

SYNTHESIS AND CHARACTERIZATION OF AMINO-CARBOXYLATO IRIIDIUM(III) COMPLEXES

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ABSTRACT: *Aminocarboxylic acids, such as 2-aminobenzoic acid, react easily with $[\text{Ir}(\text{COD})(\text{PMe}_3)_3]\text{Cl}$, (COD = 1,5-cyclooctadiene), in THF to produce hydridoaminocarboxylato iridium(III) complexes in high yields. These octahedral complexes are formed via oxidative addition reaction of the O-H bond of the carboxylic group with the central metal. The starting iridium(I) complex loses the COD molecule, the chloride is coordinated to the metal and the phosphine groups take a meridional position in the final products which are characterized by ^1H , ^{13}C and ^{31}P NMR spectroscopies.*

KEY WORDS: *Iridium(III) complexes, Hydridoaminocarboxylato iridium (III) complexes, Aminocarboxylate complexes.*

Carboxylate ligands are capable of binding to a metal in different modes. They can be either unidentate ligands or bidentate and also bridging group through both oxygen atoms of the carboxylic group [1]. There are many examples of these and other kind of bonding in the literature [2]. The chemistry of these oxygen donor ligands with the heavy metals has attracted some attention due to the difference in the size and the hardness of the oxygen and the metal [3].

One way of synthesizing complexes which contain

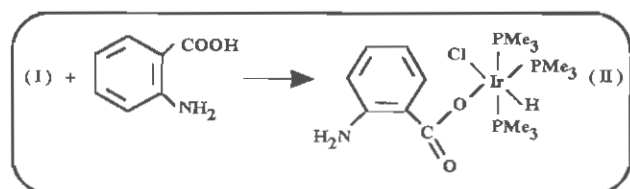
M-O moiety is the use of oxidative addition reactions of different molecules to the central metal. These kinds of reaction were studied by *Marder and Mistein* [4] using unsaturated carboxylic acids with rhodium and iridium complexes. There is also a recent report on the synthesis of hydrido phenoxy complexes of nickel group [5].

The electron rich complex $[\text{Ir}(\text{COD})(\text{PMe}_3)_3]\text{Cl}(\text{I})$, has been used as a good precursor for a variety of oxidative addition reactions with E-H bonds of various molecules (E=H, B, C, N and O) [6]. We

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have already reported the reaction of this complex with the O-H bonds from alcohols, phenols and carboxylic acids [7]. We have shown that a number of carboxylic acids reacted with complex (I) to give hydridocarboxylato iridium(III) complexes in which the carboxylato group attached to the metal through one of the oxygen atoms. Since amino acids have another donor atom in addition to the carboxylic group, we were interested in studying the reaction of these acids with complex (I). In this paper we will report our finding of these reactions.

Heating complex (I) with an excess of 2-amino-benzoic acid in THF leads to the loss of cyclo-octadiene and the protonation of the metal to yield *mer*-2-aminobenzoatochlorotris(trimethylphosphine)-hydrido iridium (III).



Complex (II) was characterized by using NMR spectroscopy. In the ^1H NMR spectrum of complex (II) there appeared a triplet at δ 1.57 and a doublet at δ 1.63 ppm, integrating in 2:1 ratio arising from the phosphorus methyl hydrogens (Fig. 1). The triplet is indicative of two *trans* PMe_3 ligands. The doublet is indicative of a PMe_3 ligand *cis* to the other two PMe_3 ligands since the methyl protons are coupled only to the phosphorus to which they are bound. Thus, the spectrum suggested a meridional arrangement of the phosphine ligands around the metal. The two mutually *trans* PMe_3 ligands are in identical environment and there is strong spin-spin coupling between them.

The high field doublet of triplets pattern at δ -21.15 ppm, in the proton spectrum, indicated the presence of a hydride ligand (Fig. 1). The overlapping doublet of triplets suggests that the hydride is in the plane of the meridional phosphines and *cis* to two nonequivalent phosphines. The central PMe_3 ligand splits the hydride into a doublet, each is further split into a triplet by the other two *trans* PMe_3 ligands. If the hydride is in the *trans* position to any of the phosphine group, as it is in *mer*-(Me_3P) $_3\text{Ir}(\text{O}_2\text{BC}_6\text{H}_4)\text{H}(\text{Cl})_9$ [8],

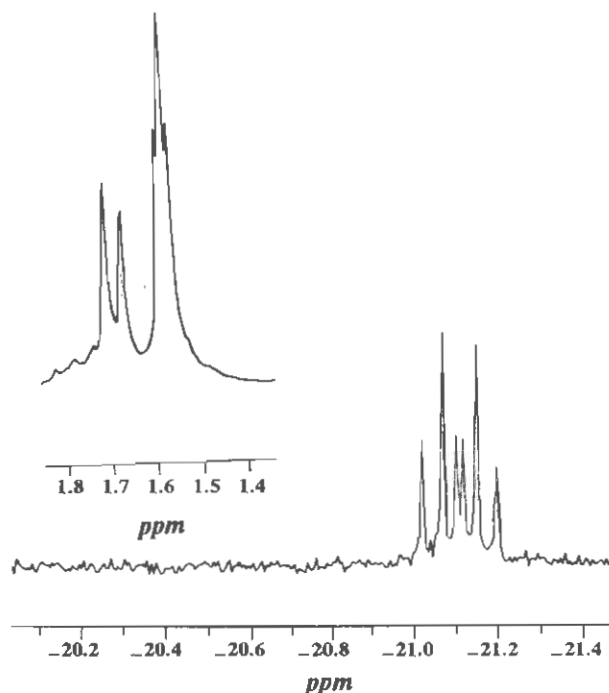


Fig. 1: ^1H NMR spectrum of complex (II) (aromatic protons are not included)

the triplets will be well separated and appear at lower field. The signals of the PMe_3 protons will be also different due to the *trans* effect of the hydride.

A pattern similar to the signals observed in the proton spectrum was observed in the ^{13}C NMR spectrum (Fig. 2). A triplet at δ 15.80 ppm ($J_{\text{C-P}} = 20$ Hz) and a doublet of triplets at δ 20.60 ppm ($J_{\text{C-P}} = 40$ Hz) further supported the meridional arrangement of the phosphines based upon arguments similar to those used for the proton spectrum.

In the ^{31}P NMR spectrum, a triplet at δ -48.04 ppm ($J_{\text{P-P}} = 52$ Hz) and a doublet at δ -30.51 ppm ($J_{\text{P-P}} = 52$ Hz) integrating in 1:2 ratio is observed (Fig. 3). This is consistent with the proposed structure. In this spectrum the triplet is due to the *cis* PMe_3 and the doublet results from the two *trans* PMe_3 ligands taking into account the coupling between these nonequivalent phosphines.

This work has shown that amino acids can form stable hydride complexes of iridium (III), through oxidative addition reaction. These novel complexes open up a wide range of possibilities for further reactions. One of the interesting reactions can be the addition of organic unsaturated compounds, such as

alkynes, to examine the complexes for insertion into the Ir-H bond. This can be followed by reductive elimination of the newly formed organic fragment. These aminocarboxylato iridium complexes might be worthy candidates for further investigation of anti-tumor activity since there are reports suggesting that some iridium complexes have anti-cancer activity [9].

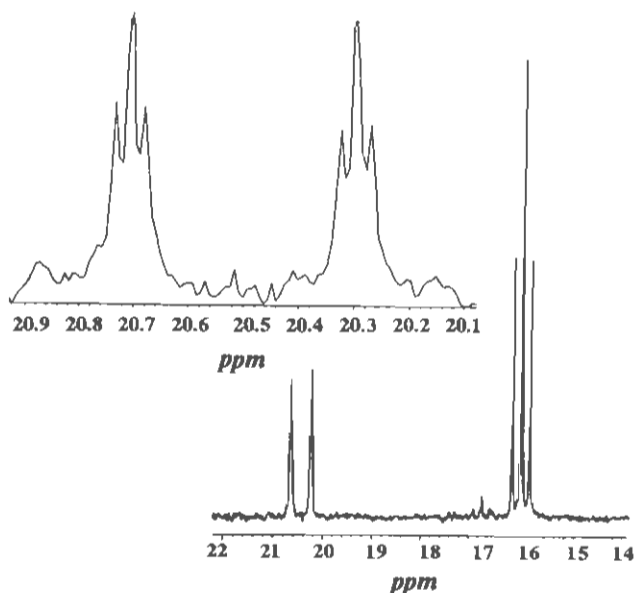


Fig. 2: ^{13}C NMR spectrum of complex (II) (only for the PMe_3 groups)

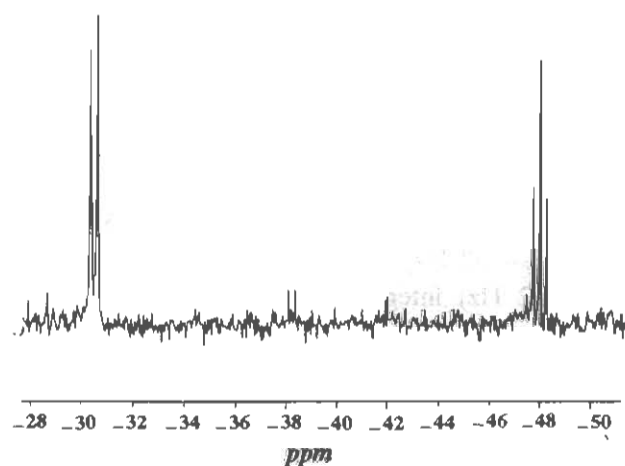


Fig. 3: ^{31}P NMR spectrum of complex (II)

EXPERIMENTAL

General

All reactions were carried out under an atmosphere of purified nitrogen using conventional glass vessels and standard Schlenk line techniques. Air sensitive

solids were stored and manipulated in a M. G. Braun Inert Atmosphere Box. Complex $[\text{Ir}(\text{COD})(\text{PMe}_3)_3]\text{Cl}$, was synthesized by the previously published method [10].

The ^1H NMR spectra were obtained on a Bruker WP 270 SY instrument and referenced to TMS via CDCl_3 resonance. The ^{13}C NMR spectra were obtained on a Varian Unity 400 instrument (at 100 MHz) and referenced to CDCl_3 resonance. ^{31}P NMR spectra were recorded on a Bruker WP 200 SY (81 MHz) instrument and referenced to an external standard of 85% H_3PO_4 . Elemental analysis were performed by Atlantic Microlab Inc. Analysis, Norcross, Georgia, U.S.A.

Synthesis of $\text{mer}-(\text{Me}_3\text{P})_3\text{Ir}(\text{O}_2\text{CC}_6\text{H}_4\text{NH}_2)(\text{H})(\text{Cl})$ (II)

A 50 mL one-necked side-armed flask, equipped with magnetic stirrer and a septum, was charged with 0.200 g (0.355 mmol) of $[\text{Ir}(\text{COD})(\text{PMe}_3)_3]\text{Cl}$ and 0.069 g (0.53 mmol, 1.5 eq) of 2-aminobenzoic acid under N_2 in a dry box. The flask was then connected to a double manifold (vacuum/nitrogen) Schlenk line and 25 mL of THF was added by syringe. The flask was then fitted with a reflux condenser attached to a N_2 inlet and the reaction mixture was heated and stirred at 60°C for 5 hours. At the end of the reaction the solution was filtered and the solvent was then removed under vacuum. The left solids were dissolved in 5 mL of CH_2Cl_2 and on addition of 20 mL of pentane the solids were reprecipitated. The white solids were collected and dried under vacuum to afford 0.170 g (0.30 mmol) of $\text{mer}-(\text{Me}_3\text{P})_3\text{Ir}(\text{O}_2\text{C}-\text{C}_6\text{H}_4\text{NH}_2)(\text{H})(\text{Cl})$ (80% yield based on the amount of $[\text{Ir}(\text{COD})(\text{PMe}_3)_3]\text{Cl}$) identified on the bases of the following data:

Analysis calculated for $\text{C}_{16}\text{H}_{34}\text{NClP}_3\text{IrO}_2$: C, 32.40; H, 5.73.

Found: C, 32.65; H, 5.82.

^1H NMR(CDCl_3): δ -21.15(dt, $J_{\text{P-H}} = 23$ Hz, 12 Hz, 1H, Ir-H), 1.57(t, $J_{\text{P-H}} = 3.5$ Hz, 18H, *trans* PMe_3), 1.63(d, $J_{\text{P-H}} = 10$ Hz, *cis* PMe_3), 6.57(m, 2H, *ortho* and *para* to NH_2), 6.80(br, 2H, NH_2), 7.18(t, 1H, *para* to COO-Ir), 7.86 ppm (d, 1H, *ortho* to COO-Ir). ^{31}P NMR(CDCl_3): δ -48.04(t $J_{\text{P-P}} = 52$ Hz, 1P, *cis* PMe_3), -30.51 ppm (d, $J_{\text{P-P}} = 52$ Hz, 2P, *trans* PMe_3).

^{13}C NMR(CDCl_3): δ 15.80(t, $J_{\text{C-P}} = 20$ Hz, 6C, *trans* PMe_3), 20.60 ppm (dt, $J_{\text{C-P}} = 40$ Hz, 5 Hz, 3C, *cis* PMe_3), 117.5(s), 118.6(s), 132.4(s), 134.2(s) (aromatic C-H carbons, quaternary C were not observed) and 149.5 ppm (brs, COO-Ir).

Synthesis of

mer-(Me_3P) $_3$ Ir[$\text{O}_2\text{CC}_6\text{H}_2\text{NH}_2(\text{OCH}_3)_2$](H)(Cl) (III)

A 100 mL one-necked side-armed flask equipped with a magnetic stir bar and a septum, was charged with 0.280 g (0.50 mmol) of $[\text{Ir}(\text{COD})(\text{PMe}_3)_3]\text{Cl}$ and 0.147 g (0.75 mmol, 1.5 eq) of 1-amino-2,5-dimethoxybenzoic acid under nitrogen in a dry box. The flask was then connected to a double manifold (vacuum/nitrogen) Schlenk line and 40 mL of THF was added by syringe. The reaction mixture was heated at 60 °C for 6 hours. At completion a light brown clear solution was observed. The solvent was stripped off under reduced pressure to give creamy white solids. The solids were dissolved in 5 mL of CH_2Cl_2 and recrystallized by addition of 15 mL of pentane to give 0.228 g of *mer*-(Me_3P) $_3$ Ir[$\text{O}_2\text{CC}_6\text{H}_2(\text{OCH}_3)_2\text{NH}_2$](H)(Cl), (70% yield based on the amount of $[\text{Ir}(\text{COD})(\text{PMe}_3)_3]\text{Cl}$) identified on the bases of the following data:

Analysis calculated for $\text{C}_{18}\text{H}_{37}\text{NCIP}_3\text{IrO}_4$: C, 33.12, H, 5.82.

Found: C, 32.96; H, 5.96.

^1H NMR(CDCl_3): δ -20.95(dt, $J_{\text{P-H}} = 22, 12$ Hz, 1H, Ir-H), 1.56(t, $J_{\text{P-H}} = 3.6$ Hz, 18H, *trans* PMe_3), 1.65(d, $J_{\text{P-H}} = 10.2$ Hz, 9H, *cis* PMe_3), 3.80(s, 3H, OMe_3 *meta* to COO-Ir), 3.90(s, 3H, OMe_3 *para* to COO-Ir), 4.8(s, 2H, NH_2), 6.2(s, 1H, *ortho* to COO-Ir), 6.9 ppm(s, 1H, *para* to COO-Ir).

^{31}P NMR(CDCl_3): δ -47.85(t, $J_{\text{P-P}} = 52$ Hz, 1P, *cis* PMe_3), -30.42 ppm (d, $J_{\text{P-P}} = 52$ Hz, 2P, *trans*

PMe_3). ^{13}C NMR(CDCl_3): δ 15.78(t, $J_{\text{C-P}} = 19$ Hz, 6C, *trans* PMe_3), 20.55 ppm (d, $J_{\text{C-P}} = 41$ Hz, 3C, *cis* PMe_3).

Attempt to synthesis

mer-(Me_3P) $_3$ Ir($\text{O}_2\text{CC}_6\text{H}_4\text{NH}_2$)(H)(Cl)

By the same method discussed above, 2-aminoethanoic acid was reacted with $[\text{Ir}(\text{COD})(\text{PMe}_3)_3]\text{Cl}$ but no identified product was obtained.

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