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DIOLEFINIC COMPLEXES OF RHODIUM(I) AND IRIDIUM(I) WITH NITROGEN-CONTAINING LIGANDS

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Summary

The synthesis and the substitution and oxidation reactions of the series of Rh^{I} and Ir^{I} complexes M(L—L)(B)Cl, [M(L—L)$(B)_2$]X and [M(L—L)(Chel)]X (L—L = *cis,cis*-cycloocta-1,5-diene, cycloocta-1,3,5,7-tetraene, bicyclo[2.2.1]-hepta-2,5-diene; Chel = 8-aminoquinoline, phenylendiamine, dipyridylketone, substituted phenanthrolines; X = Cl^-, PF_6^-, ClO_4^-) are described. The use of these complexes as anti-tumour agents is considered.

Introduction

Square planar complexes of Pt^{II} of the type *cis*-Pt$(B)_2Cl_2$ (B = nitrogen containing base) have recently been found to possess promising anti-tumour activity [1], and some of them have already been submitted to clinical trials. Studies on different complexes of Pt^{II} to correlate chemical structure with anti-tumour activity [2, 3] have demonstrated that active species must be neutral and have two *cis*-leaving-groups of a lability comparable with that of the chlorine atoms in the *cis*-Pt$(NH_3)_2Cl_2$ complex. Positive anti-tumour activity has also been found in derivatives of Rh^{III} and Ir^{IV} [2]. Furthermore, bacteriocidal and viricidal activity have been found for some complexes of Pt^{II}, Pt^{IV} and Rh^{III} [4], while complexes of transition metals with 1,10-phenanthroline and related bases have been shown to possess inhibitory or lethal action on a variety of bacteria, fungi, viruses and neoplastic cells [5].

In the light of the above results, we wondered if complexes M(L—L)(B)Cl (I), [M(L—L)$(B)_2$]X (II) and [M(L—L)(Chel)]X (III) (M = Rh^{I}, Ir^{I}; L—L = *cis,cis*-cycloocta-1,5-diene (COD), cycloocta-1,3,5,7-tetraene (COTE), bicyclo-[2.2.1]hepta-2,5-diene (NBD); Chel = bidentate nitrogen containing ligand; X = Cl^-, PF_6^-, ClO_4^-) could have useful biological activities. These complexes are also square planar d^8 species, with two reactive *cis* positions. The diolefin, as a non-labile ligand, is necessary to stabilize the +1 oxidation state of the metals.

Preliminary tests on some compounds of these series have given good results in tests for bacteriocidal [6], viricidal [7] and anti-neoplastic activity [8], and we report here details of their syntheses and chemical reactions.

Results and discussion

Both the series of complexes* M(L—L)(B)Cl and [M(L—L)(B)$_2$]Cl can be obtained by addition of a slight excess of base to the dimers [M(L—L)Cl]$_2$ in methylene chloride or in ethanol/water respectively. They are crystalline compounds, whose visible spectra are characterized by a maximum at about 380 mμ (M = Rh) and by 5 maxima in the range 480-350 mμ (M = Ir). The infrared spectra of neutral complexes show, besides the characteristic bands of the diolefin and the coordinated base, two bands at about 250 cm^{-1}, that at the higher frequency being assigned to the M—Cl and the other to the M—N bond on the basis of the results of Pannettier et al. [10]. Molecular weight measurements in dichloroethane confirm the absence of dimeric species, i.e. of bridging chlorine atoms.

Complexes of the type (III) were prepared starting from the dimer [M(L—L)Cl]$_2$, using as bidentate ligands 8-aminoquinoline (8AQ), *o*-phenylendiamine (ophen), dipyridylketone (DPK), and substituted phenanthrolines**.

With 8AQ [Rh(COD)Cl]$_2$ (IV) reacts to give a monomeric water-soluble species, in which the entering ligand is bidentate. Addition of an aqueous solution of NH_4PF_6 gives the corresponding complex [Rh(COD)8AQ]PF_6. It is interesting that in basic media, in protic solvents, the coordinated ligand loses an aminic proton easily and reversibly, to give the neutral species [Rh(COD)-8AQ(—H)]. The infrared spectrum of [Rh(COD)8AQ]PF_6 contains two bands at 3285 and 3244 cm^{-1}, which are attributable to the coordinated NH_2 group [12], while that of [Rh(COD)8AQ(—H)] shows one band at 3355 cm^{-1} (ν N—H of the free ligand 3440 and 3340 cm^{-1}). Neutral [M(COD)8AQ(—H)] compounds (M = Rh, Ir) can also be easily obtained starting from M(COD)(B)Cl and 8AQ in methanol. They show visible absorption maxima (CH_2Cl_2) at 552 (Rh) and 532 (Ir) mμ.

With *o*-phenylendiamine in methylene chloride, (IV) gives a binuclear species

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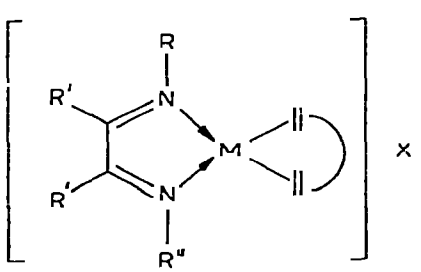
* Some of these complexes are already known [9-11].

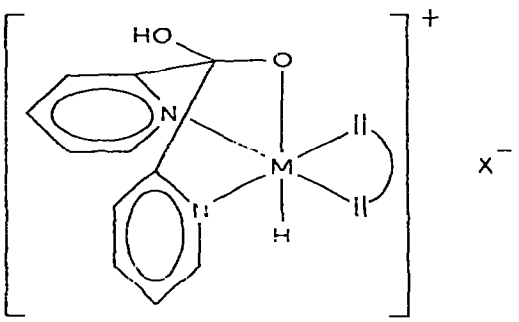
** Complexes with acetylacetone, salicylaldimine, 8-hydroxyquinoline are already known. Studies on complexes of general formula



are in progress.

$[Rh(COD)Cl]_2Chel$, which is insoluble in water. It shows a double band in the 250-280 cm^{-1} region of its infrared spectrum as for complexes of type (I).

Reaction of (IV) with DPK in protic solvents gives microcrystalline complexes of the type $[Rh^{I}(DPK)(COD)]X$ ($X = PF_6^-$, ClO_4^-). Their infrared spectra show a band at 1685 cm^{-1}, attributable to the stretching C=O in the *N,N*-coordinated DPK (ν C=O in free DPK 1675 cm^{-1}) [13]. Unexpectedly, hydridic derivatives of Ir^{III} were isolated from the corresponding iridium complex. In agreement with elemental analysis, structure (A) has been tentatively assigned to these compounds. The DPK acts here as a tridentate ligand, as already observed for complexes of Cu, Co and Ni [14].



(A)

As expected from the proposed structure (A) the infrared spectrum of the perchlorate derivative shows, besides the bands of the free anion, a hydridic band at 2181 cm^{-1}, which is shifted to 1563 cm^{-1} when the complex is prepared in a deuterated medium. The shift of the pyridinic stretching band to 1600 cm^{-1} and the absence of a ν C=O peak confirm that DPK is *N,N*-coordinated and that the keto group has undergone nucleophilic attack. Furthermore, the complexes $[Ir(COD)(PPh_3)_2]^+$ [15], $[Ir(COD)(Phen)]^+$ and $[Ir(COD)(py)_2]^+$ were isolated in reactions with triphenylphosphine, phenanthroline and pyridine respectively, demonstrating that COD is unchanged.

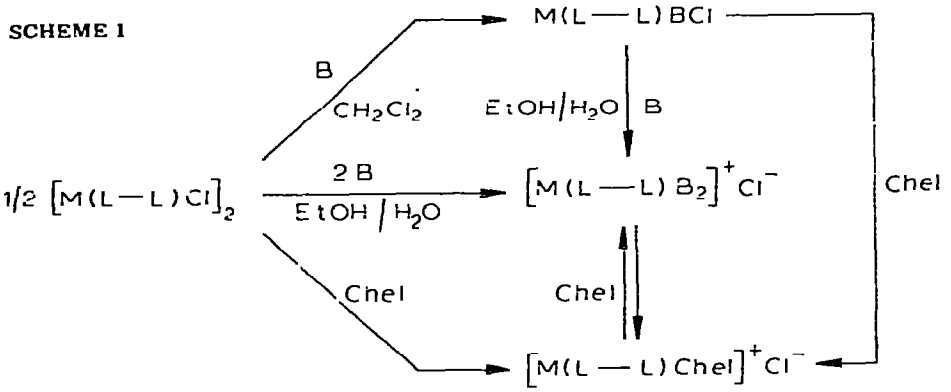
Bipy, Phen and substituted Phen (5,6-Me_2, 4,7-Me_2, 3,4,7,8-Me_4) act as bidentate chelating ligands in all the solvents, to give M(Chel)(L—L)Cl complexes with (IV). In coordinating solvents chlorine atoms exchange easily with hexafluophosphate or perchlorate anions to give the corresponding cationic complexes.

In previous papers [16, 17] we reported the synthesis and characterization of $[M(Chel)(L—L)]^+$ complexes with Chel = Bipy or Phen. The corresponding derivatives with substituted Phen can be prepared easily by the same methods (see Experimental). The complexes $[M(Chel)L—L)]^+$ are characterized by a band at about 500 mμ (Rh) or two bands at about 570 and 450 mμ (Ir). The band at 500 mμ in rhodium complexes undergoes a hypsochromic shift in going from Phen to 3,4,7,8-Me_4-Phen and from NBD to COD, while its intensity increases. Both frequency and intensity also depend on the solvent, decreasing with the increasing coordinating power of the solvent.

Substitution reactions

All the above complexes of Rh^I and Ir^I are labile. In non-coordinating solvents the complexes M(L—L)(B)Cl exchange the base easily without noticeable displacement of the coordinated chlorine, while in protogenic solvents, such as water or water/ethanol (1/1) an excess of B'* also removes the halide, giving the $[M(L—L)(B')_2]^+$ complexes indicating the presence of two labile *cis*-positions. Furthermore complexes of type (I) and (II) react rapidly with bidentate chelating ligands (Bipy, Phen, substituted Phen) to give the corresponding cationic complexes, independent of the nature of the solvent. These reactions are summarized in Scheme 1.

SCHEME 1



Recently Robb and Nicholson [18] reported a kinetic study on the reaction between Rh(COD)(B)Cl and Bipy in methanol. They found values of rate constants for solvolysis in the range 1.6-9.8 × 10^{-2} sec^{-1} (25°C), which are 10^3 times greater than those of the corresponding Pt^{II} complexes.

In complexes of type II, when M = Rh, Chel = DPK or Bipy, the reactions are clearly reversible. The complexes with DPK are more unstable than the corresponding complexes with Bipy; in fact it is possible to obtain the substitution of the Chel with triphenylphosphine only when Chel = DPK, the pentacoordinated adducts being formed when Chel = Bipy.

All the substitution reactions in complexes with nitrogen-containing ligands occur without displacement of the coordinated diolefin.

Oxidation reactions

The complexes $[M(L—L)(B)_2]Cl$ and [M(L—L)Chel]Cl are oxidized easily in the air in aqueous or methanolic solution. The reactivity was measured spectrophotometrically in the dark at 25°C, by following the decreasing intensity of the bands at about 380 mμ (Rh) or at about 460, 400, 360 mμ (Ir) for the complexes of type II and of the bands at about 460 mμ (Rh) and 570, 450 mμ (Ir) for complexes of type III.

Absorption measurements show that 1 mole of the complex takes up ½ mole of oxygen in water and about 1 mole in methanol. In general the complexes with Bipy are oxidized more rapidly than those of Phen and complexes of NBD more rapidly than those of COD. Reactions with COTE are very slow. Iridium complexes are oxidized more easily than the corresponding Rh^I com-

* B' = nitrogen containing base, different from B.

plexes. Kinetic measurements at constant oxygen pressure show an autocatalytic path for the Rh^{I} complexes in aqueous solution, while pseudo first-order kinetics are observed in methanol. Furthermore the reactions are faster in alkaline media.

The above results suggest a mechanism which involves initial formation of an oxygenated adduct as the rate determining step followed by nucleophilic attack on the coordinate olefin*, assisted by the electron-withdrawing power of the coordinated dioxygen. Subsequent steps would be the attack of the proton on coordinated oxygen, formation of a hydroperoxide derivative and its decomposition to a hydroxyderivative and hydrogen peroxide. The oxidation of the Rh^{I} complexes by H_2O_2 may be the step responsible for the autocatalysis in water.

From the above results, the fact that the anti-tumour activity observed in the tested Rh^{I} compounds is lower than that of Pt^{II} complexes, can be related to their greater lability (the corresponding Pd^{II} complexes, which react 10^5 times faster than Pt^{II} derivatives are practically inactive) and oxidisability to inert d^6 complexes (e.g. Ir^{III} complexes are completely inactive [19]). As pointed out by Cleare [2] "labile complexes react rapidly and indiscriminately, thus preventing a sufficient amount from reaching the site(s) responsible for the anti-tumour activity. Inert compounds, which reach these site(s) in higher concentration will not react sufficiently to elicit the anti-tumour response." It is probable that the introduction of suitable electron-withdrawing olefins may improve the stabilization of the +1 oxidation state, while the introduction of bulky ligands should hinder either the substitution or oxidation reactions, which both occur via an associative mechanism.

Experimental

Unless otherwise specified, preparations were performed at room temperature under nitrogen, using deaerated solvents. The complexes $[M(L{-}L)Cl]_2$ (M = Rh, Ir; L—L = COD, COT, COTE, NBD) were prepared using known methods [9, 11, 20, 21]. New compounds are listed in Table 1 along with their colours and analytical data. All the complexes were dried in vacuo.

Rh(COD)(NH_3)Cl

Concentrated ammonium hydroxide (0.3 ml, 2.37 mmol) was dropped into a suspension of $[Rh(COD)Cl]_2$ (0.49 g, 1 mmol) in methanol (50 ml). The filtered yellow solution was concentrated in vacuo. The complex, precipitated by water, was filtered off and washed repeatedly with water.

Rh(L—L)(B)Cl

A slight excess of B (0.2 ml) was added to a solution of $[Rh(L{-}L)Cl]_2$ (0.5 g) in methylene chloride (25 ml). The solvent was partially evaporated in vacuo. The precipitate, formed on adding ether, was filtered off and washed with ether.

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* Recent unpublished results show that this reaction occurs also with unsaturated molecules, such as tetracyanoethylene and fumaronitrile.

TABLE 1

ANALYTICAL DATA FOR THE COMPLEXES

Complex	Colour	Analysis found (calcd.) (%)		
		C	H	N
Rh(COD)(NH_3)Cl	Yellow	36.4 (36.45)	5.86 (5.73)	4.86 (5.31)
Rh(COD)($C_4H_9NH_2$)Cl	Yellow	44.5 (45.08)	7.30 (7.25)	4.40 (4.38)
Rh(COD)(pip)Cl [b]	Yellow	46.7 (47.07)	7.08 (6.99)	4.22 (4.22)
Rh(COD)(Mid)Cl [a]	Yellow	43.7 (43.86)	5.44 (5.52)	8.74 (8.52)
Rh(NBD)(pip)Cl	Yellow	46.3 (45.67)	5.99 (6.06)	4.34 (4.43)
Rh(COTE)(pip)Cl	Yellow	47.3 (47.66)	5.36 (5.84)	4.13 (4.27)
[Rh(COD)(Mid)$_2$]$^+PF_6^-$	Yellow	36.9 (36.94)	4.63 (4.65)	10.83 (10.87)
[Rh(NBD)(Mid)$_2$]$^+PF_6^-$	Yellow	36.1 (35.73)	4.09 (3.99)	11.3 (11.11)
[Rh(COD)Cl]$_2$ophen	Yellow	43.5 (43.95)	4.93 (5.36)	4 54 (4.66)
[Rh(COD)8AQ]$^+PF_6^-$	Yellow	41.1 (40.82)	3.81 (4.03)	5.68 (5.60)
[Rh(COD)8AQ(−H)]	Violet	58.0 (57.63)	5.2 (5.40)	8.20 (7.90)
[Rh(COD)(DPK)]$^+PF_6^-$	Orange	42.5 (42.25)	3.73 (3.73)	5.29 (5.18)
Rh(COD)(4,7(Me)$_2$Phen)Cl	Orange-red	58.4 (58.10)	5.07 (5.32)	6.09 (6.16)
Rh(COD)(3,4,7,8(Me)$_4$Phen)Cl	Orange-red	59.5 (59 7)	5.91 (5.84)	5.84 (5.80)
Rh(NBD)(Bipy)Cl	Red-violet	52.4 (52.81)	4.10 (4.17)	7.24 (7.25)
Rh(NBD)(Phen)Cl	Red	55.5 (55.37)	3.79 (3.92)	6.72 (6.82)
[Rh(COD)(5,6(Me)$_2$Phen)]$^+PF_6^-$	Orange-red	47.1 (46.83)	4 52 (4.28)	5.11 (4 96)
[Rh(COD)(4,7(Me)$_2$Phen)]$^+PF_6^-$	Yellow-orange	47.1 (46.83)	4.13 (4.28)	4.94 (4.96)
[Rh(COD)(3,4,7,8(Me)$_4$Phen)]$^+PF_6^-$	Yellow-orange	48.4 (48.66)	4.54 (4.76)	4.73 (4 73)
Ir(COD)(pip)Cl	Yellow	37.1 (37.09)	5.57 (5.51)	3.35 (3.32)
Ir(COD)(py)Cl [c]	Yellow	37.2 (37.63)	3.90 (4.13)	3.29 (3.37)
Ir(COD)(Mid)Cl	Yellow	34.3 (34.49)	4.23 (4.34)	6.80 (6.70)
Ir(COTE)(pip)Cl	Yellow	37.6 (37.45)	4.65 (4.59)	3.50 (3.36)
[Ir(COD)(py)$_2$]$^+PF_6^-$	Yellow	35.4 (35.82)	3.42 (3.67)	4.53 (4.64)
[Ir(COD)(Mid)$_2$]$^+PF_6^-$	Yellow	31.6 (31.53)	3.76 (3.96)	8.99 (9.19)
[Ir(COD)8AQ(−H)]	Violet	46.5 (46.04)	4.21 (4.31)	6.31 (6.49)
[Ir(COD)(DPKOH)H]$^+PF_6^-$	Yellow-orange	35.3 (35.24)	3.08 (3.42)	4.30 (4.32)

(continued)

TABLE 1 (continued)

Complex	Colour	Analysis found (calcd.) (%)		
		C	H	N
[Ir(COD)(DPKOH)H]$^+ClO_4^-$ · H_2O	Yellow-orange	36.9 (36.80)	3.68 (3.90)	4.35 (4.51)
Ir(COD)(5,6(Me)$_2$Phen)Cl	Red-violet	49.0 (48.57)	4.36 (4.44)	5.16 (5.15)
Ir(COD)(4,7(Me)$_2$Phen)Cl	Red-violet	48.1 (48.57)	4.38 (4.44)	5.10 (5.15)
Ir(COD)(3,4,7,8(Me)$_4$Phen)Cl	Red-violet	50.4 (50.39)	5.06 (4.93)	5.14 (4.90)
[Ir(COD)(5,6(Me)$_2$Phen)]$^+PF_6^-$	Purple	40.9 (40.43)	3.58 (3.70)	4.35 (4.28)
[Ir(COD)(4,7(Me)$_2$Phen)]$^+PF_6^-$	Purple	40.4 (40.43)	3.71 (3.70)	4.20 (4.28)
[Ir(COD)(3,4,7,8(Me)$_4$Phen)]$^+PF_6^-$	Purple	42.5 (42.28)	4.25 (4.14)	4.05 (4.11)
[Ir(NBD)(5,6(Me)$_2$Phen)]$^+PF_6^-$	Red-brown	39.2 (39.56)	2.94 (3.16)	4.30 (4.39)
[Ir(NBD)(4,7(Me)$_2$Phen)]$^+PF_6^-$	Red-brown	39.3 (39.56)	2.98 (3.16)	4.42 (4.39)
[Ir(NBD)(3,4,7,8(Me)$_4$Phen)]$^+PF_6^-$	Red-brown	41.1 (41.50)	3.62 (3.63)	4.06 (4.21)
[Ir(COTE)(Bipy)]$^+PF_6^-$	Red-brown	35.9 (36.18)	2.35 (2.70)	4.67 (4.69)
[Ir(COD)(Bipy)(OH)$_2$]$^+I^-$	Orange	35.2 (35.01)	3.33 (3.58)	4.54 (4.53)

[a] Mid = N-methylimidazole. [b] pip = piperidine. [c] py = pyridine.

[Rh(L—L)(Mid)$_2$]PF$_6$ (L—L = COD or NBD)

(1) Rh(COD)(Mid)Cl, Rh(NBD)(pip)Cl or [Rh(L—L)Cl]$_2$ (1 mmol) was suspended in EtOH/water (20/10 ml). The addition of *N*-methylimidazole in excess (2 ml) gave a clear solution, from which the complexes were precipitated by addition of a concentrated solution of NH_4PF_6. The compounds were thoroughly washed with water.

(2) *N*-methylimidazole in excess (2 ml) was added to a suspension of [Rh(COD)(DPK)]PF_6 (0.64 g, 1 mmol) in ethanol (15 ml). The complexes precipitated overnight, after addition of water.

[Rh(COD)Cl]$_2$ophen

Freshly recrystallized *o*-phenylendiamine (0.216 g, 2 mmol) was added to a solution of [Rh(COD)Cl]$_2$ (0.49 g, 1 mmol) in methylene chloride (20 ml). The complex formed was filtered off and washed with ether.

[Rh(COD)8AQ]PF$_6$

8AQ (0.29 g, 2 mmol) was added to a solution of [Rh(COD)Cl]$_2$ (0.49 g, 1 mmol) in methylene chloride (20 ml). The microcrystalline solid which separated, was filtered off and dissolved in methanol (50 ml). From this solution NH_4PF_6 precipitated [Rh(COD)8AQ]PF_6, which was filtered off and washed with water.

[Rh(COD)8AQ−H)]

(1) An aqueous solution of NaOH (10 ml N/10) was added to a methanolic solution (30 ml) of [Rh(COD)8AQ]PF_6 (0.23 g, ½ mmol). The solid precipitated was filtered off and washed with water.

(2) Alternatively, a suspension of Rh(COD)(B)Cl (1 mmol) in methanol (15 ml) was treated with 8AQ (1 mmol). The new precipitate formed was treated as above.

[Rh(COD)(DPK)]PF_6

DPK (0.36 g, 2 mmol) added to a suspension of [Rh(COD)Cl]$_2$ (0.49 g, 1 mmol) in ethanol (20 ml) gave a clear solution. The solid, formed overnight after addition of a concentrated solution of NH_4PF_6, was filtered off and washed with water.

Rh(L—L)(Chel)Cl (L—L = COD, Chel = 4,7-(Me)$_2$Phen; L—L = COD, Chel = 3,4,7,8-Me$_4$Phen; L—L = NBD, Chel = Phen; L—L = NBD, Chel = Bipy)

The stoichiometric amount of Chel, added to a solution of [Rh(L—L)Cl]$_2$ (1 g) in methylene chloride (20 ml), gave the corresponding complexes in a short time. Each was filtered off and washed with ether.

[Rh(COD)Chel]PF_6 (Chel = 5,6-Me$_2$Phen, 4,7-Me$_2$Phen, 3,4,7,8-Me$_4$Phen)

Concentrated aqueous NH_4PF_6 was added to a suspension of the corresponding chloro-derivatives in acetone/water (30/15 ml). The solid complexes were filtered off and washed with water.

Ir(COD)(B)Cl (B = pip, py, Mid)

(1) An excess of B (2 mmol) was added to a solution of [Ir(COD)Cl]$_2$ (0.67 g, 1 mmol) in methylene chloride (15 ml). The solid compounds, separated by addition of ligroin to the partially concentrated solutions, were filtered off and washed with ligroin.

(2) Alternatively, 4 mmol of B was added to a suspension of [Ir(COT)$_2$Cl]$_2$ (0.45 g, 0.5 mmol) in methylene chloride (15 ml) in the presence of a large excess of COD (2 ml, 19.64 mmol). The complex was precipitated from the solution by the addition of ligroin after partial evaporation. It was filtered off and washed with water.

Ir(COTE)(pip)Cl

See above, method 2.

[Ir(COD)B$_2$]PF_6 (B = py, Mid)

(1) An excess of B (20 mmol) was added to a suspension of [Ir(COD)Cl]$_2$ (0.67 g, 1 mmol) in ethanol (25 ml) or to a suspension of 1 mmol of Ir(COD)-(pip)Cl or Ir(COD)(py)Cl in 15 ml ethanol. Microcrystalline solids were formed by addition of a concentrated aqueous solution of NH_4PF_6, after a partial evaporation of the solvent under vacuo. The complexes were filtered off and washed with water.

(2) An excess of B was added to a suspension of [Ir(COD)(DPKOH)H]PF_6 in methanol (20 ml). The solids, which precipitated from the clear solutions by

adding water and concentrating in vacuo, were filtered off and washed with water.

[Ir(COD)(8AQ)(−H)]

A suspension of Ir(COD)(B)Cl (1 mmol) in methanol (15 ml) was treated with 8AQ (1 mmol). The crystalline precipitate formed was filtered off and washed with water.

[Ir(COD)(DPKOH)H]PF_6, [Ir(COD)(DPKOH)H]$ClO_4 \cdot H_2O$

A suspension of $[Ir(COD)Cl]_2$ (0.67 g, 1 mmol) in methanol (30 ml) was treated with DPK (0.9 g, 5 mmol), giving a clear solution. The complexes, which were precipitated by addition of concentrated aqueous NH_4PF_6 and partial evaporation of the methanol under vacuo respectively, were filtered off and washed with water.

Ir(COD)(Chel)Cl (Chel = 5,6-Me_2Phen, 4,7-Me_2Phen, 3,4,7,8-Me_4Phen)

Chel (2 mmol) was added to a solution of $[Ir(COD)Cl]_2$ (0.67 g. 1 mmol) in methylene chloride (15 ml). The solid, which formed immediately, was filtered off and washed with ether.

[Ir(COD)Chel]PF_6 (Chel = 5,6-Me_2Phen, 4,7-Me_2Phen, 3,4,7,8-Me_4Phen)

A concentrated aqueous solution of NH_4PF_6 was added to 1 mmol of Ir(COD)ChelCl (Chel = 5,6-Me_2Phen, 4,7-Me_2Phen or 3,4,7,8-Me_4Phen), partially dissolved in a mixture of acetone/water (30/15 ml). The complexes precipitated were filtered off and washed with water.

[Ir(NBD)Chel]PF_6 (Chel = 5,6-Me_2Phen, 4,7-Me_2Phen, 3,4,7,8-Me_4Phen)

A large excess of NBD (4 ml) was added to a suspension of $[Ir(COT)_2Cl]_2$ (0.9 g, 1 mmol) in acetone (60 ml). After 5 min the Chel was added and the mixture was allowed to react whilst stirring for 3 h. The precipitate was collected, washed with ether, dried in vacuo and suspended in acetone/water (25/10 ml). Addition of a concentrated aqueous solution of NH_4PF_6 to the acetone/water solution precipitated the complexes. They were filtered off and washed with water.

[Ir(COTE)Bipy]PF_6

An excess of COTE (1 ml, 8.8 mmol) was added to a suspension of $[Ir(COT)_2Cl]_2$ (0.45 g, ½ mmol) in methylene chloride (15 ml). After 5 min 2 mmol of Chel was added to the reaction mixture, which was then allowed to react with stirring for 3 h. The solid formed was collected, washed with ether, dried in vacuo and suspended in acetone/water (25/10 ml). The solid, precipitated on adding a concentrated aqueous solution of NH_4PF_6, was filtered off and washed with water.

[Ir(COD)Bipy$(OH)_2$] I

Ir(COD)(Bipy)Cl (0.2 g) was allowed to react in the air with 30 ml of water for some hours, to give a clear yellow solution. Addition of an aqueous

solution of NaI precipitated a crystalline solid which was filtered off and washed with water.

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