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

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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

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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,

$J = 22$ Hz). Elem. Anal. Calcd. for $C_{14}H_{36}ClIrNO_2P_3$: C, 29.45; H, 6.35. Found: C, 29.17; H, 6.20%.

2.9. [Ir(L-isoleucine)(H)(PMe_3)$_3$]Cl (**2g**)

Yield: 47%. ^{1}H NMR ($CDCl_3$): δ −19.77 (q, $J = 19$ Hz, 1H, IrH), 0.97 (t, $J = 7.2$ Hz, 3H, CH_3), 1.17 (d, $J = 8.4$ Hz, 3H, CH_3), 1.60 (d, $J = 6.8$ Hz, 9H, $P(CH_3)_3$), 1.61 (d, $J = 6.8$ Hz, 9H, $P(CH_3)_3$), 1.73 (m, ~3H, CH_2, NH), 1.93 (d, 9H, $J = 10.4$ Hz, $P(CH_3)_3$), 2.15 (m, 1H, CH), 3.05 (m, 1H, CH), 6.90 (br d, 1H, NH); ^{13}C NMR ($CDCl_3$): δ 12.34, 13.15, 15.81 (m, $J = 36$ Hz), 21.08 (d, $J = 40$ Hz), 24.3, 27.2, 55.6, 181.5; ^{31}P NMR ($CDCl_3$): δ −49.06 (t, $J = 16$ Hz), −33.69 (t, $J = 22$ Hz).

2.10. [Ir(L-tyrosine)(H)(PMe_3)$_3$]Cl (**2h**)

Yield: 43%. ^{1}H NMR ($CDCl_3$): δ −19.52 (q, $J = 18$ Hz, 1H, IrH), 1.34 (d, $J = 6.2$ Hz, 9H), 1.90 (d, $J = 6$ Hz, 9H), 2.02 (d, $J = 10$ Hz, 9H), 2.31 (Br s, 1H, OH), 3.35 (m, 2H, CH_2), 3.63 (br m, 1H, NH), 3.78 (d, $J = 14$ Hz, 1H, $C_\alpha H$), 7.31 (d, $J = 8.2$ Hz, 2H, ArH), 7.58 (d, $J = 8.2$ Hz, 2H, ArH), 7.62 (br s, 1H, NH); ^{31}P NMR ($CDCl_3$): δ −48.99 (t, $J = 20$ Hz), −33.71 (t, $J = 21$ Hz).

2.11. [Ir(L-serine)(H)(PMe_3)$_3$]Cl (**2i**)

Yield: 43%. ^{1}H NMR ($CDCl_3$): δ −19.9 (q, $J = 18$ Hz, 1H, IrH), 1.88 (t, $J = 6.8$ Hz, 18H, $P(CH_3)_3$), 2.09 (d, $J = 10.4$ Hz, 9H, $P(CH_3)_3$), 3.50 (m, 1H, CH), 4.26 (dq, $J = 3.6$, 9.2 Hz, 2H, CH_2), 5.21 (br t, 1H, NH), 6.20 (br s, 1H, OH), 6.60 (br t, $J = 9.6$ Hz, 1H, NH); ^{31}P NMR ($CDCl_3$): δ −47.30 (t, $J = 16$ Hz), −33.72 (t, $J = 22$ Hz).

2.12. [Ir(diphenylglycine)(H)(PMe_3)$_3$]Cl (**2j**)

Using the general procedure above with the following modifications: 1.34 mmol diphenylglycine (296.3 mg, 1.34 mmol), [Ir(COD)(PMe_3)$_3$]Cl (350 mg, 0.620 mmol). Yield: 47%. ^{1}H NMR (CH_2Cl_2): δ −8.40 (dt, $J = 174.5$, 19.9 Hz, 1H, IrH), 1.46 (d, $J = 7.7$ Hz, 9H, $P(CH_3)_3$), 1.66 (d, $J = 10.7$ Hz, 9H, $P(CH_3)_3$), 1.85 (d, $J = 10.4$ Hz, 9H, $P(CH_3)_3$), 4.76 (br s, 2H, NH_2), 6.8–8.1 (br m, 10H, ArH); ^{13}C NMR (D_2O): δ 13.2 (d, $J = 30.2$ Hz), 17.8 (dd, $J = 42.2$ Hz, $J = 3$ Hz), 18.96 (dd, $J = 42.2$ Hz, $J = 3$ Hz), 73.12, 126.94, 128.01, 128.79, 128.82, 128.90, 129.04, 138.28, 142.37, 183.04; ^{31}P NMR (D_2O): δ −44.4 (dd), −40.8 (dd), −38.0 (dd), IR: ν 2040, 1648, 947 cm^{-1}. Elem. Anal. Calcd. for $C_{23}H_{40}ClIrNO_2P_3$: C, 40.44; H, 5.90. Found: C, 40.50; H, 5.95%.

2.13. [Ir(amino acid)(H)(PMe_3)$_3$][PF_6], general procedure

An excess of KPF_6 was dissolved in distilled water, this solution was added dropwise to solution of [Ir(amino acid)(H)(PMe_3)$_3$]Cl in distilled water. A yellow-white precipitate formed immediately. The precipitate was filtered using cannula techniques to give crystals that were screened for X-ray structural analysis.

2.14. X-ray crystallography

Clear rectangular prisms of [Ir(L-valine)(H)(PMe_3)$_3$]PF_6 ($0.2 \times 0.2 \times 0.4$ mm^3) were crystallized from CH_2Cl_2 by slow diffusion into diethyl ether at room temperature. The chosen crystal was mounted on a glass fiber using epoxy cement and centered on the goniometer of a Siemens R3m/V four-circle diffractometer equipped with a scintillation counter detector. The data collection routine, unit cell refinement, and data processing were carried out with the Siemens program package SHELXTL PLUS (VMS) [7]. The Laue symmetry and systematic absences were consistent with the tetragonal space group $P4_3$. The absolute configuration was established from anomalous dispersion effects in the structure. Structure solution and refinement were performed with the graphical user interface WINGX [26]. The structure was solved by direct methods and refined using SHELX97 [27]. The asymmetric unit of the structure comprises one crystallographically independent molecule (Flack parameter = −0.010(5)). The final refinement model

Table 1
Crystal data and structure refinement for [Ir(H)(L-Valine)(PMe_3)$_3$]PF_6

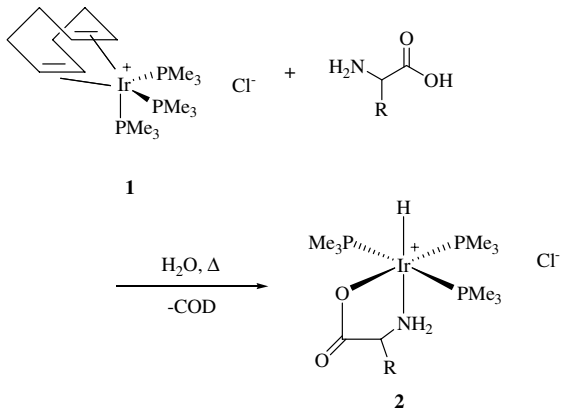
Identification code	**2c**
Empirical formula	$C_{14}H_{38}F_6IrNO_2P_4$
Formula weight	682.5
Temperature (K)	298
Wavelength (Å)	0.71073
Crystal system	Tetragonal
Space group	$P4_3$
Unit cell dimensions	
a (Å)	14.327(3)
c (Å)	14.397(4)
Volume (Å^3)	2955.3(16)
Z	4
D_{calc} (Mg/m^3)	1.534
Absorption coefficient (mm^{-1})	4.759
F(000)	1344
Crystal size (mm^3)	$0.2 \times 0.2 \times 0.4$
Theta range (°)	3.5–45.0
Index range	$0 < h < 15$, $0 < k < 15$, $-15 < l < 15$
Reflections collected	4250
Independent reflections (R_{int})	3870 (0.0263)
Observed reflections	3264 ($F > 4.0\sigma(F)$)
Absorption correction	Semi-empirical
Minimum/maximum transmission	0.5122/1.0000
Refinement method	Full-matrix least-squares
Quantity minimized	$\Sigma\omega(F_o - F_c)^2$
Number of parameters refined	254
Goodness-of-fit	1.26
Final R indices (observed data)	$R_1 = 0.0433$, $wR_2 = 0.0506$
R indices (all data)	$R_1 = 0.0560$, $wR_2 = 0.0580$
Absolute structure parameter	1.04(3)
Largest and mean Δ/σ	0.071, 0.007
Data-to-parameter ratio	12.9:1
Largest difference in peak and hole (e Å^{-3})	2.00 and −1.19

involved anisotropic displacement parameters for non-hydrogen atoms and a riding model for all hydrogen atoms. The program package ORTEP-3 was used for molecular graphics generation [28]. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 285583 for compound **2c**. A summary of the experimental details and crystallographic results can be found in Table 1.

3. Results and discussion

Metal hydrides have assumed an important role in transition metal catalysis [29]. It is our desire to exploit the Ir–H bonds in amino acid complexes of iridium in an attempt to explore their catalytic activity. We initially prepared and characterized a number of naturally and unnaturally occurring amino acid complexes (Table 2). These complexes are of interest because most of them possess excellent water solubility which may lend themselves to use in "green" processes. Additionally, a variety of binding modes of amino acids to metals have been demonstrated [30]. Therefore, we wished to fully understand the structure of amino acid complexes of iridium and undertook a comprehensive study of these complexes.

Since we knew that amino acids are not very soluble in organic solvents and that C–H activation frequently occurs with $[Ir(cod)(PMe_3)_3]Cl$ upon heating [31], we chose to react amino acids with $[Ir(cod)(PMe_3)_3]Cl$ (**1**) in aqueous solution. Water is an excellent solvent for complex **1** and most amino acids. The reaction of α-amino acids with complex **1** at 100 °C in water leads to formation of hydridoiridium amino acid complexes (**2a–2j**) in good to excellent yields (Table 1). These complexes are the first examples of amino acid iridium hydrido species.



When L-valine was added to complex **1**, a meridional product, **2**, was formed upon heating (Table 2). Initially, L-valine was chosen as the amino acid ligand because the isopropyl group gives a distinct NMR signal which can be used in determining its binding to the metal. In the ^1H NMR spectrum of a simple mixture of L-valine and complex **1**, the resonances of the free amino acid and the iridium complex are easily discerned (Fig. 1). The resonances

Table 2
Yields, chemical shift, δ, of the hydride peak in the ^1H NMR spectrum, spin–spin coupling and coupling constants, *J*, for the complexes $[Ir(aa)(H)(PMe_3)_3]Cl$. Spin–spin coupling q is a quartet, dt is a doublet of triplets

Complex	Amino acid	Yield (%)	δ of Hydride (ppm)	Spin–spin coupling, *J* (Hz)
2a	Glycine	96	−19.15	q, 19
2b	L-Alanine	79	−19.39	q, 17
2c	L-Valine	71	−19.10	q, 17
2d	L-Phenylalanine	67	−19.48	q, 12
2e	L-Tryptophan	64	−19.42	q, 19
2f	L-Proline	61	−20.32	q, 20
2g	L-Isoleucine	47	−19.77	q, 19
2h	L-Tyrosine	43	−19.50	q, 18
2i	L-Serine	43	−19.90	q, 18
2j	Diphenylglycine	47	−8.40	dt, 174.5, 20

at 0.82 ppm correspond to the isopropyl methyl protons of L-valine. The multiplet at 2.1 ppm is due to the isopropyl methine proton and the doublet at 3.53 ppm corresponds to the proton of the α carbon of valine. The resonance at 1.5 ppm corresponds to the methyl groups on the trimethyl phosphines of complex **1**, and at 2.0 and 3.3 ppm to the aliphatic and olefinic protons of the 1,5 COD ligand, respectively.

From the ^1H NMR spectrum (Fig. 2) of the mixture after heating at 100 °C for 18 h, it is clear that the L-valine is attached to the metal center. The isopropyl methyl groups of the bound valine are present as two distinct sets of doublets, one set shifted upfield and the other shifted downfield, bordering the resonances of the excess L-valine still present in the solution. The resonance of the proton on the α carbon remains a doublet shifted slightly upfield from its free amino acid counterpart. Therefore, the amino acid had formed a complex with the iridium.

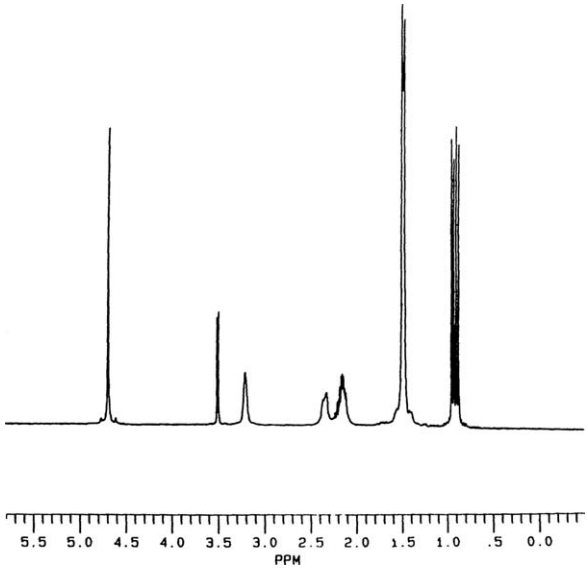


Fig. 1. ^1H NMR spectrum of a 2:1 mixture of L-valine and $[Ir(COD)(PMe_3)_3]Cl$ (**1**).

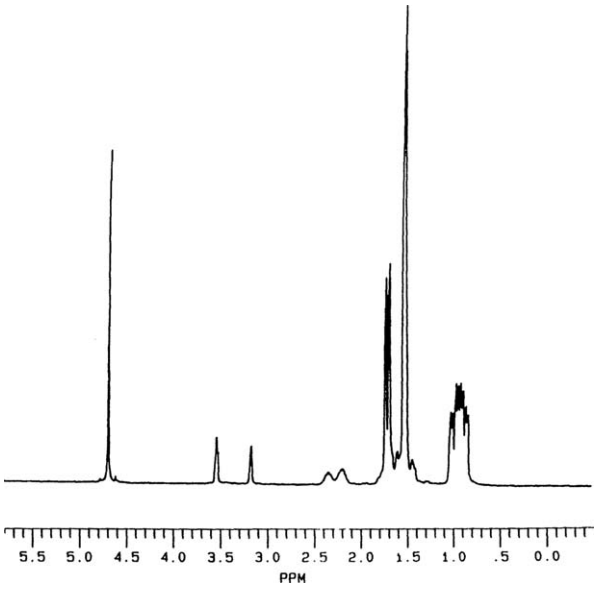


Fig. 2. ^{1}H NMR spectrum of a 2:1 mixture of L-valine and [Ln(COD)(P-Me$_3$)$_3$]Cl (**1**) heated at 100 °C for 18 h.

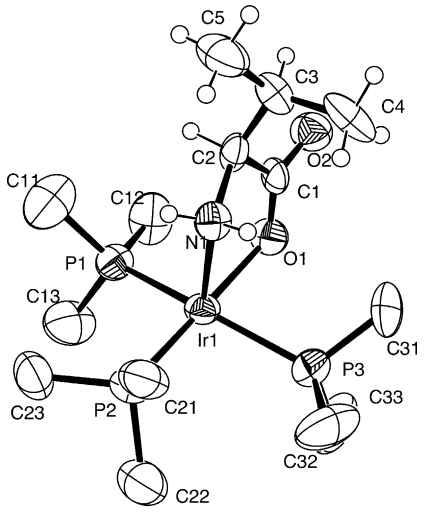


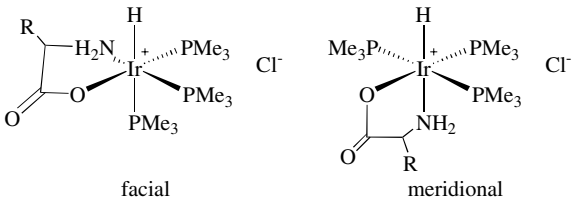
Fig. 3. ORTEP drawing of [Ir(L-valine)(H)(PMe$_3$)$_3$]PF$_4$ derived from compound **2c**. The hydride ligand was not located in the mixture determination and is not shown.

The complex appears to be the meridional complex (Scheme 1) from the coupling pattern of the hydride proton. The hydride resonance of the L-valine complex is a quartet with a chemical shift of −19.1 ppm. The quartet is due to P–H spin–spin coupling of three *cis* phosphorus neighbors, indicative of a meridional arrangement of phosphines in the octahedral Ir(III) complex. The chemical shift of the hydride is consistent with the hydride *trans* to either N or O of the amino acid ligand [23].

The ORTEP plot from the single crystal diffraction study of [Ir(L-valine)(H)(PMe$_3$)$_3$]PF$_6$ clearly shows the meridional arrangement with the hydride *trans* to the amino acid nitrogen (Fig. 3). All of the other amino acid complexes synthesized showed a peak at approximately the same chemical shift and identical spin–spin coupling pattern (Table 2) and, therefore, were assigned as meridional isomers.

Examination of the structural solution for **2c**, it appeared that the cation shown in Fig. 3 along with the PF$_6$ anion did not account for enough volume in the crystal lattice. Attempts to locate additional electron density from possible solvent inclusion were unsuccessful. The PLATON program SQUEEZE [32] found a total void volume of approximately 590 Å^2 which is a space that could accommodate quite a number of solvent molecules. Attempts to locate additional electron density from possible disordered solvent inclusion were unsuccessful. SQUEEZE did not find sufficient electron density in the void to account for solvent molecules. The highest electron density peak was only 0.79 e/Å^3 and it was 1.03 Å away from the iridium. A reasonable hypothesis based on the size of the void space is that the ions crystallized with one mole of diethyl ether per cation/anion pair but the volatile solvent escaped from the lattice before the diffraction experiment. This raises the interesting question: if solvent was lost, why did the crystal lattice remain intact and not collapse?

Examination of intermolecular contacts and the crystal packing of **2c** gives an answer to this question as well as showing a fascinating extended-lattice. Complex **2c** crystallizes in the chiral tetragonal space group $P4_3$. The cation/anion pairs lie around the 4_3 screw axis. The two hydrogen atoms attached to the coordinated valine nitrogen atoms are both hydrogen-bonded. One of the N hydrogen atoms is bonded to a fluorine atom of the PF$_6$ counter ion with a N···F distance of 3.227 Å. The second N hydrogen atom is bonded to the carbonyl oxygen of a second cation with a N···O distance of 2.913 Å. The N–H–O hydrogen bonding leads to the 43 helix shown in Fig. 4.



Scheme 1. Meridional and facial isomers of [Ir(aa)(H)(PMe$_3$)$_3$].

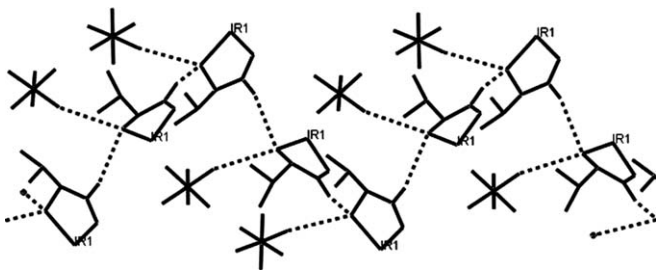


Fig. 4. Helical extended structure of **2c** (PMe$_3$ ligands removed for clarity).

Along with the hydride at −19.6 ppm, the ^{1}H NMR spectrum of **2j** shows an additional multiplet at −8.40 ppm. This hydride peak is consistent with the hydride being *trans* to the less electronegative phosphorus atom. Additionally, this proton is a doublet of triplets with one coupling constant of 20 Hz which is consistent with P–H coupling *cis* and a second coupling constant of 175 Hz, consistent with P–H coupling *trans*. Additionally, we observed small amounts of other hydride peaks: a doublet of quartets at −11.4 and a triplet at −21.0 (t) ppm. We have postulated that these peaks are due to other iridium complexes which contain four PMe_3 ligands and two PMe_3 ligands, respectively. We have as of yet been unable to isolate and further analyze these compounds.

Further examination of the proton NMR spectra of several of the amino acid complexes in the region of −9.0 ppm, showed that trace amounts of the facial isomer, by evidence of the same doublet of triplet patterns as with the facial isomer of the diphenylglycine complex **2j**, were present. As can be seen from Table 3, all of the mono substituted α-amino acid complexes give predominantly the meridional isomer, while the α,α-disubstituted amino acid gives significant amounts of the facial, meridional and other complexes.

Interestingly, the ratio of hydrides for the diphenylglycine complex changes with time when the compound is kept in a $CDCl_3$ solution. A solution of freshly prepared **2j** in $CDCl_3$ was prepared and the NMR spectrum was obtained over time. The integration areas of the hydride corresponding to the *fac* and *mer* isomers as well as the hydride of the other isomers (isomer 1 and isomer 2) were normalized compared to an internal standard. As can be seen from Table 4, the *mer* isomer is not inert. However, it does not appear that the *mer* isomerizes to the *fac* isomer. Instead, the material that forms is one with a hydride chemical shift of −21.0 ppm and is a triplet. Presumably, the *mer* isomer has a PMe_3 ligand exchanged with another ligand, perhaps chloride.

The same experiment was performed on the D-phenylglycine complex. Here, the ratio of facial, *mer* and other complexes remained constant over time. We conclude that monosubstituted amino acids, while giving predominately meridional isomers, are also much more inert.

Table 3
Distribution of *mer* and *fac* isomers and other complexes of the [Ir(aminoacid)(H)(PMe_3)$_3$]Cl system as determined by the relative integration of the corresponding hydride signals in the ^{1}H NMR spectra from freshly prepared samples in $CDCl_3$

Amino acid	*fac* (%)	*mer* (%)	Other (%)
L-Leucine	6	91	3
L-Isoleucine[a]	8	86	6
L-*tert*-Leucine	6	84	9
L-Proline	3	85	12
D-Phenylglycine	5	84	12
Diphenylglycine	35	27	37

[a] Spectrum obtained in D_2O.

Table 4
Distribution of *mer*, *fac* and other isomers of [Ir(diphenylglycine)(H)(PMe_3)$_3$]Cl complexes as determined by the integration areas of the corresponding hydride signals in the ^{1}H NMR spectra compared to an internal standard

Day	*fac* isomer (%)	Other isomer 1 (%)	*mer* isomer (%)	Other isomer 2 (%)
1	35	6	27	31
2	36	6	19	39
6	36	7	5	52
8	36	4	5	56

Our studies have indicated that these complexes are not completely inert. The amino acid ligand can be replaced with a less sterically hindered amino acid. For example, when free glycine is added to an aqueous solution of the L-valine complex, **2c**, at 100 °C, the formation of the glycine complex, **2a**, and free valine is observed by ^{1}H NMR spectroscopy. A series of reactions was performed in which glycine replaced the alanine ligand and alanine replaced the valine ligand. The bulk of the side chain dictated which amino acid complex was formed.

4. Conclusion

We have found that hydrido amino acid complexes of iridium can easily be formed in water and that their isomeric forms can be monitored by proton NMR spectroscopy. Both meridional and facial isomers can form and their ratios are dependent upon the degree of substitution of the amino acid; α-monosubstituted amino acids give predominantly meridional isomers, while α,α-disubstituted amino acid give both meridional and facial isomers.

We continue to explore the possibilities of using these iridium amino acid complexes as possible catalysts. The potential use of these complexes as catalysts is under investigation. The water solubility of these complexes as well as the presence of the chiral amino acid ligands creates new possibilities for catalytic systems.

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