were obtained on a Bruker WP200SY instrument operating at 81 MHz and referenced using an internal standard of 85% H_3PO_4. All elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA. X-ray crystal structures were obtained using a Siemens R3m/v diffractometer and Mo Kα ($\lambda = 0.71071$ Å) radiation at 303 K.

2.2. Synthesis of [Ir(aa)(H)(PMe$_3$)$_3$]Cl, general procedure

A 100 mL reaction flask equipped with a stir bar and septum, was charged with the amino acid (1.0 mmol) and $[Ir(COD)(PMe_3)_3]Cl$ (0.5 mmol) under inert atmosphere in a drybox. The flask was connected to a double manifold Schlenk line and distilled water (25 mL) was added via syringe. The solution was heated with stirring. After 18 h at reflux, the reaction was cooled and the solvent removed in vacuo. The white solid residue was extracted with CH_2Cl_2 (3×10 mL). The CH_2Cl_2 extracts were combined and the solvent removed in vacuo. The solids were further dried under reduced pressure to give the amino acid complex. Yields and spectral data are given below.

2.3. [Ir(glycine)(H)(PMe$_3$)$_3$]Cl (**2a**)

Yield: 96%. ^1H NMR ($CDCl_3$): δ −19.15 (q, $J = 18.7$ Hz, 1H, IrH), 1.62 (t, $J = 3.5$ Hz, 18H, $P(CH_3)_3$), 1.78 (d, $J = 10.5$ Hz, 9H, $P(CH_3)_3$), 3.39 (t, 2H, CH_2), 6.11 (br s, 2H, NH_2); ^{13}C NMR ($CDCl_3$): δ 18.71 (vt, $J = 10$ Hz, $P(CH_3)_3$), 20.63 (d, $J = 39$ Hz, $P(CH_3)_3$), 43.09, 185.43 ppm; ^{31}P NMR ($CDCl_3$): δ −47.52 (t, $J = 20$ Hz), −33.78 (d, $J = 18$ Hz). Elem. Anal. Calcd. for $C_{11}H_{32}ClIrNO_2P_3$: C, 24.88%; H, 6.07%. Found: C, 24.70%; H, 6.18%.

2.4. [Ir(L-alanine)(H)(PMe$_3$)$_3$]Cl (**2b**)

Yield: 79%. ^1H NMR ($CDCl_3$): δ −19.36 (q, $J = 17$ Hz, IrH), 1.65 (d, $J = 10$ Hz, 9H, $P(CH_3)_3$), 1.73 (d, $J = 10$ Hz, 9H, $P(CH_3)_3$), 1.80 (m, 3H, CH_3), 1.92 (d, $J = 6$ Hz, 9H, $P(CH_3)_3$), 3.09 (m, 1H, CH), 3.26 (br s, 1H, NH), 6.69 (br s, 1H, NH); ^{13}C NMR ($CDCl_3$): δ 17.25 (t, $J = 20$ Hz), 21.5 (d, $J = 40$ Hz), 21.1, 52.3, 181.5; ^{31}P NMR ($CDCl_3$): δ −48.31 (t, $J = 20$ Hz), −34.52 (t, $J = 21$ Hz). Elem. Anal. Calcd. for $C_{12}H_{34}ClIrNO_2P_3$: C, 26.45; H, 6.29. Found: C, 26.44; H, 6.44%.

2.5. [Ir(L-valine)(H)(PMe$_3$)$_3$]Cl (**2c**)

Yield: 71%. ^1H NMR ($CDCl_3$): δ −19.10 (q, $J = 17$ Hz, 1H, IrH), 1.10 (dd, 6H, $C(CH_3)_2$), 1.57 (t, $J = 5.6$ Hz, 9H, $P(CH_3)_3$), 1.65 (d, $J = 5.8$ Hz, 9H, $P(CH_3)_3$), 1.92 (d, $J = 10.4$ Hz, 9H, $P(CH_3)_3$), 2.55 (m, 1H, $CH(Me)_2$), 2.98 (m, 1H, $C_\alpha H$), 3.22 (br s, 1H, NH), 6.89 (br s, 1H, NH); ^{13}C NMR ($CDCl_3$): δ 18.16 (t, $J = 17$ Hz), 21.17 (d, $J = 37$ Hz), 19.43, 54.28, 109.31, 181.51; ^{31}P NMR ($CDCl_3$): δ −49.35 (t, $J = 20$ Hz), −35.02 (d, $J = 20$ Hz). Elem. Anal. Calcd. for $C_{14}H_{38}ClIrNO_2P_3$: C, 29.34; H, 6.68. Found: C, 29.74; H, 6.58%.

2.6. [Ir(L-phenylalanine)(H)(PMe$_3$)$_3$]Cl (**2d**)

Yield: 67%. ^1H NMR ($CDCl_3$): δ −19.48 (q, $J = 12$ Hz, 1H, IrH), 0.96 (d, $J = 6.4$ Hz, 9H, $P(CH_3)_3$), 1.64 (d, $J = 6.2$ Hz, 9H, $P(CH_3)_3$), 1.76 (d, $J = 10.2$ Hz, 9H, $P(CH_3)_3$), 2.92 (br t, 1H, NH), 3.20 (dd, $J = 6$, 13.6 Hz, 1H, $PhCH_a$), 3.41 (m, 1H, $C_\alpha H$), 3.62 (d, $J = 13.6$ Hz, 1H, $PhCH_b$), 7.19 (t, 1H, ArH), 7.28 (t, 2H, ArH), 7.54 (d, 2H, ArH), 7.75 (br t, 1H, NH); ^{13}C NMR ($CDCl_3$): δ 15.11 (d, $J = 17$ Hz), 18.80 (t, $J = 17$ Hz), 21.66 (d, $J = 42$ Hz), 55.66, 58.94, 132.9, 134.66, 137.37, 142.05, 189.38; ^{31}P NMR ($CDCl_3$): δ −48.6 (t, $J = 21$ Hz), −34.51 (d, $J = 19$ Hz). Elem. Anal. Calcd. for $C_{18}H_{38}ClIrNO_2P_3$: C, 34.81; H, 6.17. Found: C, 34.26; H, 6.33%.

2.7. [Ir(L-tryptophan)(H)(PMe$_3$)$_3$]Cl (**2e**)

Yield: 64%. ^1H NMR ($CDCl_3$): δ −19.42 (q, $J = 19$ Hz, IrH), 0.69 (d, $J = 6.8$ Hz, 9H, $P(CH_3)_3$), 1.59 (d, $J = 10.4$ Hz, 9H, $P(CH_3)_3$), 1.64 (d, $J = 6.05$ Hz, 9 Hz, $P(CH_3)_3$), 3.17 (br s, 1H, NH), 3.42 (m, 2H, CH_2), 3.63 (m, 1H, $C_\alpha H$), 7.08 (m, 2H, ArH), 7.41 (m, 2H, ArH), 7.63 (br s, 1H, NH), 8.10 (m, 1H, ArH); ^{31}P NMR ($CDCl_3$): δ −48.39 (t, $J = 20$ Hz), −34.34 (t, $J = 21$ Hz). Elem. Anal. Calcd. for $C_{20}H_{39}ClIrN_2O_2P_3$: C, 36.39; H, 5.95. Found: C, 34.10; H, 5.82%.

2.8. [Ir(L-proline)(H)(PMe$_3$)$_3$]Cl (**2f**)

Yield: 61%. ^1H NMR ($CDCl_3$): δ −20.32 (q, $J = 20$ Hz, 1H, IrH), 1.45 (d, $J = 6.3$ Hz, 9H, $P(CH_3)_3$), 1.58 (d, $J = 6.6$ Hz, 9H, $P(CH_3)_3$), 1.76 (d, $J = 10.2$ Hz, 9H, $P(CH_3)_3$), 2.11 (br m, 3H), 2.37 (m, 1H), 2.52 (m, 1H), 2.60 (m, 1H), 3.65 (q, 1H), 3.85 (br m, 1H), 7.70 (br m, 1H, NH); ^{13}C NMR ($CDCl_3$): δ 18.06 (t, $J = 17$ Hz), 21.17 (d, $J = 41$ Hz), 26.81, 30.45, 53.20, 57.72, 18.89; ^{31}P NMR ($CDCl_3$): δ −48.59 (t, $J = 20$ Hz), −35.38 (d,