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COMPLEXES OF RHODIUM(I) AND IRIDIUM(I) WITH OPTICALLY ACTIVE SCHIFF BASES

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Summary

The synthesis and the reactions of cationic complexes of rhodium(I) and iridium(I) of the type [M(N—N')(COD)]$^+$ and [M(N—N')(CO)$_2$]$^+$ (N—N' = Schiff bases of pyridine-2-aldehyde; COD = *cis,cis*-1,5-cyclooctadiene) are reported.

Introduction

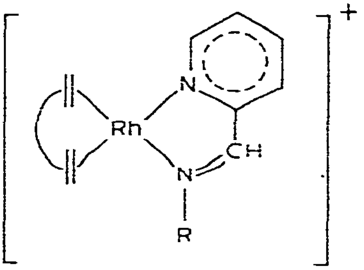
In recent years several complexes of rhodium(I), ruthenium(II), and other transition metals have been found to be active catalysts for the hydrogenation of ketones and olefins [1]. By using optically active complexes it is possible to obtain asymmetric hydrogenation reactions [2,3]. Usually these catalysts contain phosphines or diphosphines in different metal/ligand ratios [3—5], but recently we observed that complexes of the type [M(Chel)ED]PF$_6$ (M = Rh, Ir; Chel = 2,2'-bipyridine, 1,10-phenanthroline or methyl substituted phenanthrolines; ED = hexadiene) are also active hydrogenation catalysts for olefins and ketones at room temperature and atmospheric pressure [6]. Furthermore we obtained satisfactory results by using the complex *cis*-[Rh(Bipy)$_2$Cl$_2$]Cl · 2H$_2$O or the system [Rh(cyclooctene)$_2$Cl]$_2$/Chel in different ratios [7].

With the aim of examining the use of complexes with nitrogen-containing ligands in asymmetric catalysis we have studied the reactions of rhodium(I) and iridium(I) complexes with Schiff bases derived from pyridine-2-aldehyde and several primary amines, including the optically-active α-phenylethylamine. These ligands were chosen on the basis of their structural analogy with Bipy and similar compounds, and have already been extensively studied as ligands for other transition metals, especially the first row [8]. Of particular interest are the tetragonal pyramidal [M(η^5-C$_5$H$_5$)(N—N')(CO)$_2$]PF$_6$ complexes (M = V [9], Mo and W [10,11]; N—N' = 2-pyridinal-*S*-(—)α-phenylethylimine), in which, in addition to the asymmetric centre of the ligand, a second chiral centre is formed in the complexation on the metal. They exist therefore in two diastereoisomeric forms, and they were separated in the case of the molybdenum complex [11]. The absolute configuration of one of them has been determined [12]. The separation of the two diastereoisomers has also been carried out for analogous cobalt derivatives [13].

Results and discussion

In this paper we describe the synthesis and reactions of complexes of the type $[Rh(N{-}N')COD)]PF_6$ (I) ($N{-}N' = C_6H_4NCH{=}NR$, 2-pyridinalmethylimine (PMI), 2-pyridinalethylimine (PEI), 2-pyridinalisopropylimine (PiPI); 2-pyridinal-n-butylimine (PBuI); 2-pyridinalbenzylimine (PBI); (+)- and (—)-2-pyridinal-phenylethylimine (PPEI)). The complexes with PPEI have been isolated also for iridium. The two enanthiomeric forms of this chelating ligands are easy to obtain, the amine being commercially available in *dextro* or *levo* form.

The rhodium complexes can be isolated as microcrystalline solids by treatment of a methanol solution of $[Rh(COD)Cl]_2$ with the chelating ligand, followed by precipitation as hexafluorophosphates (COD = *cis,cis*-cyclooctadiene). Elemental analyses (Table 1) and IR spectra ($\nu(C{=}N)$ of medium weak intensity at about 1590 cm^{-1}) agree with formulation I



(I)

Complexes I show a reactivity very similar (see Scheme 1) to that found for the analogous compounds with Bipy or Phen [14,15]. Thus they react with carbon monoxide to give the dicarbonyl derivatives $[Rh(N{-}N')(CO)_2]^+$ (II), which can easily be isolated as microcrystalline solids, from which the starting complexes are recovered by treatment with COD. Compounds II lose one CO mole when nitrogen is bubbled into their methyl cyanide solutions. As shown by the IR spectra, the two bands in the 2100—2040 cm^{-1} region, typical of the dicarbonyl derivatives, disappear and a new band appears at about 2010 cm^{-1}. The stretching frequencies of the CO group for the complexes II and the monocarbonyl derivatives are listed in Table 2 *.

Addition of KI to the solutions of monocarbonyl derivatives gives the neutral complexes $[Rh(N{-}N')(CO)I]$ (III), one of which has been isolated and characterized ($N{-}N'$ = PBuI, $\nu(CO)$ 1962 cm^{-1}). These complexes react rapidly

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* For the carbonyl derivatives with Bipy and Phen we erroneously reported the presence of an equilibrium between di- and tri-carbonyl complexes, associated with the appearance of two new bands at about 2100 and 1976 cm^{-1} [15]. We have now established that the latter band, which is present also in the (N—N') complexes, is due to a reaction with the NaCl glasses of the IR cell and hence to the formation of [Rh(Chel)(CO)Cl] derivatives. The high percentages of carbon and nitrogen we found, were probably attributable to the presence of low amounts of MeCN. The data for CO uptake are, however, always much higher than those required for dicarbonyl formation.

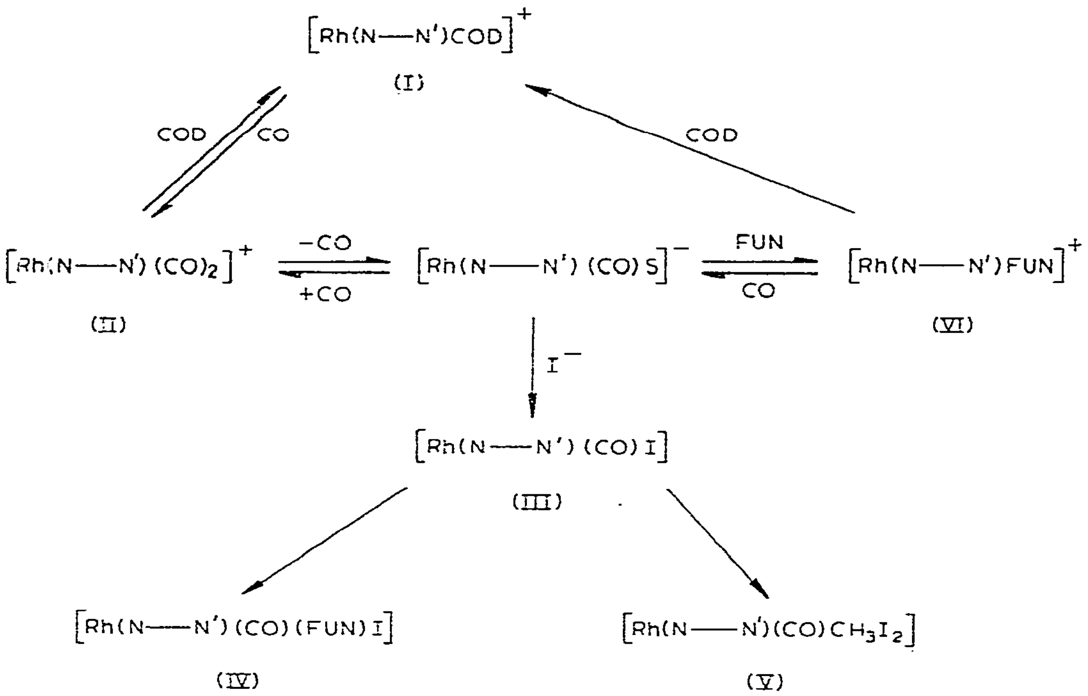
TABLE 1

ANALYTICAL DATA FOR THE COMPLEXES

No.	Complex	Colour	Analysis (Found (calcd.) (%))		
			C	H	N
1	$[Rh(PMI)COD]PF_6$	Green-brown	36.7 (37.83)	4.01 (4.30)	5.84 (5.88)
2	$[Rh(PEI)COD]PF_6$	Brown	38.5 (39.19)	4.64 (4.52)	5.48 (5.71)
3	$[Rh(PiPI)COD]PF_6$	Red	39.6 (40.49)	5.14 (4.79)	5.36 (5.55)
4	$[Rh(PBu)COD]PF_6$	Deep red	41.9 (41.71)	5.12 (5.06)	5.31 (5.40)
5	$[Rh(PBI)COD]PF_6$	Deep red	45.8 (45.66)	4.52 (4.38)	5.10 (5.07)
6	$[Rh(PEA)(COD)Cl]$ (D) [a]	Yellow	51.8 (52.26)	6.31 (6.30)	3.69 (3.80)
7	$[Rh(PEA)(COD)Cl]$ (L)	Yellow	52.2 (52.26)	6.31 (6.30)	3.82 (3.80)
8	$[Rh(PPEI)(COD)]PF_6$ (D)	Red	46.3 (46.65)	4.82 (4.62)	5.02 (4.95)
9	$[Rh(PPEI)(COD)]PF_6$ (L)	Red	46.7 (46.65)	4.61 (4.62)	5.04 (4.95)
10	$[Rh(PMI)(CO)_2]PF_6$	Yellow-green	25.4 (25.49)	1.93 (1.90)	6.28 (6.60)
11	$[Rh(PEI)(CO)_2]PF_6$	Blue	26.9 (27.42)	2.33 (2.30)	6.13 (6.39)
12	$[Rh(PiPI)(CO)_2]PF_6$	Ochre-yellow	28.8 (29.22)	2.72 (2.67)	6.07 (6.19)
13	$[Rh(PBuI)(CO)_2]PF_6$	Yellow-green	30.8 (30.92)	2.74 (3.03)	5.75 (6.01)
14	$[Rh(PBI)(CO)_2]PF_6$	Ochre yellow	35.7 (36.02)	2.35 (2.42)	5.36 (5.60)
15	$[Rh(PPEI)(CO)_2]PF_6$ (D)	Yellow-green	36.9 (37.37)	2.57 (2.74)	5.25 (5.45)
16	$[Rh(PPEI)(CO)_2]PF_6$ (L)	Yellow-green	36.9 (37.37)	2.55 (2.74)	5.22 (5.45)
17	$[Rh(PBuI)(CO)I]$	Violet	30.6 (31.45)	3.45 (3.36)	6.35 (6.67)
18	$[Rh(PMI)(CO)CH_3I_2]$	Yellow	21.6 (20.79)	2.37 (3.13)	5.04 (5.38)
19	$[Rh(PEI)(FUN)(CO)I]$	Yellow	32.8 (33.22)	2.79 (2.57)	11.5 (11.92)
20	$[Rh(PBI)FUN]PF_6$	Yellow	39.2 (39.10)	2.82 (2.70)	11.1 (10.75)
21	$[Ir(PEA)(COD)Cl]$ (D)	Yellow	41.9 (42.05)	4.42 (5.07)	3.01 (3.06)
22	$[Ir(PEA)(COD)Cl]$ (L)	Yellow	42.4 (42.05)	4.67 (5.07)	2.94 (3.06)
23	$[Ir(PPEI)(COD)I]$ (D)	Violet	41.2 (41.44)	4.11 (4.11)	4.36 (4.39)
24	$[Ir(PPEI)COD]ClO_4$ (L)	Deep blue	43.6 (43.31)	4.14 (4.29)	4.52 (4.59)
25	$[Ir(PPEI)(COD)FUN]PF_6$	Cream	40.1 (42.56)	3.42 (3.85)	7.27 (7.64)

[a] (D) and (L) refer to the free basis.

SCHEME 1



S = solvent

in coordinative and oxidative addition. For example, with fumaronitrile (FUN) they form the pentacoordinate adduct IV, and with methyl iodide a hexacoordinated species of rhodium(III) (V), in which the methyl group is *cis* to the carbonyl [15]. Samples of the above products have been isolated and characterized (IV: N—N' = PEI, ν(CO) 2042 cm^{-1}, ν(C≡N) 2209 cm^{-1}, ν(C=N) 1595 cm^{-1}; V: N—N' = PMI, ν(CO) 2070 cm^{-1}, ν(C=N) 1596 cm^{-1}) **. Furthermore complexes II react with FUN with complete displacement of carbon monoxide, as demonstrated by the disappearance in the IR spectrum (MeCN solution) of the two bands of the coordinated CO. The elemental analyses of the new complexes are in agreement with formulae [Rh(N—N')FUN]PF$_6$ (VI) (e.g., N—N' = PBI, ν(CN) of the coordinated olefin at 2210 and 2225 cm^{-1}). Complexes VI react with carbon monoxide to give the dicarbonyl derivatives, as confirmed by the IR spectra, and with COD to reform complexes I.

The iridium complexes of the kind [Ir(N—N')(COD)]X (VII) (e.g. N—N' = PPEI; X = ClO$_4^-$, I$^-$) have been obtained via a template reaction between Ir(COD)(PEA)Cl (PEA = (+)- or (—)-α-phenylethylamine) and pyridine-2-aldehyde, followed by addition of an aqueous anionic solution. Complexes VII

** The intensity of the CO-stretching band of the latter compound decreases with time, while a new band appears at 1691 cm^{-1}. This fact is probably due to migration of the methyl group to the coordinated CO, with formation of an acylic group. The reaction is very slow at room temperature.

TABLE 2

IR CO STRETCHING FREQUENCIES (cm^{-1}, MeCN) OF COMPLEXES [Rh(N—N')(CO)$_2$]PF$_6$

Complex	ν(CO)	Δν(CO)	ν(CO) [a]
[Rh(PMI)(CO)$_2$]$^+$	2102, 2042	60	2012
[Rh(PEI)(CO)$_2$]$^+$	2101, 2042	59	2013
[Rh(PiPI)(CO)$_2$]$^+$	2100, 2039	61	2012
[Rh(PBuI)(CO)$_2$]$^+$	2100, 2041	59	2012
[Rh(PBI)(CO)$_2$]$^+$	2102, 2041	61	2013
(+)- or (—)-[Rh(PPEI)(CO)$_2$]$^+$	2099, 2039	60	2012

[a] After N$_2$ bubblement (monocarbonyl derivative).

are easily isolated as intensely coloured microcrystals and, like the corresponding rhodium complexes, show a fair solubility in some common organic solvents, such as acetone, methanol, methyl cyanide. Their IR spectra show many bands in the 1600 cm^{-1} region, where ν(C=N) frequencies are expected, and the assignment of these was not attempted.

Like the iridium complexes with Bipy and Phen [16], derivatives VII give easily coordinative and oxidative addition reactions. In fact pentacoordinated adducts (VIII), probably with a trigonal bipyramidal structure [17], are formed with ethylene, activated olefins (acrylonitrile, fumaronitrile, tetracyanoethylene) and acetylene. The reactions with ethylene, acrylonitrile and fumaronitrile are reversible. The [Ir(PPEI)(COD)FUN]PF$_6$ adduct has been isolated (ν(C≡N) 2221 cm^{-1}, ν(C=N) 1598 cm^{-1}). Only in the presence of iodide ions [16] do complexes VIII react with methyl iodide to give the corresponding neutral iridium(III) derivatives [Ir(N—N')(COD)CH$_3$I]$^+$.

Optical activity

The optical activity data for the chiral complexes are listed in Table 3. They are not very accurate, because of the small values of α and the low concentrations necessitated by the high absorbance of the solutions. It is noteworthy that in [Rh(PEA)(COD)Cl] complexes the sign of the optical rotation of the coordinated amine is opposite to that of the free base, as already observed in complexation [18] or in organic condensation reactions [19] with chiral substrates. So pyridinal-2-phenylethylimine, obtained by condensation of pyridine-2-aldehyde with D(+)-phenylethylamine, is levorotatory but complexation causes a change in the sign of rotation, as shown in Scheme 2.

SCHEME 2

$$\begin{tikzcd}
\text{PEA (D)} \arrow[r] \arrow[d, "(+)"] & \text{[Rh(COD)(PEA)Cl]} \arrow[d, "(-)"] \\
\text{PPEI} \arrow[r] & \text{[Rh(COD)PPEI]}^+ \\
(-) & (+)
\end{tikzcd}$$

The iridium pentacoordinated (VIII) and rhodium hexacoordinated derivatives (V) must be mixtures of diastereoisomers, since the metal is an asymmetric centre. The isomers have not yet been separated.

TABLE 3

OPTICAL ACTIVITY [a] OF THE COMPLEXES

Complex	Solvent	g/100 ml	$[\alpha]_{435\text{Hg}}$
[Rh(PEA)(COD)Cl] (D)	CH_2Cl_2	0.01840	−147 [b]
[Rh(PEA)(COD)Cl] (L)	CH_2Cl_2	0.01840	+125 [b]
[Rh(PPEI)COD]PF_6 (D)	CH_2Cl_2	0.0140	+143 [b]
[Rh(PPEI)COD]PF_6 (L)	CH_2Cl_2	0.0140	−143
[Rh(PPEI)$(CO)_2$]PF_6 (D)	MeOH	0.0128	+312
[Rh(PPEI)$(CO)_2$]PF_6 (L)	MeOH	0.0128	−312
[Ir(PPEI)COD]ClO_4 (D)	CH_2Cl_2	0.01530	+224
[Ir(PPEI)COD]ClO_4 (L)	CH_2Cl_2	0.01530	−229

[a] Perkin—Elmer Polarimeter 141. [b] $[\alpha]_{404\text{Hg}}$

Given the analogy between the chemical behaviour of rhodium(I) and iridium(I) complexes with Schiff bases and those of the corresponding Bipy or Phen derivatives, we should expect the compounds [Rh(N—N')ED]$^+$ and the system $[Rh(ED)Cl]_2$/(N—N') (in different ratios) to have catalytic activity for the hydrogenation of olefins and ketones. In particular, the complexes with N—N' = PPEI should permit asymmetric catalysis. Examination of this possibility is in progress in our laboratories.

Experimental

Preparation of the ligands

The Schiff bases PMI, PEI, PiPI, PBuI, PBI and PPEI were prepared by published methods [19—21]. The amines and pyridine-2-aldehyde (1.4 ml) in 1/1 ratio were dissolved in MeOH (5 ml) and allowed to react for 1 h at room temperature or at 40°C (PPEI). The chelating ligands were not isolated, the above solutions being used directly for the subsequent reactions.

Preparation of the complexes

The complexes were prepared under nitrogen using deaerated solvents, and were dried in vacuo at room temperature. Compounds $[Rh(COD)Cl]_2$ and $[Ir(COD)Cl]_2$ were synthesized by published methods [22,23]. The elemental analyses and the colours of the new complexes are listed in Table 1.

[Rh(N—N')COD]PF_6 (N—N' = PMI (1), PEI (2), PiPI (3), PBuI (4), PBI (5), PPEI (8,9)).

0.49 m (1 mmol) of $[Rh(COD)Cl]_2$ suspended in MeOH (10 ml) and treated with a methanol solution of the imine, gave a clear deep-red solution. Addition of solid NH_4PF_6 caused immediate precipitation of the microcrystalline complexes which were collected and washed with water and ether.

[Rh(PEA)(COD)Cl] (6,7)

0.25 g (0.5 mmol) of $[Rh(COD)Cl]_2$ suspended in anhydrous EtOH (13 ml), were treated with excess of D(+)- or L(—)-PEA (0.4 ml). The monobasic derivative, which began to precipitate within few minutes, was filtered off after 2 h stirring and washed with ether.

*[Rh(N—N')(CO)$_2$]PF$_6$ (N—N' = PMI (***10***), PEI (***11***), PiPI (***12***) PBuI (***13***), PBI (***14***), PPEI (***15,16***)*

1 mmol of [Rh(N—N')(COD)]PF$_6$, suspended in absolute EtOH, was allowed to react under CO pressure, until the starting complex was transformed into the differently coloured dicarbonyl derivative. The microcrystalline solid was isolated and washed with ether.

*[Rh(PBuI)(CO)I] (***17***)*

0.5 mmol of **13** were dissolved in MeCN (7 ml). After bubbling of nitrogen for 10 min to form the monocarbonyl derivative, the solution was saturated with KI, turning to deep red. Addition of water precipitated a sticky black product, which was decanted and redissolved in acetone. The precipitation was repeated twice, under a nitrogen stream, and the microcrystalline solid obtained was filtered off and washed with water.

*[Rh(PMI)(CO)CH$_3$I$_2$] (***18***)*

0.5 mmol of **10** were dissolved in a MeOH/MeCN mixture (12/5 ml) and nitrogen was bubbled into the solution for 10 min to form the monocarbonyl derivative. The solution was then saturated with KI and an excess of methyl iodide (1 ml) was added. The precipitate was washed with water and ether.

*[Rh(PEI)(FUN)(CO)I] (***19***)*

0.5 mmol of **11** were dissolved in MeCN (12 ml) and the monocarbonyl derivative prepared as described above. The solution was then saturated with KI and excess of FUN (0.15 g) was added. The microcrystalline solid which was precipitated by addition of water was filtered off and washed with water and ether.

*[Rh(PBI)FUN]PF$_6$ (***20***)*

0.5 mmol of **14** dissolved in MeCN (12 ml) were treated with excess of FUN. The solution was allowed to react for 2 h and the evolved CO was removed in vacuo. Addition of ether to the concentrated solution precipitated the complex, which was filtered off and washed with ether.

*[Ir(PEA)(COD)Cl] (***21,22***)*

0.5 g (1.5 mmol) of [Ir(COD)Cl]$_2$, suspended in absolute EtOH (18 ml) were treated with excess of D(+)- or L(—)-PEA (0.5 ml) to give an immediate precipitate. After stirring for 1 h, this was filtered off and washed with ether.

*[Ir(PPEI)(COD)I] (***23***) and [Ir(PPEI)(COD)]ClO$_4$ (***24***)*

0.45 g (1 mmol) of **21** were suspended in absolute EtOH (15 ml) and treated with an excess of pyridine-2-aldehyde (0.25 ml). Addition of few ml (ca. 4) of aqueous saturated solutions of NaI or NaClO$_4$ to the deep-violet solution (partially concentrated in vacuo in the case of the perchlorate derivative), precipitated the corresponding complexes, which were washed with water.

*[Ir(PPEI)(COD)FUN]PF$_6$ (***25***)*

0.19 g (0.3 mmol) of **23**, suspended in MeOH (10 ml), were treated with solid NH_4PF_6 and then with FUN, both in excess. The pentacoordinated adduct, was precipitated immediately, and it was filtered off and repeatedly washed with water and ether.

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