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COMPLEXES OF IRIDIUM(I) WITH 2,2'-BIPYRIDINE AND 1,10-PHENANTHROLINE: SYNTHESIS AND REACTIONS OF CATIONIC COMPLEXES WITH DIOLEFINS

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Summary

The synthesis and reactions of Ir^I complexes of the type $[IrChel(L—L)]^+$ (Chel = Bipy or Phen; L—L = cyclooctadiene or 2,5-norbornadiene) are described. Coordinative- and oxidative-addition, and substitution reactions are compared with those of the corresponding Rh^I derivatives.

Introduction

In previous papers we described the synthesis and reactions of rhodium(I) complexes of the type [Rh(Chel)(L—L)]X [1], $[Rh(Chel)(CO)_2]X$ and Rh(Chel)(CO)Y [2] (Chel = Bipy or Phen; L—L = cyclooctadiene (COD) or 2,5-norbornadiene (NBD); X^- = ClO_4^- or PF_6^-; Y^- = Cl^-, Br^-, I^-). The present paper reports the results obtained with $[Ir^I(Chel)(L—L)]^+$ complexes*.

Results

The complexes [Ir(Chel)(L—L)]Cl can be synthesized, as in the case of the corresponding Rh^I compounds, starting from $[Ir(L—L)Cl]_2$, which in turn were prepared from $H_2[IrCl_6]$ [5]**. When L—L = COD, we have found that the cheaper reagent $IrCl_3 \cdot 3H_2O$ can be used instead, following the method reported for the preparation of $[Ir(COT)_2Cl]_2$ (COT = cyclooctene) [6]. $[Ir(COT)_2Cl]_2$ itself is a very good starting material for the synthesis of the complexes [Ir(Chel)(L—L)]Cl, which can be prepared either by treating a solution of $[Ir(COD)Cl]_2$ in methylene chloride with Bipy or Phen, or by treating a solution of $[Ir(COT)_2Cl]_2$ in methylene chloride (L—L = COD) or

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* This type of complex has been mentioned by us in a previous communication [3]. The complex $[Ir(Bipy)(COD)]BF_4$ [4] is also known.

** The complex $[Ir(NBD)Cl]_2$ could be obtained only in very low yield (5%) [5b].

acetone (L—L = NBD) with the diolefin and then with the bidentate chelating system.

An excess of Chel or L—L respectively does not cause displacement of the other coordinated ligand, but the chlorine atom in [IrChel(L—L)]Cl exchanges rapidly with X^- (X^- = Br^-, I^-, N_3^-, SCN^-, ClO_4^-, PF_6^-) in aqueous acetone. In the solid state the chloro-, bromo-, perchlorato- and hexafluorophosphato- derivatives are tetracoordinated, probably with a square planar structure (there are no infrared absorptions for coordinated halides above 200 cm^{-1}, while the absorption frequencies for the ClO_4^- and PF_6^- groups are characteristic of non-coordinated ligands). The iodo-, azido- and thiocyanato-derivatives are probably pentacoordinated (the visible spectra of the iodo-derivatives are quite different from those of the other halido compounds; the patterns of infrared spectra for the azido and thiocyanato groups are those of coordinated ligands). In solution the type of coordination depends on the solvent. For example in aqueous solution the chloro derivatives are 1/1 electrolytes, like the perchlorato and hexafluorophosphato derivatives in dichloroethane, while the conductivities of the halo derivatives in the latter solvent are in contrast very low, suggesting the presence of an equilibrium between tetra- and penta-coordinated species, which is shifted towards penta-coordination on going from chloro to iodo derivatives. Substitution, and coordinative- and oxidative-addition reactions of [IrChel(L—L)]X (X^- = ClO_4^-, PF_6^-) (I) were studied.

Substitution reactions

Phen reacts with the compounds [Ir(Bipy)(L—L)]X (X^- = ClO_4^-, PF_6^-), as with Rh^I, to displace Bipy but not the diolefin, while carbon monoxide displaces only coordinated L—L with formation of $[Ir(Chel)(CO)_3]X$. COD does not displace coordinated NBD in (I), nor does the reverse reaction occur.

Coordinative addition reactions

Unlike the corresponding Rh^I compounds, the complexes (I) give penta-coordinated adducts with a variety of small molecules at room temperature and atmospheric pressure. With monoolefins (ethylene, propylene, 1-butene, 1-hexene, cyclohexene), maleic anhydride (MA), acrylonitrile (AN), fumaronitrile (FUN) and tetracyanoethylene (TCNE), solutions of (I) in methylene chloride rapidly change from red-violet to yellow with the formation of the corresponding penta-coordinated adduct. Absorption measurements in acetonitrile show that one mole of ethylene is taken up per mole of complex and that the reaction is reversible: when argon is bubbled through a solution of adduct, the original compound is obtained, and this cycle can be repeated many times, as shown by visible spectra. Propylene and 1-butene show similar behaviour. With MA, and FUN the adducts were isolated, and elemental analysis and infrared spectra are in agreement with the proposed formulae. All these adducts except for those of TCNE, react with sodium iodide to give the corresponding iodo-derivatives, with displacement of the coordinated olefin.

Cis- and *trans*-butene interact appreciably only with the NBD complexes and NBD or COD complexes react with acetylene and butadiene to give the corresponding adducts. Butadiene can easily be removed by sweeping the solutions with nitrogen, but acetylene (L—L = COD) requires an intermediate treatment with ethylene, which can then in turn be removed by inert gas.

The behaviour of the [Ir(Chel)(L—L)] X complexes with carbon monoxide is interesting. At first they give the corresponding pentacoordinated adducts, but then a slow displacement of L—L occurs, with formation of tricarbonyl derivatives. The reaction can be followed qualitatively using the colour changes of the solutions: the initial red-violet solutions rapidly turn yellow, and then slowly turn brown, while microcrystalline solids separate. Elemental analysis, infrared spectra and absorption measurements are in agreement with the formation of tricarbonyl derivatives as final products. When L—L = COD the first reaction step is reversible, so that by sweeping the yellow solutions with nitrogen the starting compounds are formed.

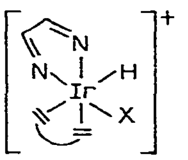
With triethyl- and triphenyl-phosphine only adducts of complexes (I) were isolated, even with excess of reagent.

Oxidative-addition reactions

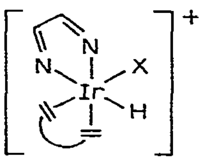
The complexes (I) react rapidly in methyl cyanide or methanol with dilute HY ($Y^- = Cl^-$) to give the corresponding hydrido complexes [Ir(Chel)(L—L)HY] X The synthesis of [Ir(Chel)(L—L)HY] ClO_4 (II) ($Y^- = Cl^-$, Br^-, I^-) can also be achieved by addition of concentrated $HClO_4$ to the complexes Ir(Chel)(L—L)Y. Only impure compounds could be isolated by addition of perchloric acid and excess sodium halide to complexes (I), owing to reductive elimination, which occurs during the washing with water which is necessary to remove excess halide. Even in the absence of Y^-, complexes (I) react with concentrated perchloric acid in methyl cyanide to give complexes which we suppose to be of the type [IrChel(L—L)(CH_3CN)H] $(ClO_4)_2$, as suggested by the isolation of the complex [IrPhen(COD)(PEt_3)H] $(ClO_4)_2$ from the parallel reaction with the corresponding penta-coordinated adduct of Ir^I *.

As mentioned above, solutions of complexes (II) in methyl cyanide readily undergo reductive elimination reactions on adding water, but, exceptionally, [IrPhen(COD)(PEt_3)H]$^{2+}$ requires an alkaline aqueous solution.

For the complexes (II) the following isomers are possible



(A)



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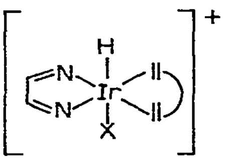

(C)

The IR spectra of the perchlorato derivatives show ν(Ir—H) frequencies which decrease on going from chloro- to iodo-derivatives, the values for NBD derivatives being on average 70 cm^{-1} lower than those for COD (Chel = Bipy; L—L = COD: $Y^- = Cl^-$ 2241, Br^- 2226, I^- 2207; L—L = NBD: $Y^- = Cl^-$ 2169, Br^- 2157, I^- 2127 cm^{-1}). These observations point to structure (C) as the most probable; however in the hexafluorophosphato derivatives, synthesized by a different procedure (see Experimental), the Ir—H bands are split, so the presence of isomers is probable.

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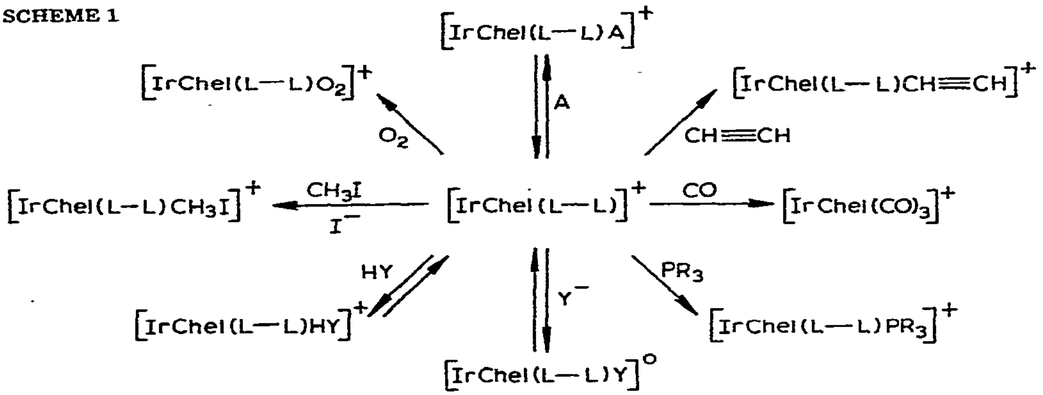
* Some examples of synthesis by oxidative addition of σ-bonded dicationic hydrido and organometallic complexes have been recently reported [7].

SCHEME 1



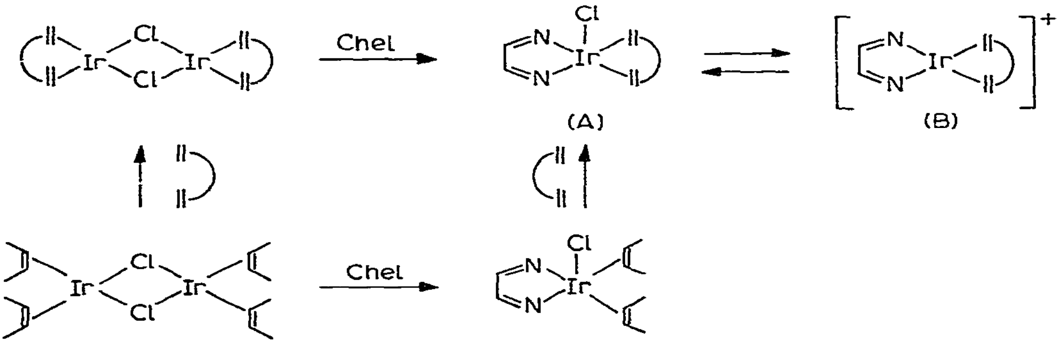
A = ethylene, propylene, AN, FUN, TCNE, butadiene.

A similar but irreversible reaction to that of HX is observed for HgY_2 ($Y^- = Cl^-$, Br^-) with (I). Complexes (I) react slowly, and only in the presence of I^-, with methyl iodide to give hexa-coordinated [IrChel(L—L)(CH_3)(I)]X derivatives. There is also evidence for irreversible reactions of (I) with molecul oxygen and hydrogen (in alkaline media). These reactions will be further investigated to elucidate the mechanism of absorption and the nature of the fin products. We hope that the series of corresponding complexes with substitute phenanthrolines, which we are now preparing, may offer more suitable characteristics for these studies.

The reactions of complexes (I) are summarized in Scheme 1. It is interes ing that when $X^- = Cl^-$, several of these reactions can also be carried out in aqueous media.

Discussion

For the synthesis of complexes (I) we suggest the following reaction pat



As reported, conductivity measurements support the presence of the equ librium between the penta- and tetra-coordinated species (A ⇌ B), and during the synthesis of [IrPhen(COD))]Cl we noted the formation of an intermediat blue-violet microcrystalline solid (which we assume to be A), which then turn into a green compound (B).

In general complexes with NBD react more rapidly than the corresponding COD derivatives (e.g. reactions with dioxygen and CH_3I). They also give more stable pentacoordinated adducts (see reaction with carbon monoxide) and oxidative-addition products [e.g., the [IrChel(NBD)(HY)]X complexes are less acid than the corresponding complexes with COD, in accord also with the lower values of ν(Ir—H) frequencies].

As was shown in our previous communication [3], the complexes [IrChel(L—L)]X show a behaviour similar to that of Vaska's complex. The oxidative-addition reactions with HY, HgY_2 and CH_3I in the presence of cationic complexes, implies the possibility of two reaction mechanisms. For example, with HY it is possible that either electrophilic attack by the proton (followed by coordination of halide) or coordination of halide (followed by protonation) is the first step. With CH_3I the second path is preferred since the reaction occurs only in the presence of iodide.

The greater reactivity of these complexes of iridium compared with those of rhodium is in agreement with the general behaviour of these two metals in oxidation state +1.

Experimental

Unless otherwise specified preparations were performed at room temperature and atmospheric pressure under nitrogen, using deaerated solvents. The new compounds dealt with in the present investigation are listed in Table 1 along with their colours and analytical data.

$[Ir(COD)Cl]_2$

This product was prepared using the procedure of Herde and Senoff [6]. The IR spectrum is identical with that reported by Pannetier et al. [5a]. Yield 82%.

[IrBipy(COD)]Cl (1)

(a). A solution of Bipy (0.4 g, 2.5 mmole) in methylene chloride (10 ml) was added to a solution of $[Ir(COD)Cl]_2$ (0.7 g, 1 mmole) in the same solvent (10 ml). The solid, which rapidly precipitated from the blue-violet solution, was filtered off after 30 min and washed with ether. Yield 67%. The complex is soluble in methylene chloride, methyl cyanide, methanol, water.

(b). COD (1 ml, 9 mmole) was added to a suspension of $[Ir(COT)_2Cl]_2$ (0.45 g, 1 mmole) in methylene chloride (25 ml). After 20 min Bipy (0.4 g, 2.5 mmole) was added to the clear orange-brown solution, which rapidly turned to deep violet. The isolation of the complex followed as above. Yield 91%. Conductivity (0.001 *M*): $\Lambda = 108\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$ (water), $5.7\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$ (dichloroethane).

IrBipy(COD)Y: $Y^- = Br^-$ (2), I^- (3), N_3^- (4), SCN^- (5); [IrBipy(COD)]X: $X^- = ClO_4^-$ (6), PF_6^- (7)

An excess of solid NaX or NaY was added to a water/acetone (5 + 25 ml) solution of 0.2 g of (1). Microcrystalline deeply-coloured solids precipitated immediately or after a partial evaporation of the acetone (2,4). They were

TABLE 1

ANALYTICAL DATA FOR THE COMPLEXES

Number	Complex	Colour	Analyses found (calcd.) (%)		
			C	H	N
(1)	[IrBipy(COD)]Cl	Violet-blue	43.3 (43.94)	3.79 (4.10)	5.54 (5.69)
(2)	[IrBipy(COD)]Br	Red-violet	39.9 (40.31)	3.55 (3.75)	4.97 (5.22)
(3)	IrBipy(COD)I	Violet	36.9 (37.06)	3.27 (3.45)	4.82 (4.80)
(4)	IrBipy(COD)N_3	Orange-red	43.0 (43.37)	4.09 (4.04)	13.81 (14.05)
(5)	IrBipy(COD)SCN	Violet	43.9 (44.35)	3.94 (3.91)	8.26 (8.16)
(6)	[IrBipy(COD)ClO_4	Red-violet	38.5 (38.88)	3.42 (3.62)	4.91 (5.03)
(7)	[IrBipy(COD)]PF_6	Red-violet	35.4 (35.94)	3.31 (3.35)	4.56 (4.65)
(8)	[IrPhen(COD)]Cl	Green	46.5 (46.55)	3.71 (3.91)	5.56 (5.43)
(9)	IrPhen(COD)Br	Green	42.4 (42.86)	3.39 (3.59)	5.08 (4.99)
(10)	IrPhen(COD)I	Violet	38.9 (39.54)	3.40 (3.31)	4.71 (4.50)
(11)	IrPhen(COD)N_3	Violet	45.5 (45.97)	3.85 (3.85)	13.01 (13.40)
(12)	IrPhen(COD)SCN	Red-violet	45.9 (46.82)	3.61 (3.74)	8.02 (7.80)
(13)	[IrPhen(COD)]ClO_4	Green	41.1 (41.42)	3.20 (3.47)	4.96 (4.83)
(14)	[IrPhen(COD)]PF_6	Green	38.1 (38.40)	3.12 (3.22)	4.51 (4.47)
(15)	[IrBipy(NBD)]Cl	Violet	42.9 (42.90)	3.33 (3.38)	5.73 (5.88)
(16)	IrBipy(NBD)Br	Violet	39.0 (39.23)	3.01 (3.09)	5.12 (5.38)
(17)	IrBipy(NBD)I	Violet	35.7 (35.98)	2.92 (2.84)	4.81 (4.94)
(18)	[IrBipy(NBD)]PF_6	Brown	33.4 (34.88)	2.64 (2.75)	4.60 (4.78)
(19)	IrPhen(NBD)Cl	Violet	43.8 (45.64)	2.99 (3.22)	5.47 (5.60)
(20)	IrPhen(NBD)I	Violet	38.1 (38.58)	2.72 (2.72)	4.66 (4.73)
(21)	[IrPhen(NBD)]PF_6	Brown	37.8 (37.44)	2.57 (2.64)	4.70 (4.59)
(22)	[IrBipy(COD)(FUN)]PF_6	White	38.5 (38.88)	3.15 (3.26)	8.14 (8.24)
(23)	[IrPhen(COD)(FUN)]ClO_4	White	43.7 (43.80)	3.44 (3.52)	8.43 (8.52)
(24)	[IrBipy(NBD)(FUN)]PF_6	White	38.0 (38.01)	3.01 (2.73)	8.66 (8.44)
(25)	[IrPhen(COD)(TCNE)]PF_6	Light green	40.7 (41.43)	2.56 (2.67)	11.10 (11.15)
(26)	[IrBipy(COD)(MA)]PF_6	Light yellow	37.3 (37.77)	3.11 (3.17)	3.86 (4.00)
(27)	[IrPhen(COD)(MA)]PF_6	Light yellow	39.1 (39.89)	2.76 (3.07)	3.80 (3.88)
(28)	[IrBipy(COD)(PPh_3)]ClO_4	Orange	52.2 (52.84)	4.26 (4.31)	3.37 (3.42)
(29)	[IrPhen(COD)(PPh_3)]ClO_4	Orange	53.4 (54.19)	4.31 (4.19)	3.40 (3.32)
(30)	[IrPhen(NBD)(PPh_3)]PF_6	Red	51.1 (50.98)	3.47 (3.58)	3.20 (3.21)
(31)	[IrBipy(COD)(PEt_3)]PF_6	Red	39.8 (40.05)	4.97 (4.90)	3.82 (3.89)
(32)	[IrPhen(COD)(PEt_3)]PF_6	Red	41.3 (41.99)	4.67 (4.74)	3.89 (3.76)
(33)	[IrBipy(COD)HCl]PF_6	White	33.9 (33.89)	3.25 (3.31)	4.18 (4.39)
(34)	[IrPhen(COD)HCl]PF_6	White	36.5 (36.29)	3.36 (3.19)	4.05 (4.23)
(35)	[IrBipy(COD)HCl]ClO_4	White	36.6 (36.40)	3.72 (3.57)	4.63 (4.73)
(36)	[IrBipy(COD)HBr]ClO_4	White	33.5 (33.94)	3.17 (3.32)	4.20 (4.39)
(37)	[IrBipy(COD)HI]ClO_4	Light cream	31.3 (31.62)	3.02 (3.09)	4.05 (4.09)
(38)	[IrPhen(NBD)HCl]PF_6	Cream	34.1 (35.35)	2.70 (2.65)	4.03 (4.34)
(39)	[IrBipy(NBD)HI]ClO_4	Green	29.2 (30.57)	2.55 (2.56)	4.09 (4.19)
(40)	[IrPhen(COD)(PEt_3)H]$(ClO_4)_2$ [a]	White	37.1 (39.1)	4.11 (4.54)	3.29 (3.51)
(41)	[IrBipy(COD)CH_3I]PF_6	Orange	30.7 (30.70)	3.10 (3.11)	[illegible]
(42)	[IrBipy(NBD)CH_3I]PF_6				

filtered off, washed thoroughly with water and dried in vacuo at room temperature. Conductivity of (6) (0.001 *M*): $\Lambda = 28.4\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$ (dichloroethane).

[IrPhen(COD)] Cl (8)

(a). A solution of Phen (0.5 g, 2.5 mmole) in methylene chloride (30 ml) was added to a solution of $[Ir(COD)Cl]_2$ (0.67 g, 1 mmole) in the same solvent (30 ml) to give a blue colour. The microcrystalline solid of the same colour, which immediately precipitated, however turned green within 15 min. The compound was isolated and washed with acetone and ether. Yield 68%. The complex is soluble in methylene chloride, methyl cyanide, methanol, water.

(b). Phen (0.5 g, 2.5 mmole) was added to the orange-brown solution obtained from COD (1 ml, 9 mmole) and $[Ir(COT)_2Cl]_2$ (0.45 g, 1 mmole) in methylene chloride (25 ml). Again the solution rapidly turned violet and then slowly went green. The complex was isolated as above. Yield 87%. Conductivity (0.001 *M*): $\Lambda = 98.7\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$ (water), $4.6\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$ (dichloroethane).

IrPhen(COD)Y: $Y^- = Br^-$ (9), I^- (10), N_3^- (11), SCN^- (12); [IrPhen(COD)] X: $X^- = ClO_4^-$ (13), PF_6^- (14)

The above complexes were prepared following the procedure described for the corresponding Bipy derivatives. Conductivity of (13) (0.001 *M*): $\Lambda = 32.9\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$ (dichloroethane).

IrChel(NBD)Cl: Chel = Bipy (15), Phen (19)

A suspension of $[Ir(COT)_2Cl]_2$ (0.9 g, 2 mmole) in acetone (60 ml) was treated with NBD (4 ml, 20 mmole) and, after a few minutes, with Chel (2.5 mmole). The precipitated complexes were filtered off after 4 h, washed with ether and dried in vacuo.

IrChel(NBD)Y: Chel = Bipy, $Y^- = Br^-$ (16), I^- (17); Chel = Phen, $Y^- = I^-$ (20); [IrChel(NBD)]PF_6: Chel = Bipy (18), Phen (21)

Solid NaI or NH_4PF_6 were added to a solution of IrChel(NBD)Cl (0.3 g) in acetone/water (15 + 5 ml). The microcrystalline precipitates were filtered off after 20 min, washed with water and dried in vacuo. The iodo derivatives were recrystallized from acetone/water under nitrogen.

[IrChel(COD)(FUN)]X: Chel = Bipy, $X^- = PF_6^-$ (22); Chel = Phen, $X^- = ClO_4^-$ (23)

A suspension of [IrChel(COD)] X (0.2 g) in methylene chloride (20 ml) was treated with FUN (0.1 g). The colour was discharged and a white solid was formed which was filtered off after 20 min and washed with ether.

[IrBipy(NBD)(FUN)]PF_6 (24)

FUN (0.2 g) was added to a solution of (18) (0.25 g) in methyl cyanide (15 ml). The complex was precipitated from the filtered yellow solution by addition of ether.

[IrPhen(COD)(TCNE)]PF$_6$ (25)

A suspension of (14) (0.2 g) in methylene chloride (20 ml), was treated with the stoichiometric amount of TCNE. The solid, which precipitated immediately, was washed with a little methylene chloride.

[IrChel(COD)(MA)]PF$_6$: Chel = Bipy (26), Phen (27)

MA (0.2 g) was added to a solution of [IrChel(COD)]PF$_6$ (0.2 g) in methylene chloride (50 ml). The precipitate was washed with a little methylene chloride and petroleum ether.

[IrChel(COD)(PPh$_3$)]ClO$_4$: Chel = Bipy (28), Phen (29)

Triphenylphosphine (0.1 g) was added to a suspension of [IrChel(COD)]-ClO$_4$ (0.2 g) in methyl cyanide/ether (10 + 30 ml). The solid, which precipitated slowly from the orange solution, was filtered off and washed with ether.

[IrPhen(NBD)(PPh$_3$)]PF$_6$ (30)

Triphenylphosphine (0.1 g) was added to a suspension of (21) (0.2 g) in methyl cyanide/ether (10 + 30 ml). The orange solution was evaporated to dryness in vacuo and the residue was crystallized from acetone/water.

[IrChel(COD)(PEt$_3$)]PF$_6$: Chel = Bipy (31), Phen (32)

Triethylphosphine (0.55 mmole) was added to [IrChel(COD)]PF$_6$ (0.5 mmole) suspended in ether/methanol (30 + 10 ml). The solids, which precipitated immediately, were filtered off after 30 min and washed with ether.

[IrChel(COD)HCl]PF$_6$: Chel = Bipy (33), Phen (34); [IrBipy(NBD)HCl]PF$_6$ (38)

A suspension of [IrChel(L—L)]PF$_6$ (0.5 mmole) in methanol (30 ml) was treated with 4 drops of conc. hydrochloric acid to give immediate discharge of colour and precipitation of white solid.

[IrBipy(L—L)HY]ClO$_4$: L—L = COD, Y^- = Cl^- (35), Br^- (36), I^- (37); L—L = NBD, Y^- = I^- (39)

(a). A suspension of IrBipy(L—L)Y, (0.5 mmole) in methanol (30 ml), was treated with 3 drops of conc. perchloric acid. The microcrystalline precipitate was filtered off and washed with ether.

(b). A suspension of [IrBipy(L—L)]ClO$_4$, (5 mmole) in methanol (30 ml) was treated with 3 drops of conc. perchloric acid and then with LiY in excess. An inversion in the addition order of the reagents did not affect the nature of the products.

[IrPhen(COD)(PEt$_3$)H](ClO$_4$)$_2$ (40)

A suspension of [IrPhen(COD)(PEt$_3$)]ClO$_4$ (0.15 g) in methanol (10 ml) was treated with 1 drop of conc. perchloric acid. The white solid formed was isolated, washed thoroughly with water and dried in vacuo at room temperature.

[IrBipy(COD)CH_3I]PF_6 (41)

To a solution of (7) (0.1 g) in methyl cyanide (15 ml), were added 0.C5 g of NaI and after a few minutes 2 ml of methyl iodide. The precipitate, formed overnight, was separated and washed with water and methanol.

[IrBipy(NBD)CH_3I]PF_6 (42)

A suspension of (17) (0.2 g) in methyl cyanide (20 ml) treated with 2 ml of methyl iodide and after 5 min with solid NH_4PF_6, gave an orange solution. On adding water a microcrystalline precipitate was formed, which was isolated, washed thoroughly with water and dried in vacuo at room temperature.

Acknowledgements

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