Inorganica Chimica Acta, *73* (1983) 275–279

Cationic Iridium(I) Complexes with 1,5-Cyclooctadiene and Nitrogen Ligands

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Received January 5, 1983

The preparation and catalytic properties of cationic tetracoordinated iridium complexes with 1,5-cyclooctadiene and mono- or bidentate nitrogen donor ligands are described. The related [Ir(COD)(π-PhNPh$_2$)]BF$_4$ and [Ir(COD)(π-PhNHPh)]BF$_4$ complexes, containing the amine group coordinated to the metal via *π-interaction of an arene ring, have been also prepared. On the other hand five-coordinated complexes of formula [Ir(OClO$_3$)(COD)(TFB)] and [Ir(COD)(TFB)(nitrile)]$^+$ are reported.*

Introduction

The preparation of several cationic diolefin iridium(I) complexes with nitrogen donor ligands of general formulae [Ir(diolefin)L$_2$]$^+$ (L = MeCN [1, 2] and pyridine type ligands [3, 4]; L$_2$ = 2,2′-bipyridine, 1,10-phenanthroline or Schiff-base type ligands [1, 4–10], have been reported. In the present paper we describe the synthesis and properties of new square-planar or pentacoordinated iridium 1,5-cyclooctadiene complexes with nitrogen donor ligands, as well as, the ability of a phenyl ring of NPh$_3$ or NHPh$_2$ to coordinate to the iridium atom.

Results and Discussion

Complexes with Monodentate Nitrogen Ligands

The reaction of the dimeric complex [IrCl(COD)]$_2$ [11] with silver tetrafluoroborate in the presence of an excess of nitrile ligands leads to the formation of species of the type [Ir(COD)L$_2$]BF$_4$ (eqn. (1)):

$$\tfrac{1}{2}[\mathrm{IrCl(COD)}]_2 + \mathrm{AgBF_4} + 2\mathrm{L} \longrightarrow [\mathrm{Ir(COD)L_2}]\mathrm{BF_4} + \mathrm{AgCl} \qquad (1)$$

L = benzonitrile (bzn), phenylacetonitrile (PhCH$_2$CN), 4-methylbenzonitrile(4-Mebzn), 4-methoxybenzonitrile(4-MeObzn), 2-chlorobenzonitrile(2-Clbzn).

The IR spectra (in Nujol mulls) of the resulting complexes show a band in the 2289–2251 cm^{-1} region, corresponding to the stretching vibration ν(C≡N), which is shifted 25–34 cm^{-1} towards higher energies relative to the vibration of the free nitrile, being consistent with the coordination of the ligand *via* the free electron pair of the nitrogen [12].

The reaction of the previously described complex [Ir(COD)(MeCN)$_2$]BF$_4$ [1, 2] and the analogous perchlorate complex prepared according to eqn. (1), with pyridine- or quinoline-type ligands gives rise to the displacement of the coordinated acetonitrile (eqn. (2)):

$$[\mathrm{Ir(COD)(MeCN)_2}]\mathrm{A} + 2\mathrm{L} \longrightarrow [\mathrm{Ir(COD)L_2}]\mathrm{A} + 2\mathrm{MeCN} \qquad (2)$$

A = BF$_4^-$, L = 2-methylpyridine(2-Mepy), 2-ethylpyridine(2-Etpy), 5-nitro, 6-methylquinoline(5-NO$_2$, 6-Mequin).

A = ClO$_4^-$, L = quinoline(quin), 4,7-dichloroquinoline(4,7-Cl$_2$quin).

Alternatively, this type of complex can also be prepared by reacting [IrCl(COD)]$_2$ with silver tetrafluoroborate in the presence of the corresponding ligand (L = 2-methoxypyridine(2-MeOPy), 6-methylquinoline(6-Mequin), 5-NO$_2$, 6-Mequin).

Complexes with Bidentate Nitrogen Ligands

Whilst the addition of monodentate aromatic nitriles to solutions of the [Ir(COD)(MeCN)$_2$]$^+$ complex does not lead to the displacement of the coordinated acetonitrile, the addition of the potentially bidentate ligand succinonitrile yields the [Ir(COD)(sucn)]$^+$ derivative. A similar behaviour is observed for chelating bidentate nitrogen ligands (eqn. (3)):

$$[\mathrm{Ir(COD)(MeCN)_2}]\mathrm{A} + \mathrm{L{-}L} \longrightarrow [\mathrm{Ir(COD)(L{-}L)}]\mathrm{A} + 2\ \mathrm{MeCN} \qquad (3)$$

0020-1693/83/$3.00

A = ClO_4^-, L–L = succinonitrile(sucn), 8-aminoquinoline (8-NH_2quin), ethylenediamine(en), N,N,N′,N′-tetramethylethylenediamine(tmeda), 1,2-diphenylethylenediamine(stien).

A = BF_4^-, L–L = sucn, en.

A significant shift to lower frequencies of the ν(N–H) bands of the diamine ligand was found after coordination. These diamine derivatives decompose in air.

Pentacoordinated Complexes

Attempts to prepare [Ir(COD)(TFB)]ClO_4 by the reaction of $[IrCl(COD)]_2$ with silver perchlorate in the presence of tetrafluorobenzobarrelene (TFB) led to the formation of the pentacoordinated complex [Ir($OClO_3$)(COD)(TFB)]. The presence of the Ir–$OClO_3$ bond is revealed by bands which are characteristic of the $OClO_3$ group (C_{3v}) [13].

The coordinated perchlorate group can be displaced by acetonitrile or phenylacetonitrile. The reactions give rise to the formation of the pentacoordinated complexes [Ir(COD)(TFB)(MeCN)]ClO_4 and [Ir(COD)(TFB)($PhCH_2CN$)]ClO_4. The acetonitrile complex can also be prepared according to eqn. (4):

$$[Ir(COD)(MeCN)_2]ClO_4 + TFB \longrightarrow [Ir(COD)(TFB)(MeCN)]ClO_4{}^* + MeCN \qquad (4)$$

π-Arene Complexes

An interesting reaction takes place when di- or triphenylamine are added to dichloromethane–acetone suspensions of $[IrCl(COD)]_2$ and silver tetrafluoroborate. The silver chloride formed is filtered off and white solids are obtained from the filtrates. Their IR spectra reveal the presence of the uncoordinated tetrafluoroborate anion and the coordinated amine ligand. Analytical results suggest the presence of only one molecule of the amine per iridium atom (Table I). Their molar conductivities are as expected for 1:1 electrolytes. Their ^1H NMR spectra in deuterochloroform show, along with the protons of the coordinated 1,5-cyclooctadiene three complex multiplets centered at δ = 7.4, 6.6 and 6.0 ppm, in the triphenylamine complex and two complex multiplets centered at δ = 7.4 and 6.4 ppm in the diphenylamine derivative.

All these data support the formulation of the complexes as arene compounds, *via* the π-coordination of one of the aromatic rings of the amine ligand (eqn. (5)):

$$\tfrac{1}{2}[IrCl(COD)]_2 + AgBF_4 + NRPh_2 \longrightarrow [Ir(COD)(\pi\text{-}PhNRPh)]BF_4 + AgCl \qquad (5)$$

R = H or Ph

This type of coordination is particularly common in the tetraphenylborate anion and the reported ^1H NMR data for these complexes [14] are in agreement with the spectra described above for the di- and triphenylamine complexes. On the other hand, some iron-diphenylamine complexes, where the diphenylamine ligand is coordinated *via* a phenyl ring have been reported [15].

Table I lists analytical results, yields, colours and relevant IR data for all the complexes reported in this paper.

Catalytic Activity

The obtained tetracoordinated complexes catalyze the hydrogen transfer from isopropanol to acetophenone and cyclohexene, their catalytic behaviour being dependent upon the nitrogen donor ligand (Table II). Those containing nitrile type ligands give rise to moderately active systems, whereas those with pyridine- or quinoline-type ligands lead generally to only little-active catalysts, except for the complex [Ir(COD)(5-NO_2, 6-Mequin)$_2$]BF_4 which shows a relatively high capacity for the reduction of acetophenone to 1-phenylethanol.

The complexes with bidentate nitrogen ligands give rise to systems which are more active than the others described in the present study. They are generally more active in the hydrogen transfer from isopropanol to acetophenone than to cyclohexene. As has already been observed [16] for analogous rhodium complexes the best results for diamine type ligands are obtained with primary diamines (Table III). In general, these iridium complexes are less readily reduced to metal than the corresponding rhodium derivatives.

The herein-mentioned complexes are comparatively less active than those with ligands of the Me_x-Phen-type studied extensively by Mestroni *et al.* [17–19].

Experimental

All reactions were carried out under nitrogen atmosphere at room temperature. Solvents were dried and distilled before use. The C, H and N analyses were made with a Perkin-Elmer 240 microanalyzer. The IR spectra (4000–200 cm^{-1} range) were recorded on a Perkin-Elmer 577 spectrophotometer, using nujol mulls between polyetheylene sheets. The ^1H NMR spectra were obtained with a Perkin-Elmer R-12B spectrometer. The analyses of the catalytic reactions were carried out with a Perkin-Elmer 3920

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*The analogous [Ir(COD)(TFB)(bzn)]BF_4 was similarly prepared starting from [Ir(COD)(bzn)$_2$]BF_4.

TABLE I. Analytical Results, Yields, Colours and IR Data[a] for the New Isolated Complexes.

Complex		Found (calcd.) (%)			Yield (%)	Colour	IR data (cm^{-1})
		C	H	N			
1	$[Ir(COD)(bzn)_2]BF_4$	44.5 (44.5)	4.2 (3.7)	4.9 (4.7)	62	orange	2256(s)[b]
2	$[Ir(COD)(PhCH_2CN)_2]BF_4$	46.9 (46.4)	4.4 (4.2)	4.6 (4.5)	60	yellow	2289(m)[b]
3	$[Ir(COD)(4\text{-}Mebzn)_2]BF_4$	46.7 (46.4)	4.3 (4.2)	4.6 (4.5)	70	orange	2261(s)[b]
4	$[Ir(COD)(4\text{-}MeObzn)_2]BF_4$	44.7 (44.1)	4.4 (4.0)	4.4 (4.3)	61	yellow	2251(s)[b]
5	$[Ir(COD)(2\text{-}Clbzn)_2]BF_4$	39.3 (39.9)	3.1 (3.0)	4.0 (4.2)	84	red	2261(w)[b]
6	$[Ir(COD)(2\text{-}Mepy)_2]BF_4$	41.4 (41.9)	4.9 (4.6)	4.8 (4.9)	77	yellow	
7	$[Ir(COD)(2\text{-}Etpy)_2]BF_4$	43.2 (43.9)	5.3 (5.0)	4.7 (4.7)	78	yellow	
8	$[Ir(COD)(5\text{-}NO_2, 6\text{-}Mequin)_2]BF_4$	43.9 (44.0)	4.0 (3.7)	7.0 (7.3)	80	yellow	
9	$[Ir(COD)(quin)_2]ClO_4$	46.7 (47.4)	4.2 (4.0)	4.0 (4.3)	80	yellow	
10	$[Ir(COD)(4,7\text{-}Cl_2quin)_2]ClO_4$	38.4 (39.2)	2.8 (2.8)	3.4 (3.5)	55	yellow	
11	$[Ir(COD)(2\text{-}MeOpy)_2]BF_4$	39.8 (39.7)	4.5 (4.3)	4.3 (4.6)	67	yellow	
12	$[Ir(COD)(6\text{-}Mequin)_2]BF_4$	50.0 (49.9)	4.9 (4.5)	4.0 (4.2)	62	yellow	
13	$[Ir(COD)(sucn)]BF_4$	30.3 (30.8)	3.5 (3.4)	5.9 (6.0)	76	yellow	2310(w), 2295(sh)[b]
14	$[Ir(COD)(8\text{-}NH_2quin)]ClO_4$	37.1 (37.6)	3.6 (3.5)	4.6 (5.2)	83	red	3206(m), 3176(w)[c] 3106(m), 3076(m)[c]
15	$[Ir(COD)(en)]BF_4$	26.0 (26.8)	4.5 (4.5)	6.9 (6.3)	77	yellow	
16	$[Ir(COD)(tmeda)]ClO_4$	32.4 (32.6)	5.6 (5.5)	5.6 (5.4)	72	yellow	
17	$[Ir(COD)(stien)]ClO_4$	42.5 (43.2)	4.5 (4.6)	4.5 (4.6)	73	yellow	3290(s), 3231(s)[c]
18	$[Ir(COD)(sucn)]ClO_4$[d]	29.1 (29.6)	3.4 (3.3)	5.2 (5.7)	59	yellow	
19	$[Ir(COD)(en)]ClO_4$	26.5 (26.1)	4.4 (4.4)	7.0 (6.1)	76	yellow	3291(s), 3245(s)[c]
20	$[Ir(OClO_3)(COD)(TFB)]$	38.2 (38.4)	3.1 (2.9)		57	pink	1130(vs), 1025(vs), 620(s)(br)[e]
21	$[Ir(COD)(TFB)(MeCN)]ClO_4$	39.6 (39.6)	3.4 (3.2)	2.0 (2.1)	73	white	2310(w)[b]
22	$[Ir(COD)(TFB)(bzn)]BF_4$	44.9 (45.3)	2.8 (3.3)	1.9 (1.9)	37	white	2250(w)[b]
23	$[Ir(COD)(TFB)(PhCH_2CN)]ClO_4$	44.4 (45.2)	2.2 (3.9)	1.8 (1.9)	37	white	2290(w)[b]
24	$[Ir(COD)(\pi\text{-}PhNPh_2)]BF_4$	48.9 (49.4)	4.3 (4.3)	2.3 (2.2)	59	white	1100(vs)(br), 525(s)[f]
25	$[Ir(COD)\pi\text{-}PhNHPh)]BF_4$	43.7 (43.2)	3.8 (4.2)	2.5 (2.5)	57	white	1100(vs)(br), 525(s)[f]

[a] Nujol mulls. [b] $\nu(C{\equiv}N)$. [c] $\nu(N{-}H)$. [d] This complex is explosive in the solid state. [e] $-OClO_3$ group. [f] BF_4^- group.

TABLE II. Hydrogen Transfer Reduction of Acetophenone and Cyclohexene Catalyzed by Cationic Iridium(I) Complexes.

Complex	Conversion (%) after two hours	
	acetophenone	cyclohexene
$[Ir(COD)(bzn)_2]BF_4$	27	6
$[Ir(COD)(PhCH_2CN)_2]BF_4$	10	5
$[Ir(COD)(4\text{-}Mebzn)_2]BF_4$	23	8
$[Ir(COD)(4\text{-}MeObzn)_2]BF_4$	22	10
$[Ir(COD)(2\text{-}Clbzn)_2]BF_4$	23	7
$[Ir(COD)(2\text{-}MeOpy)_2]BF_4$	0	5
$[Ir(COD)(2\text{-}Mepy)_2]BF_4$	3	13
$[Ir(COD)(2\text{-}Etpy)_2]BF_4$	0	6
$[Ir(COD)(6\text{-}Mequin)_2]BF_4$	5	6
$[Ir(COD)(quin)_2]ClO_4$	6	6
$[Ir(COD)(4,7\text{-}Cl_2quin)_2]ClO_4$	0	0
$[Ir(COD)(5\text{-}NO_2,6\text{-}Mequin)_2]BF_4$	69	0
$[Ir(COD)(sucn)]BF_4$	17	0
$[Ir(COD)(8\text{-}NH_2quin)]ClO_4$	51	0
$[Ir(COD)(en)]BF_4$	92	12
$[Ir(COD)(stien)]ClO_4$	57	3
$[Ir(COD)(tmeda)]ClO_4$	5	7

TABLE III. Hydrogen Transfer Reduction of Acetophenone Catalyzed by $[M(diolefin)(diamine)]^+$ Complexes.

M[a]	Conversion (%) after two hours		
	primary diamine	secondary diamine	tertiary diamine
Rh	95 (stien)	28 (tpen)[b]	6 (tmeda)
Ir	92 (en) 57 (stien)		5 (tmeda)

[a] M = Rh, diolefin = NBD; M = Ir, diolefin = COD. [b] 2,N,N'-triphenylethylenediamine.

B chromatograph, connected to a Perkin-Elmer M-2 calculation integrator.

Preparation of the Compounds of the $[Ir(COD)L_2]BF_4$-Type (L = Nitrile Ligand (1–5))

To dichloromethane solutions of $[IrCl(COD)]_2$ were added stoichiometric amounts of silver tetrafluoroborate in dichloromethane and large excess of the nitrile (L = bzn, $PhCH_2CN$, 4-Mebzn) or Ir/L = 1/2.5 molar ratio (L = 4-MeObzn, 2-Clbzn). The mixtures were stirred for 30 minutes and the silver chloride formed was filtered off. Concentration of the filtrates and slow addition of diethylether led to the precipitation of the required complexes.

Preparation of the Compounds of the $[Ir(COD)L_2]A$ Type (L = Pyridine or Quinoline-type Ligand; A = BF_4^-, ClO_4^-) (6–12)

These complexes were prepared by the two different routes described below.

i) To stirred solutions of $[Ir(COD)(MeCN)_2]A$ in acetone were added the respective ligands L in 1/3 molar ratio. After stirring for 30 minutes, the resulting yellow solutions were concentrated under reduced pressure. Addition of diethylether led to the precipitation of the required complexes.

ii) To dichloromethane solutions of $[IrCl(COD)]_2$ were added stoichiometric amounts of silver tetrafluoroborate in acetone and the respective ligands L in 1/2.5 molar ratio. The mixtures were stirred for 30 minutes, and the silver chloride formed was filtered off. Concentration of the filtrates and slow addition of diethylether led to the precipitation of the required complexes.

Preparation of the Compounds of the [Ir(COD)(L–L)]A type (L–L = Bidentate Nitrogen Ligand; A = BF_4^-, ClO_4^-) (13–19)

To stirred solutions of $[Ir(COD)(MeCN)_2]A$ in acetone or dichloromethane were added stoichiometric amounts of the respective ligands L–L. The resulting solutions were stirred for 30 minutes and then concentrated under reduced pressure. Subsequent addition of diethylether led to the precipitation of the required complexes.

Preparation of [Ir(OClO$_3$)(COD)(TFB)] (20)

Silver perchlorate (50.3 mg, 0.24 mmol), suspended in dichloromethane was added to a dichloromethane solution of 81.5 mg (0.12 mmol) of $[IrCl(COD)]_2$ containing 162.8 mg (0.72 mmol) of tetrafluorobenzobarrelene. The mixture was stirred for 30 minutes and the silver chloride formed was filtered off. Concentration of the filtrate and addition of diethylether led to the precipitation of the formulated complex (85.4 mg).

Preparation of the Compounds of the [Ir(COD)(TFB)L]A Type (L = Nitrile Ligand; A = BF_4^-, ClO_4^-) (21–23)

These complexes were prepared by the two different routes described below.

i) To stirred solutions of $[Ir(COD)L_2]A$ (L = MeCN, A = ClO_4^-; L = bzn, A = BF_4^-) in dichloromethane, tetrafluorobenzobarrelene was added in 1/1.5 molar ratio. After stirring for one hour, the resulting solutions were concentrated under reduced pressure. Addition of diethylether led to the precipitation of the required complexes.

ii) To stirred solutions of $[Ir(OClO_3)(COD)(TFB)]$ in dichloromethane MeCN or $PhCH_2CN$ was added in 1/1 molar ratio. After stirring for one hour, the resulting solutions were concentrated under reduced pressure. Addition of diethylether led to the precipitation of the required complexes.

Preparation of the Compounds [Ir(COD)(π-Ph-NRPh)]BF$_4$ (R = H, Ph) (24–25)

Stoichiometric amounts of silver tetrafluoroborate in acetone were added to dichloromethane solutions of $[IrCl(COD)]_2$ containing the corresponding $NRPh_2$ ligand in $Ir/NRPh_2$ = 1/3 molar ratio. The mixtures were stirred for 30 minutes and the silver chloride was filtered off. Concentration of the filtrates and addition of diethylether led to the precipitation of the required complexes.

Catalytic Activity

The transfer hydrogenation reactions were carried out under argon in refluxing isopropanol with magnetic stirring. The equipment consisted of a 50 ml round bottom flask, fitted with a condenser and provided with a serum cap. The catalysts were prepared by adding 0.1 mmol of potassium hydroxide in 1 ml of isopropanol to a solution (8 ml) of $[Ir(COD)L_2]A$ or $[Ir(COD)(L–L)]A$ (0.02 mmol). The resulting solution was refluxed for 1 hour and 2 mmol of the substrate in 1 ml of isopropanol was injected.

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