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Synthesis and Hydrogenation Reaction of Iridium Complexes Containing L-Methionine Methyl Ester

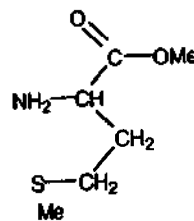
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Chemistry of transition metal complexes of sulfur-containing amino acid ligands such as *l*-cysteine, *l*-cysteine methyl-ester and *l*-methionine has been studied due to the biological significance of the interaction between metal ion and sulfur-containing amino-acids.¹⁻¹⁰ Those ligands can chelate through -NH₂ and carbonyl, -NH₂ and sulfur, or all of three sites. Amino acids exist in living systems in one enantiomeric form predominantly, since nature prefers for a particular enantiomer which complements the life. Reactions of transition metals with asymmetric ligands can lead to the catalysis for asymmetric hydrogenation. Although various complexes of sulfur containing amino acids have been prepared, iridium(I) complexes of those ligands have not been made. We report herein the synthesis and hydrogenation reactions of iridium complexes containing *l*-methionine methyl ester (MME) li-

gand to investigate the coordination sites of MME as well as the possibility as catalysts.



MME

Synthesis. The reaction of [IrCl(COD)]₂ (COD=1,5-cyclooctadiene) with MME·HCl by 1:2 mole ratio of Ir to MME ligand in the mixture of methanol and ether at 25 °C gives a yellow crystalline product (**1**). The absorption bands at 1744 cm⁻¹ and 3190 cm⁻¹ in the IR spectrum of **1** are assigned to the uncoordinated carbonyl group of the ester and the coordinated amine respectively, indicating the MME ligand is bonded through amine and sulfur. In the free MME ligand, ν_{CO} is found at 1744 cm⁻¹, however, ν_{NH₂} can not be observed since the ligand exists as the ammonium salt (ν_{RNH₂⁺} is found as strong multiple bands at 2720, 2614 and 2510 cm⁻¹). The uncoordinated NH₂ is observed in the range of 3300-3450 cm⁻¹, while the coordinated NH₂ is observed in the range of 3000-3200 cm⁻¹ in the literature.⁵⁻⁸ The bands for Ir-N at 528 cm⁻¹ and Ir-S at 361 cm⁻¹ also confirm the ligand is coordinated through amine and sulfur.⁴⁻¹¹ The ¹H NMR spectral data of the complexes in this work are shown in Table 1. Comparing with the free MME ligand, the resonance of the S-CH₃ in **1** is slightly shifted downfield by 0.10 ppm on coordination of sulfur to iridium. Elemental analyses of all the complexes of this work are listed in Table 2 and the data indicates two MME ligands are included in the complex **1** and the electrical conductivity in methanol is 92 cm²ohm⁻¹mol⁻¹, which is typical of 1:1 electrolytes in methanol.¹² Thus, the chloride is anionic and the molecular formula of the complex is considered to be Ir[MME]₂Cl (**1**). The molecular structure can be **1a** with two MME ligands being trans to each other or **1b** with cis configuration, but **1a** may be more probable due to the steric hindrance of both S-methyl groups on the same side in **1b**. The reaction of [IrCl(COE)]₂ (COE=cyclooctene) with MME by 1:2 mole ratio in the presence of NaAsF₆ produces a yellow compound (**2**). The IR spectrum of **2** shows a band

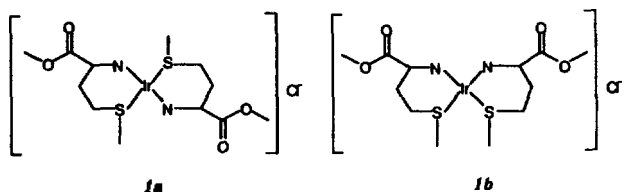
Table 1. Characteristic ¹H NMR Spectral Data of the Complexes^a

Compound	S-CH ₃	O-CH ₃	-CH ₂	S-CH ₂	-NH ₂	-CH	-CH
1	2.25, s	3.87, s	2.30-2.40, m	2.70, t	3.30, s	4.30, t	
2^c	2.23, s	3.80, s	1.80-2.80, m	b	3.30, s	4.20, t	5.32, t
3^d	2.25, s	3.83, s	2.30-2.40, m	b	3.35, s	4.30, t	5.62, t
			(MME)				
			[1.50-1.80, m				
			2.60-2.80, m				
			(COE)				

^as, singlet; t, triplet; m, multiplet. ^bnot separately found due to the multiplet of -CH₂. ^cwater peak; δ 4.80 ppm, s. ^dtriphenylphosphine; δ 7.20-7.80 ppm.

Table 2. Elemental Analysis of the Iridium Complexes

Compound		%C	%H	%N
1	Calcd.	26.0	4.70	5.06
	Found	26.3	5.12	4.78
2	Calcd.	30.4	5.57	3.54
	Found	30.4	5.63	2.90
3	Calcd.	39.5	4.95	1.44
	Found	38.9	4.86	1.47



at 1746 cm^{-1} for an uncoordinated carbonyl, and the strong and broad band around 3428 cm^{-1} region for asymmetric stretch of water. Water molecules might be included in this complex because NaCl from the reaction of $[\text{IrCl}(\text{COE})_2]_2$ with NaAsF_6 is washed by water and drying under vacuum for 6 hours could not remove the moisture. A weak band at 1550 cm^{-1} is assigned to the bonded olefin, a strong band at 700 cm^{-1} to AsF_6^- and the one at 529 cm^{-1} to Ir-N. The above data indicates the MME ligand is bonded through amine and sulfur and COE is also bonded to the metal. The ^1H NMR spectral data also indicates that both MME and COE are coordinated to iridium and the water peak appears at δ 4.80 ppm. The broad peak at δ 3.30 ppm is assigned to $-\text{NH}_2$ and peaks for CH_2 's of COE, MME and S- CH_2 are shown as multiplets altogether in the 1.80-2.80 ppm range. Elemental analysis of **2** corresponds to the 5-coordinated cationic complex, $[\text{Ir}(\text{MME})_2(\text{COE})]\text{AsF}_6 \cdot 2\text{H}_2\text{O}$ and the electrical conductivity in methanol is $85\text{ }\mu\text{ohms/cm}$ based on this formula. Due to the difficulty in crystal growing for all the compounds in this work, crystal structure has not been determined. The possible structure for **2** is square pyramid or trigonal bipyramid. Whether COE ligand is on the axial or equatorial site is not clear at this moment.

When the reaction is proceeded by the 1:1 mole ratio of iridium complex to MME with an excess of triphenylphosphine in the presence of NaAsF_6 , a yellow crystalline product (**3**) is obtained. Again, the free carbonyl group is observed at 1736 cm^{-1} , water at 3448 cm^{-1} , coordinated amine at 3150 cm^{-1} , coordinated olefin at 1540 cm^{-1} , AsF_6^- at 700 cm^{-1} , and Ir-N at 526 cm^{-1} . Together with the ^1H NMR data, the MME ligand is bonded through nitrogen and sulfur. The

elemental analysis suggests the molecular formula of **3** be a 4-coordinated complex, $[\text{Ir}(\text{COE})(\text{MME})(\text{PPh}_3)]\text{AsF}_6 \cdot 3\text{H}_2\text{O}$. The electrical conductance data based on this formula ($87\text{ }\mu\text{ohms/cm}$ in methanol) confirms **3** is a 1:1 electrolyte.

Hydrogenation Reaction. Hydrogenation reactions of styrene using the cationic iridium complexes have been carried out at $55\text{ }^\circ\text{C}$ under 5 atmospheric pressure of H_2 , with the styrene to iridium mole ratio of 800 to 1. The composition of the product was characterized by gas chromatography using Apiezon L column. The hydrogenation reaction has been completed after 5 hours with 97% yield of ethylbenzene and 3% of unreacted styrene for all three iridium complexes. Therefore, the iridium complexes in this work are acting as the catalysts for hydrogenation. Further reaction such as asymmetric hydrogenation of α -acetamido-cinnamic acid will be attempted at higher temperature and pressure since the iridium complexes in this work contains an asymmetric carbon center in the MME ligand, thus the complexes are potential asymmetric hydrogenation catalysts.

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