*Journal of Organometallic Chemistry*, 251 (1983) 369–375
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# DIOLEFIN CATIONIC IRIDIUM(I) COMPLEXES WITH SULFUR LIGANDS

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(Received February 8th, 1983)

## Summary

The preparation and properties of cationic iridium(I) complexes of the types $[Ir_2(\mu\text{-}L)_2(COD)_2](ClO_4)_2$ and $[Ir_2\{\mu\text{-}(L\text{-}L)\}_2(COD)_2](ClO_4)_2$ (COD = 1,5-cyclooctadiene, L and L–L = mono- and bi-dentate sulfur donor ligand, respectively) are described. The mononuclear complexes $[Ir(COD)L_2]ClO_4$ are also described. Reaction with triphenylphosphine gives pentacoordinated mixed complexes of the types $[Ir_2(\mu\text{-}L)_2(COD)_2(PPh_3)_2](ClO_4)_2$, $[Ir(COD)L_2(PPh_3)]ClO_4$ and $[Ir(COD)L(PPh_3)_2]ClO_4$.

## Introduction

We recently reported the ability of some sulfur ligands to give mononuclear or dinuclear diolefin cationic rhodium(I) complexes. Only rhodium(I) square planar derivatives were obtained when 1,5-cyclooctadiene was present as a ligand, but pentacoordinated complexes were obtained with 2,5-norbornadiene [1]. The use of iridium(I) should favour pentacoordination [2].

As far as we know, only one iridium(I) complex containing a sulfur ligand, viz. $[Ir(COD)(SCH_2CH_2SPh)_2]Cl$, has been described [3]. However, several cationic diolefin iridium(I) compounds of formula $[Ir(diolefin)L_2]^+$ with L = nitrogen or phosphorus ligands have been reported [4–8]. Some of them are very effective catalysts for the homogeneous hydrogenation of olefins [6–9]. In this paper we describe the preparation of new cationic complexes mono- and di-nuclear containing sulfur ligands of the types $[Ir(COD)L_2]ClO_4$, $[Ir_2(\mu\text{-}L)_2(COD)_2](ClO_4)_2$ and $[Ir_2\{\mu\text{-}(L\text{-}L)\}_2(COD)_2](ClO_4)_2$, and some related pentacoordinated complexes of iridium(I).

## Results and discussion

Dinuclear complexes $[Ir_2(\mu\text{-}L)_2(COD)_2](ClO_4)_2$ and $[Ir_2\{\mu\text{-}(L\text{-}L)\}_2(COD)_2](ClO_4)_2$ with bridging sulfur ligands can be prepared by addition of

0022-328X/83/$03.00

$AgClO_4$ to dichloromethane solutions of $[IrCl(COD)]_2$ [10] containing a stoichiometric amount of a monodentate (L) or bidentate (L–L) sulfur ligand:

$$[IrCl(COD)]_2 + 2L + 2AgClO_4 \rightarrow [Ir_2(\mu\text{-}L)_2(COD)_2](ClO_4)_2 + 2AgCl \qquad (1)$$

(L = tetrahydrothiophen (tht), trimethylene sulfide (tms), $SMe_2$, or $SEt_2$)

$$[IrCl(COD)]_2 + 2L\text{–}L + 2AgClO_4 \rightarrow [Ir_2\{\mu\text{-}(L\text{–}L)\}_2(COD)_2](ClO_4)_2 + 2AgCl \qquad (2)$$

(L–L = 1,4-dithiacyclohexane (dt), $(t\text{-}BuS)_2(CH_2)_2$, or $(CH_3S)_2$)

It is noteworthy that these dinuclear complexes are also formed in the presence of an excess of L = $SMe_2$, $SEt_2$ or L–L = dt, $(t\text{-}BuS)_2(CH_2)_2$ or $(CH_3S)_2$. However, mononuclear complexes $[Ir(COD)L_2]ClO_4$ with L are formed when an excess of the ligand tht or tms is present.

An alternative method of preparation of $[Ir_2(\mu\text{-}L)_2(COD)_2](ClO_4)_2$ and $[Ir_2\{\mu\text{-}(L\text{–}L)\}_2(COD)_2](ClO_4)_2$ complexes, where L = $SMe_2$ or $SEt_2$ and L–L = dt, $(t\text{-}BuS)_2(CH_2)_2$, or $(CH_3S)_2$, involves the addition to dichloromethane solutions of $[Ir(COD)_2]ClO_4$ [4,6] of the stoichiometric amount or excess of the corresponding monodentate or bidentate sulfur ligand.

$$2[Ir(COD)_2]ClO_4 + 2L \rightarrow [Ir_2(\mu\text{-}L)_2(COD)_2](ClO_4)_2 + 2COD \qquad (3)$$

(L = $SMe_2$, $SEt_2$)

$$2[Ir(COD)_2]ClO_4 + 2L\text{–}L \rightarrow [Ir_2\{\mu\text{-}(L\text{–}L)\}_2(COD)_2](ClO_4)_2 + 2COD \qquad (4)$$

(L–L = dt, $(t\text{-}BuS)_2(CH_2)_2$, $(CH_3S)_2$)

As expected this reaction give mononuclear compounds of formula $[Ir(COD)L_2]ClO_4$ when the tetrahydrothiophen or trimethylene sulfide is used in 2/1 ligand/Ir ratio.

The isolated complexes are moderately stable in the solid state but decompose in solutions exposed to air. The C, H and S elemental analyses, molar conductivities in acetone, melting points, and yields of the isolated complexes are listed in Table 1.

The nuclearity of the dinuclear complexes were established by measuring the conductivities of acetone or nitromethane solutions of different concentrations. The values of $A$ in Onsager's equation ($\Lambda_e = \Lambda_0 - A\sqrt{c}$) [11], measured in the concentration range ca. $10^{-3}$–$10^{-5}$ $M$, lie between 600 and 1100 in acetone and between 300 and 650 in nitromethane, confirming the binuclear nature of the complexes (2/1 electrolytes) [11,12]. Conductance studies on the previously described $[Rh(COD)L_2]ClO_4$ complexes [1] in acetone, show that they can also be regarded as dinuclear species ($L_2$ = dt, $(t\text{-}BuS)_2(CH_2)_2$; $A$ = 1100, 900). It should be noted, however, that $SEt_2$ and dt can act as bridging ligands in rhodium complexes [1,13].

The reaction of $[Ir(COD)L_2]ClO_4$ (L = tht, tms) with one or two mols of triphenylphosphine gives pentacoordinated derivates of formula $[Ir(COD)L_2(PPh_3)]ClO_4$ or $[Ir(COD)L(PPh_3)_2]ClO_4$ (Scheme 1). Under the same conditions analogous $[Rh(COD)L_2]ClO_4$ complexes react with $PPh_3$ with formation of the square-planar $[Rh(COD)L(PPh_3)]ClO_4$ complexes [14] and $[Rh(COD)(PPh_3)_2]ClO_4$ [15], in keeping with the low tendency of rhodium(I) to form pentacoordinated complexes when 1,5-cyclooctadiene is used as a ligand [16].

On the other hand the binuclear complexes $[Ir_2(\mu\text{-}L)_2(COD)_2](ClO_4)_2$ (L = $SMe_2$,

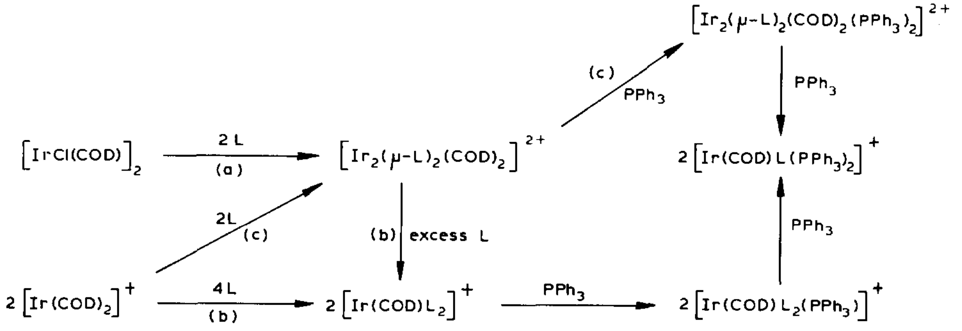
TABLE 1

ANALYTICAL RESULTS, CONDUCTIVITIES, MELTING POINTS AND YIELDS OF THE COMPLEXES $[Ir_2(\mu\text{-}L)_2(COD)_2](ClO_4)_2$, $[Ir_2(\mu\text{-}(L\text{-}L))_2(COD)_2](ClO_4)_2$ AND $[Ir(COD)L_2](ClO_4)$

| Complex | | Found(calcd.) (%) | | | Conductivity data | | Yield (%) | M.p. [a] (°C) | Colour |
|---|---|---|---|---|---|---|---|---|---|
| | | C | H | S | $A$ [b] | $\Lambda_M$ (ohm$^{-1}$ cm$^2$ mol$^{-1}$) | | | |
| I | $[Ir_2(\mu\text{-tht})_2(COD)_2](ClO_4)_2$ | 28.92<br>(29.50) | 4.23<br>(4.10) | 6.82<br>(6.55) | 610 [c] | 223 [d] | 85 | 80–85 | orange |
| II | $[Ir_2(\mu\text{-tms})_2(COD)_2](ClO_4)_2$ | 28.62<br>(27.85) | 3.93<br>(3.79) | 7.20<br>(6.75) | 475 [c] | 182 [d] | 60 | 90–95 | orange |
| III | $[Ir_2(\mu\text{-SMe}_2)_2(COD)_2](ClO_4)_2$ | 25.02<br>(25.97) | 3.96<br>(3.89) | 7.12<br>(6.92) | 305 [c] | 233 [d] | 90 | 70–75 | yellow |
| IV | $[Ir_2(\mu\text{-SEt}_2)_2(COD)_2](ClO_4)_2$ | 29.26<br>(29.39) | 4.55<br>(4.49) | 6.67<br>(6.53) | 520 [c] | 198 [d] | 85 | 65–70 | orange |
| V | $[Ir_2(\mu\text{-dt})_2(COD)_2](ClO_4)_2$ | 27.88<br>(27.69) | 3.96<br>(3.84 | 11.99<br>(12.30) | 1070 [d] | 248 [d] | 90 | 170–175 | white |
| VI | $[Ir_2(\mu(\text{t-BuS})_2(CH_2)_2)_2(COD)_2](ClO_4)_2$ | 35.02<br>(35.64) | 5.40<br>(5.61) | 10.32<br>(10.56) | 720 [d] | 202 [d] | 90 | 140–145 | orange |
| VII | $[Ir_2(\mu\text{-}(CH_3S)_2)_2(COD)_2](ClO_4)_2$ | 24.06<br>(24.29) | 3.76<br>(3.64) | 13.42<br>(12.95) | 835 [d] | 200 [d] | 75 | 125–130 | pink |
| VIII | $[Ir(COD)(tht)_2]ClO_4$ | 32.90<br>(33.31) | 4.92<br>(4.86) | 11.56<br>(11.10) | – | 132 [d] | 85 | 145–148 | yellow |
| IX | $[Ir(COD)(tms)_2]ClO_4$ | 30.12<br>(30.65) | 4.40<br>(4.37) | 11.48<br>(11.68) | – | 116 [d] | 85 | 115–120 | yellow |

[a] Decomposes. [b] Slope found for Onsager's equation $\Lambda_e = \Lambda_o - A\sqrt{c}$ [11]. [c] Measured in nitromethane solution. [d] Measured in acetone solution.

SCHEME 1. Monodentate sulfur ligands. (a) L = tht, tms, $SMe_2$, $SEt_2$; (b) L = tht, tms; (c) L = $SMe_2$, $SEt_2$.



$SEt_2$) react with a stoichiometric amount of $PPh_3$ to give the dinuclear derivatives $[Ir_2(\mu\text{-}L)_2(COD)_2(PPh_3)_2](ClO_4)_2$. Conductance studies give values of $A$ corresponding to binuclear species ($A = 630$, 855 in acetone). If the sulfur is assumed to be bridging, these compounds probably have the iridium in a pentacoordinated environment.

Mononuclear pentacoordinated $[Ir(COD)L(PPh_3)_2]ClO_4$ complexes are formed by addition of the stoichiometric amount of $PPh_3$ to the dinuclear $[Ir_2(\mu\text{-}L)_2(COD)_2(PPh_3)_2](ClO_4)_2$ complexes. The latter complexes $[Ir(COD)L(PPh_3)_2]ClO_4$ are also obtained by addition of triphenylphosphine in 2/1 $PPh_3$/Ir ratio to $[Ir_2(\mu\text{-}L)_2(COD)_2](ClO_4)_2$ (L = $SMe_2$ or $SEt_2$).

At the complexes containing both $PPh_3$ and sulfur ligands are air stable. Their C, H, and S elemental analyses, molar conductivities in acetone [17], melting points, and yields are listed in Table 2.

The IR spectra of all the complexes isolated show bands due to the coordinated diolefin 1,5-cyclooctadiene together with those due to the relevant sulfur ligands and triphenylphosphine coordinated. The spectra of the perchlorates show bands due to the uncoordinated perchlorate anion (1100s and 620m $cm^{-1}$) [18].

## Experimental

All reactions were carried out at room temperature, under nitrogen in deoxygenated solvents. The C, H and S analyses were carried out with a Perkin–Elmer 240B microanalyzer. The IR spectra were recorded on a Beckman IR4260 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in acetone solutions, in the concentration range ca.$1 \times 10^{-4}$–$5 \times 10^{-4}$, with a Red. Copenh. CDM3 Radiometer conductimeter. Values of $A$ in Onsager's equation $\Lambda_e = \Lambda_0 - A\sqrt{c}$ were calculated from measurements at several concentrations in acetone or nitromethane in the $5 \times 10^{-3}$–$5 \times 10^{-5}$ $M$ range. Melting points were determinated with a Buchi 510 apparatus.

### *Preparation of $[Ir_2(\mu\text{-}L)_2(COD)_2](ClO_4)_2$ and $[Ir_2\{\mu\text{-}(L\text{–}L)\}_2(COD)_2](ClO_4)_2$ complexes*

(i) A slight excess of ligand L or L–L (0.22 mmol) and the stoichiometric amount of $AgClO_4$ (0.20 mmol) were added to dichloromethane solutions of $[IrCl(COD)]_2$ (0.1 mmol). The mixture was stirred in the absence of light for 1 h, then the solution

TABLE 2

ANALYTICAL RESULTS, CONDUCTIVITIES DATA, MELTING POINTS, COLOURS, AND YIELDS OF THE COMPLEXES $[Ir(COD)L_2(PPh_3)]ClO_4$, $[Ir_2(\mu\text{-}L)_2(COD)_2(PPh_3)_2](ClO_4)_2$ and $[Ir(COD)L(PPh_3)_2]ClO_4$

| Complex | | Found(calcd.)(%) | | | Conductivity Data | | Yield (%) | M.p. [a] (°C) | Colour |
|---|---|---|---|---|---|---|---|---|---|
| | | C | H | S | $A$ [b] | $\Lambda_M$ ($ohm^{-1}$ $cm^2$ $mol^{-1}$) | | | |
| X | $[Ir(COD)(tht)_2(PPh_3)]ClO_4$ | 49.25<br>(48.67) | 5.37<br>(5.13) | 7.25<br>(7.63) | – | 142 | 85 | 155 | orange |
| XI | $[Ir(COD)(tms)_2(PPh_3)]ClO_4$ | 48.20<br>(47.40) | 4.66<br>(4.81) | 7.60<br>(7.90) | – | 150 | 75 | 165 | orange |
| XII | $[Ir_2(\mu\text{-}SMe_2)_2(COD)_2(PPh_3)_2](ClO_4)_2$ | 47.02<br>(46.40) | 4.78<br>(4.56) | 4.68<br>(4.42) | 630 [d] | 271 | 70 | 85–90 | orange |
| XIII | $[Ir_2(\mu\text{-}SEt_2)_2(COD)_2(PPh_3)_2](ClO_4)_2$ | 48.30<br>(47.87) | 5.20<br>(4.92) | 4.12<br>(4.25) | 855 [d] | 257 | 70 | 95–100 | pink |
| XIV | $[Ir(COD)(tht)(PPh_3)_2]ClO_4$ | 57.86<br>(56.91) | 4.76<br>(4.94) | 2.98<br>(3.16) | – | 148 | 75 | 150–155 | pink |
| XV | $[Ir(COD)(tms)(PPh_3)_2]ClO_4$ | 57.60<br>(56.50) | 5.02<br>(4.81) | 3.02<br>(3.20) | – | 148 | 55 | 125–130 | pink |
| XVI | $[Ir(COD)(SMe_2)(PPh_3)_2]ClO_4$ | 54.70<br>(56.00) | 4.95<br>(4.86) | 2.92<br>(3.24) | – | 150 | 60 | 140–145 | pink |
| XVII | $[Ir(COD)(SEt_2)(PPh_3)_2]ClO_4$ | 55.26<br>(56.80) | 5.22<br>(5.13) | 2.84<br>(3.15) | – | 154 | 60 | 165–170 | red |

[a] Decomposes. [b] Slope found for Onsager's equation $\Lambda_e = \Lambda_o - A\sqrt{c}$ [11]. [d] Measured in acetone solution.

was filtered through Kieselghur. Addition of diethyl ether to the filtrate gave a precipitate, which was filtered off, washed with ether, and vacuum dried. All the $[Ir_2(\mu\text{-}L)_2(COD)_2](ClO_4)_2$ and $[Ir_2\{\mu\text{-}(L\text{-}L)\}_2(COD)_2](ClO_4)_2$ complexes were prepared by this route.

(ii) Addition of a slight excess over the stoichiometric amount of ligand, L = $SMe_2$, $SEt_2$ or L–L (0.12 mmol), to dichloromethane solutions of $[Ir(COD)_2]ClO_4$ (0.1 mmol) resulted in an immediate reaction. The complexes produced were precipitated by adding ether, then filtered off, washed with ether, and vacuum dried.

### *Preparation of $[Ir(COD)L_2]ClO_4$ complexes (L = tht or tms)*

(i) When the method (i) (above) was used with a 2/1 L/Ir ratio for L = tht or tms, the mononuclear $[Ir(COD)L_2]ClO_4$ complexes were isolated.

(ii) A slight excess (0.22 mmol) of tht or tms was added to a solution of $[Ir(COD)_2]ClO_4$ (0.1 mmol) in dichloromethane. Addition of ether gave a precipitate, which was filtered off, washed with ether, and vacuum dried.

### *Preparation of $[Ir(COD)L_2PPh_3]ClO_4$ complexes (L = tht or tms)*

A stoichiometric amount of $PPh_3$ (0.1 mmol) was added to a solution of the $[Ir(COD)L_2]ClO_4$ complex (0.1 mmol), in dichloromethane, prepared "in situ" as described above (ii) in the presence of an excess of the sulfur ligand. The product was precipitated by addition of diethyl ether, filtered off, washed with ether, and vacuum dried.

### *Preparation of $[Ir_2(\mu\text{-}L)_2(COD)_2(PPh_3)_2](ClO_4)_2$ complexes (L = $SMe_2$ or $SEt_2$)*

A stoichiometric amount of $PPh_3$ (0.1 mmol) was added to a dichloromethane solution of the $[Ir_2(\mu\text{-}L)_2(COD)_2](ClO_4)_2$ complex (0.05 mmol) prepared "in situ". Addition of diethyl ether gave the corresponding $[Ir_2(\mu\text{-}L)_2(COD)_2(PPh_3)_2](ClO_4)_2$ complex. The solid was filtered off, washed with ether, and vacuum dried.

### *Preparation of $[Ir(COD)L(PPh_3)_2]ClO_4$ complexes*

$PPh_3$ in 2/1 $PPh_3$/Ir ratio was added to a dichloromethane solution of $[Ir(COD)L_2]ClO_4$ (L = tht or tms) and $[Ir_2(\mu\text{-}L)_2(COD)_2](ClO_4)_2$ (L = $SMe_2$ or $SEt_2$), prepared "in situ" in the presence of excess of ligand. The pentacoordinate $[Ir(COD)L(PPh_3)_2]ClO_4$ complex was precipitated by addition of diethyl ether, washed with ether, and vacuum dried.

## Acknowledgements

We thank Prof. Dr. L.A. Oro for many helpful discussions.

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