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IRIDIUM(I) COMPLEXES WITH TETRAFLUOROBENZOBARRELENE

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Summary

Fifty three neutral and cationic iridium complexes containing tetrafluorobenzobarrelene and N-, P-, As-, Sb-, O- or S-donors as ancillary ligands, are described. Representative general formulae are: $IrCl(TFB)L_x$ ($x = 1$ or 2), $Ir(SnCl_3)(TFB)L_2$, $Ir(OClO_3)(TFB)_2$, $[Ir(TFB)_2L]^+$, $[Ir(TFB)L_2]^+$ and $[Ir(TFB)(CO)_3]^+$.

Introduction

The ready accessibility of $[IrCl(COD)]_2$ (COD = 1,5-cyclooctadiene) has promoted the development of an extensive chemistry of neutral and cationic complexes containing the iridium-cyclooctadiene moiety [1]. In addition, several compounds with other diolefins have been described [2].

Recent work [3] in our laboratory has revealed the capacity of the ligand tetrafluorobenzobicyclo[2.2.2]octatriene, (TFB) to stabilize pentacoordinated iridium complexes, such as $Ir(OClO_3)(COD)(TFB)$, $[Ir(COD)(TFB)(nitrile)]^+$ and $IrCl(TFB)_2$. Moreover, the last offers an opportunity for preparing new iridium complexes containing one or two tetrafluorobenzobarrelene ligands.

Herein we describe the synthesis and properties of new pentacoordinated or square planar iridium complexes containing TFB and N-, P-, As-, Sb-, O- or S-donors as ancillary ligands.

Results and discussion

Neutral complexes

Addition of an excess of 2-methylpyridine (2-Mepy) or quinoline (quin) to an acetone suspension of $IrCl(TFB)_2$ [3b] leads to displacement of one tetrafluorobenzobarrelene molecule and to the formation of a square-planar complex of the general formula IrCl(TFB)L, according to eq. 1:

$$IrCl(TFB)_2 + L \xrightarrow{Me_2CO} IrCl(TFB)L + TFB \quad (1)$$

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The resulting complexes of the IrCl(TFB)L type react with a stoichiometric amount of triphenylphosphine to give $IrCl(TFB)(PPh_3)$, which can also be obtained directly by reacting $IrCl(TFB)_2$ with an equimolar amount of triphenylphosphine.

Pentacoordinated complexes of the general formula $IrCl(TFB)L_2$ can be prepared according to eq. 2:

$$IrCl(TFB)_2 + 2L\ (\text{or } L{-}L) \xrightarrow{Me_2CO} IrCl(TFB)L_2 + TFB \qquad (2)$$

L = PPh_3, $AsPh_3$, $SbPh_3$; L–L = bis(1,2-diphenylphosphino)ethane (dppe), 1,10-phenanthroline (phen), 2,2′-bipyridine (bipy)

$IrCl(TFB)(AsPh_3)_2$ and $IrCl(TFB)(SbPh_3)_2$ react with triphenylphosphine to give mixed complexes of the general formula $IrCl(TFB)(PPh_3)L$, which alternatively are obtained as represented in eq. 3:

$$IrCl(TFB)(PPh_3) + L \xrightarrow{CH_2Cl_2} IrCl(TFB)(PPh_3)L \qquad (3)$$

(L = $AsPh_3$, $SbPh_3$)

Square-planar complexes of the type IrCl(TFB)L, as well as the analogous 1,5-cyclooctadiene compounds [4–6], are monomeric in chloroform. Their IR spectra show a single Ir–Cl stretching mode at 318 cm^{-1}, characteristic of an iridium–chloro terminal bond *trans* to a C=C double bond, and shifted by ca. 23 cm^{-1} towards higher frequencies relative to IrCl(COD)L [5].

On the other hand, refluxing of an ethanol suspension of $IrCl(TFB)_2$ with $SnCl_2 \cdot 2H_2O$, during 3 days, gives rise to the formation of $Ir(SnCl_3)(TFB)_2$ in 80% yield. The resulting complex reacts slowly with PPh_3 or dppe to form the corresponding $Ir(SnCl_3)(TFB)L_2$ derivatives. By contrast, one molecule of 1,5-cyclooctadiene is promptly displaced in the related $Ir(SnCl_3)(COD)_2$ [7].

A more appropriate preparative route is the addition of $SnCl_2 \cdot 2H_2O$ to acetone solutions of complexes of the type $IrCl(TFB)L_2$, as represented in eq. 4:

$$IrCl(TFB)L_2 + SnCl_2 \xrightarrow{Me_2CO} Ir(SnCl_3)(TFB)L_2 \qquad (4)$$

(L = PPh_3, $AsPh_3$, $SbPh_3$; L_2 = dppe, phen, bipy)

$Ir(SnCl_3)(COD)(phen)$, which is far less stable than the homologous compound $Ir(SnCl_3)(TFB)(phen)$, has been prepared similarly. Together with $Ir(SnCl_3)(TFB)(bipy)$ these are the first complexes containing trihalotin groups along with nitrogen donor ligands. Moreover, $Ir(SnCl_3)(TFB)(SbPh_3)_2$ is the first compound of this type containing a Sb-donor ligand.

In acetone, the mixed complexes $IrCl(TFB)(PPh_3)L$ do not react with $SnCl_2 \cdot 2H_2O$, whilst in methanol (which seems to favour the formation of ionic species of the type $[Ir(TFB)(PPh_3)L]^+Cl^-$) the addition of $SnCl_2 \cdot 2H_2O$ leads to the instantaneous precipitation of $Ir(SnCl_3)(TFB)(PPh_3)L$. Some related complexes of the type $Ir(SnCl_3)(COD)(CO)(PPh_3)$ have recently been reported [8].

The IR spectra of the trichlorotin complexes show two or three absorptions in the ν(Sn–Cl) region, similar to those observed for analogous compounds [9]. The displacement of the absorption due to ν(Sn–Cl) towards higher frequencies ($\Delta\nu = \nu(Sn{-}Cl)_{coordinated} - \nu(Sn{-}Cl)_{free} = 65{-}30\ cm^{-1}$) confirms that the $SnCl_3^-$ group is linked to the iridium atom [10].

The molecular weights and molar conductivities of complexes of the types $IrCl(diolefin)L_2$ and $Ir(SnCl_3)(diolefin)L_2$ (diolefin = COD [4,9,11] and TFB (this work; Table 1) point to a notable preference of the complexes containing TFB to be pentacoordinated, with a lower tendency to dissociate any of the ligands than those containing $SbPh_3$. This may also be seen from a comparison of the $[Ir(diolefin)_2]ClO_4$ complexes: when diolefin = COD, a cationic four-coordinated complex $[Ir(COD)_2]ClO_4$ is isolated [12,13], whilst when diolefin = TFB, we find that the complex (obtained by the reaction of $IrCl(TFB)_2$ with $AgClO_4$) contains a bonded perchlorate ligand $Ir(OClO_3)(TFB)_2$, as is revealed by the IR spectrum which is characteristic for this covalent bonded group (C_{3v} symmetry) [14]. In acetone

$$Ir(OClO_3)(TFB)_2 \overset{Me_2CO}{\rightleftharpoons} [Ir(TFB)_2]ClO_4$$

solution the perchlorate ligand is displaced and the measured conductivities are as expected for a 1:1 electrolyte. The same behaviour has also been observed for $Ir(OClO_3)(COD)(TFB)$ [3a].

Neutral complexes of the type Ir(A)(TFB) (A = acetylacetonate (acac) or 8-oxyquinolate (oq)) can be prepared by reacting $IrCl(TFB)_2$ with Tl(acac) or Na(oq). The latter, as well as the analogous 1,5-cyclooctadiene derivative [15], reacts with PPh_3 to give $Ir(oq)(TFB)(PPh_3)$, according to eq. 5:

$$Ir(oq)(TFB) + PPh_3 \xrightarrow{CH_2Cl_2} Ir(oq)(TFB)(PPh_3) \qquad (5)$$

Table 1 lists the analytical data, molar conductivities in acetone, molecular weights in chloroform, yields and colour for the neutral complexes.

Cationic complexes

Addition of an excess of 2-methylpyridine or quinoline, or of stoichiometric amounts of triphenylphosphine or 1,10-phenanthroline, to dichloromethane suspensions of $Ir(OClO_3)(TFB)_2$ leads to the displacement of one molecule of TFB and formation of square-planar complexes of the general formula $[Ir(TFB)L_2]ClO_4$* (eq. 6):

$$Ir(OClO_3)(TFB)_2 + 2\,L \xrightarrow{CH_2Cl_2} [Ir(TFB)L_2]ClO_4 + TFB \qquad (6)$$

Whilst, addition of an excess or a stoichiometric amount of ligands such as triphenylarsine, triphenylstibine, acetonitrile, dimethylsulphoxide **, diethylsulphide or triphenylphosphinesulphide merely leads to the displacement of the perchlorate group from its coordination site, and to the formation of pentacoordinated complexes of the type $[Ir(TFB)_2L]ClO_4$ (eq. 7):

$$Ir(OClO_3)(TFB)_2 + L \xrightarrow{CH_2Cl_2} [Ir(TFB)_2L]ClO_4 \qquad (7)$$

($L = AsPh_3, SbPh_3, MeCN, Me_2SO, SEt_2, SPPh_3$)

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* Analogous complexes $[Ir(TFB)L_2]BF_4$ are obtained on treating $IrCl(TFB)_2$ with $AgBF_4$, in presence of the corresponding ligand.

** In the IR spectrum, the presence of a strong band at 1020 cm^{-1} points to its coordination through the oxygen atom [16].

TABLE 1

COLOUR, ANALYTICAL RESULTS, MOLAR CONDUCTIVITIES, MOLECULAR WEIGHTS AND YIELDS FOR NEUTRAL COMPLEXES

Complex	Colour	Analyses (Found (calcd.) (%))			Λ_M (ohm^{-1} cm^2 mol^{-1})	Mol.wt.(CHCl$_3$) (Found(calcd.))	Yield (%)
		C	H	N			
IrCl(TFB)(2-Mepy)	yellow	40.33	2.83	2.47	1	595	75
(I)		(39.53)	(2.39)	(2.56)		(547)	
IrCl(TFB)(quin)	yellow	43.99	2.87	2.42	4	590	59
(II)		(43.26)	(2.25)	(2.40)		(583)	
IrCl(TFB)(PPh$_3$)	orange	50.41	3.09	–	0	756	70
(III)		(50.31)	(2.95)			(716)	
IrCl(TFB)(PPh$_3$)$_2$	yellow	59.34)	4.43	–	1	782	95
(IV)		(58.92)	(3.71)			(978)	
IrCl(TFB)(AsPh$_3$)$_2$	yellow	53.82	3.59	–	0	663	69
(V)		(54.08)	(3.40)			(1066)	
IrCl(TFB)(SbPh$_3$)$_2$	yellow	50.57	3.47	–	1	1130	72
(VI)		(49.70)	(3.13)			(1160)	
IrCl(TFB)(dppe)	yellow	53.28	3.99	–	2	927	96
(VII)		(53.55)	(3.55)			(852)	
IrCl(TFB)(phen)	violet	45.63	2.47	4.51	6	664	83
(VIII)		(45.46)	(2.22)	(4.42)		(634)	
IrCl(TFB)(bipy)	violet	43.34)	2.53)	4.27	3	662	80
(IX)		(43.32)	(2.31)	(4.59)		(610)	
IrCl(TFB)(PPh$_3$)(AsPh$_3$)	yellow	56.23	4.28	–	0	674	87
(X)		(56.39)	(3.55)			(1022)	

IrCl(TFB)(PPh$_3$)(SbPh$_3$)	yellow	53.76	3.47	–	0	692	78
(XI)		(53.92)	(3.39)			(1069)	
Ir(SnCl$_3$)(TFB)$_2$	white	33.41	1.62	–	0	–	80
(XII)		(33.15)	(1.39)				
Ir(SnCl$_3$)(TFB)(PPh$_3$)$_2$	yellow	49.08	3.26	–	6	1186	55
(XIII)		(49.36)	(3.11)			(1168)	
Ir(SnCl$_3$)(TFB)(AsPh$_3$)$_2$	yellow	45.70	3.18	–	13	1204	66
(XIV)		(45.90)	(2.89)			(1256)	
Ir(SnCl$_3$)(TFB)(SbPh$_3$)$_2$	yellow	42.73	2.86	–	3	1472	50
(XV)		(42.72)	(2.69)			(1350)	
Ir(SnCl$_3$)(TFB)(dppe)	yellow	43.75	2.86	–	2	–	59
(XVI)		(43.81)	(2.90)				
Ir(SnCl$_3$)(TFB)(phen)	violet	35.12	2.16	3.29	5	–	77
(XVII)		(35.00)	(1.71)	(3.40)			
Ir(SnCl$_3$)(TFB)(bipy)	violet	33.08	2.12	3.51	5	–	63
(XVIII)		(33.04)	(1.76)	(3.50)			
Ir(SnCl$_3$)(TFB)(PPh$_3$)(AsPh$_3$)	yellow	47.07	2.94	–	0	1145	67
(XIX)		(47.57)	(2.99)			(1212)	
Ir(SnCl$_3$)(TFB)(PPh$_3$)(SbPh$_3$)	yellow	45.71	2.90	–	0	1220	70
(XX)		(45.80)	(2.88)			(1259)	
Ir(OClO$_3$)(TFB)$_2$	yellow	38.97	1.80	–	112	–	74
(XXI)		(38.74)	(1.62)				
Ir(acac)(TFB)	yellow	40.13	2.84	–	1	560	80
(XXII)		(39.46)	(2.53)			(518)	
Ir(oq)(TFB)	red	44.40	2.69	2.83	0	–	38
(XXIII)		(44.84)	(2.15)	(2.49)			
Ir(oq)(TFB)(PPh$_3$)	orange	57.35	3.74)	1.78	0	799	46
(XXIV)		(56.79)	(3.30)	(1.70)		(824)	

TABLE 2

COLOUR, ANALYTICAL RESULTS, MOLAR CONDUCTIVITIES AND YIELDS FOR CATIONIC COMPLEXES

Complex	Colour	Analyses (Found (calcd.) (%))			Λ_M (ohm^{-1} cm^2 mol^{-1})	Yield (%)
		C	H	N		
($[Ir(TFB)(PPh_3)_2]ClO_4$	red	54.95	3.71	–	140	61
(XXV)		(55.31)	(3.48)			
$[Ir(TFB)(phen)]ClO_4$	red	40.81	2.60	3.72	106	95
(XXVI)		(41.30)	(2.02)	(4.01)		
$[Ir(TFB)(quin)_2]ClO_4$	yellow	46.72	3.22	3.50	122	72
(XXVII)		(46.42)	(2.60)	(3.61)		
$[Ir(TFB)(2\text{-}Mepy)_2]ClO_4$	yellow	40.61	3.96	3.49	130	86
(XXVIII)		(40.94)	(2.86)	(3.98)		
$[Ir(TFB)(AsPh_3)_2]ClO_4$	red	51.09	4.14	–	119	67
(XXIX)		(51.00)	(3.21)			
$[Ir(TFB)(SbPh_3)_2]ClO_4$	orange	46.54	3.37	–	103	65
(XXX)		(47.10)	(2.96)			
$[Ir(TFB)(phen)]BF_4$	red	40.98	2.98	4.10	132	95
(XXXI)		(42.06)	(2.06)	(4.09)		
$[Ir(TFB)(quin)_2]BF_4$	yellow	47.04	3.30	3.69	136	69
(XXXII)		(47.19)	(2.64)	(3.67)		
$[Ir(TFB)(2\text{-}Mepy)_2]BF_4$	yellow	41.29	3.50	3.96	139	74
(XXXIII)		(41.69)	(2.92)	(4.05)		
$[Ir(TFB)(sucn)]BF_4$	yellow	33.63	2.34	4.53	–	83
(XXXIV)		(32.83)	(1.72)	(4.79)		
$[Ir(TFB)(4\text{-}MeObzn)_2]BF_4$	yellow	44.35	3.08	3.66	–	78
(XXXV)		(43.59)	(2.61)	(3.63)		
$[Ir(TFB)(SEt_2)_2]BF_4$	orange	35.06	3.70	–	110	68
(XXXVI)		(35.04)	(3.82)			
$[Ir(TFB)_2(AsPh_3)]ClO_4$	white	48.28	3.40	–	132	75
(XXXVII)		(48.03)	(2.59)			

$[Ir(TFB)_2(SbPh_3)]ClO_4$	white	45.41	3.12	–	132	53
(XXXVIII)		(45.98)	(2.48)			
$[Ir(TFB)_2(MeCN)]ClO_4 \cdot \frac{1}{2}CH_2Cl_2$	white	38.47	2.03	1.59	124	73
(XXXIX)		(38.46)	(1.95)	(1.69)		
$[Ir(TFB)_2(OSMe_2)]ClO_4$	white	37.62	2.00	–	129	83
(XL)		(37.98)	(2.21)			
$[Ir(TFB)_2(SEt_2)]ClO_4$	white	41.18	3.26	–	122	80
(XLI)		(40.31)	(2.66)			
$[Ir(TFB)_2(SPPh_3)]ClO_4$	white	47.60	2.44	–	127	87
(XLII)		(48.58)	(2.62)			
$[Ir(TFB)_2(MeCN)]BF_4$	white	39.98	2.04	1.74	140	44
(XLIII)		(40.43)	(1.96)	(1.81)		
$[Ir(TFB)(PPh_3)(AsPh_3)]ClO_4$	red	53.26	3.91	–	113	72
(XLIV)		(53.07)	(3.34)			
$[Ir(TFB)(PPh_3)(SbPh_3)]ClO_4$	orange	50.30	3.80	–	101	66
(XLV)		(50.88)	(3.20)			
$[Ir(TFB)(quin)(PPh_3)]BF_4$	orange	51.96	4.14	1.79	129	60
(XLVI)		(52.24)	(3.15)	(1.56)		
$[Ir(TFB)(2\text{-}Mepy)(PPh_3)]BF_4$	orange	49.79	4.31	1.73	141	68
(XLVII)		(50.24)	(3.28)	(1.63)		
$[Ir(TFB)(4\text{-}MeObzn)(PPh_3)]BF_4$	orange	50.78	3.11	1.62	112	65
(XLVIII)		(50.68)	(3.13)	(1.56)		
$[Ir(TFB)(phen)(PPh_3)]BF_4$	red	53.11	3.53	3.11	128	70
(XLIX)		(53.23)	(3.08)	(2.96)		
$[Ir(TFB)(phen)(AsPh_3)]ClO_4$	red	49.92	3.10	2.59	119	66
(L)		(50.23)	(2.91)	(2.79)		
$[Ir(TFB)(phen)(SbPh_3)]ClO_4$	red	47.90	3.13	2.74	121	61
(LI)		(47.99)	(2.78)	(2.66)		
$[Ir(TFB)(phen)(P(OPh)_3)]ClO_4$	yellow	49.29	2.84	2.91	126	78
(LII)		(50.03)	(2.90)	(2.78)		
$[Ir(TFB)(CO)_3]ClO_4$	white	29.88	0.98	–	–	94
(LIII)		(29.93	(1.00)			

These complexes (L = MeCN, $AsPh_3$ or $SbPh_3$) can also be prepared by the reaction of $IrCl(TFB)_2$ with the corresponding ligand in the presence of silver salts, whereas the reaction between $IrCl(TFB)_2$ and the ligands $AsPh_3$ or $SbPh_3$ gives rise to the displacement of one molecule of TFB and to formation of $IrCl(TFB)L_2$ (see eq. 2). These compounds allow the synthesis of complexes of the type $[Ir(TFB)L_2]ClO_4$, obtained by treating $IrCl(TFB)L_2$ (L = $AsPh_3$ or $SbPh_3$) with $AgClO_4$ in CH_2Cl_2 (eq. 8):

$$IrCl(TFB)L_2 + AgClO_4 \xrightarrow{CH_2Cl_2} [Ir(TFB)L_2]ClO_4 + AgCl \quad (8)$$

$(L = AsPh_3, SbPh_3)$

On comparing these reactions of the iridium tetrafluorobenzobarrelene derivatives with those of complexes containing 1,5-cyclooctadiene, we can again observe an increased tendency of the former to give pentacoordinated species. Thus, $[Ir(COD)_2]^+$ reacts with an excess of MeCN to give the square-planar complex $[Ir(COD)(MeCN)_2]^+$ [17], and with a stoichiometric amount of SEt_2 to yield the binuclear complex $[Ir_2(COD)_2(SEt)_2](ClO_4)_2$ [12], in contrast to the formation of the pentacoordinated complexes $[Ir(TFB)_2L]ClO_4$ (L = MeCN or SEt_2).

Moreover, square planar complexes $[Ir(TFB)L_2]BF_4$, containing relatively weak ligands, incapable of displacing TFB from $IrCl(TFB)_2$ or $Ir(OClO_3)(TFB)_2$ (eqs. 2 and 6) can be obtained by treating Ir(acac)(TFB) with HBF_4, in the presence of the corresponding ligand, according to eq. 9:

$$Ir(acac)(TFB) + 2L\ (or\ L\text{–}L) + HBF_4 \rightarrow [Ir(TFB)L_2]BF_4 + Hacac \quad (9)$$

(L = 4-methoxybenzonitrile (4-MeObzn), SEt_2; L–L = succinonitrile (sucn))

Whilst addition of stoichiometric amounts of PPh_3 to $[Ir(TFB)(phen)]BF_4$ affords the pentacoordinated species $[Ir(TFB)(phen)(PPh_3)]BF_4$, the addition of PPh_3 to $[Ir(TFB)L_2]^+$ (L = 2-Mepy, quin, 4-MeObzn, $AsPh_3$ or $SbPh_3$) leads to displacement of one molecule of the respective monodentate ligand and to the formation of square-planar derivatives of the type $[Ir(TFB)L(PPh_3)]^+$. The reaction of $AsPh_3$, $SbPh_3$ or $P(OPh)_3$ with $[Ir(TFB)(phen)]ClO_4$ gives the corresponding pentacoordinated species.

Finally, it seems of interest to report that bubbling carbon monoxide (760 Torr) through a dichloromethane suspension of $Ir(OClO_3)(TFB)_2$ leads to a white, stable substance of the formula $[Ir(TFB)(CO)_3]ClO_4$.

All the above-mentioned observations suggest that the tetrafluorobenzobarrelene ligand shows a higher tendency to stabilize five-coordinated iridium complexes than the usual 1,5-cyclooctadiene ligand.

The analytical data, conductivities in acetone, yields and colour for the cationic complexes are collected in Table 2.

Experimental

C, H and N analyses were carried out with a Perkin–Elmer 240 microanalyzer. IR spectra were recorded on a Perkin–Elmer 577 spectrophotometer (over the range 4000–200 cm^{-1}) using Nujol mulls between polyethylene sheets. Conductivities were measured in 5×10^{-4} *M* acetone solutions with a Philips 9501/01 conductimeter.

Molecular weights were determined osmometrically with a Perkin–Elmer 115 instrument.

Preparation of complexes of the type IrCl(TFB)L (I,II)

A suspension of $IrCl(TFB)_2$ [3b] (62.0 mg, 0.09 mmol) in 25 ml of acetone was treated with a large excess of L (0.5 ml) for 15 min. The resulting yellow solution was evaporated under reduced pressure to ca. 0.5 ml. Slow addition of hexane led to the precipitation of a yellow solid, which was filtered off, washed with hexane and vacuum-dried.

Preparation of $IrCl(TFB)(PPh_3)$ (III)

This complex was prepared by two different routes:

(a) PPh_3 (29.9 mg, 0.11 mmol) in 5 ml of acetone was added to a solution of 0.11 mmol of IrCl(TFB)L (I,II) in 20 ml of acetone. The resulting orange coloured solution was vacuum-concentrated to ca. 0.5 ml. Slow addition of hexane precipitated an orange solid, which was filtered off, washed with hexane and vacuum-dried.

(b) A suspension of $IrCl(TFB)_2$ (58.3 mg, 0.08 mmol) in 20 ml of acetone was treated with PPh_3 (21.0 mg, 0.08 mmol) for 30 min. The resulting orange coloured solution was concentrated to 0.5 ml, and slow addition of hexane led to the precipitation of an orange solid, which was filtered off, washed with hexane and vacuum-dried.

Preparation of complexes of the type $IrCl(TFB)L_2$ (IV–IX)

A suspension of $IrCl(TFB)_2$ (62.0 mg, 0.09 mmol) in 25 ml of acetone was treated with L or, L–L (0.18 mmol of L, or 0.09 mmol of L–L) for 15 min. The resulting solution was evaporated under reduced pressure to ca. 0.5 ml. Slow addition of hexane led to the precipitation of the required complex, which was filtered off, washed with hexane and vacuum-dried.

Preparation of complexes of the type $IrCl(PPh_3)L$ (X,XI)

These complexes were prepared by two different routes:

(a) A solution of 0.06 mmol of $IrCl(TFB)L_2$ (V,VI) in 25 ml of dichloromethane was treated with PPh_3 (14.0 mg, 0.06 mmol) for 1 h. The resulting solution was concentrated under reduced pressure to ca. 0.5 ml. Slow addition of pentane/hexane (1/1,v/v) led to precipitation of a yellow solid, which was filtered off, washed with pentane and vacuum-dried.

(b) A solution of $IrCl(TFB)(PPh_3)$ (69.2 mg, 0.10 mmol) in 25 ml of dichloromethane was treated with 0.20 mmol of L for 10 min. The resulting solution was concentrated under reduced pressure to ca. 0.5 ml. Slow addition of pentane-hexane (1/1,v/v) led to precipitation of a yellow solid, which was treated as above.

Preparation of $Ir(SnCl_3)(TFB)_2$ (XII)

Under nitrogen, a stoichiometric amount of $IrCl(TFB)_2$ (309.8 mg, 0.45 mmol) was added to a solution of $SnCl_2 \cdot 2H_2O$ (102.8 mg, 0.45 mmol) in 25 ml of ethanol. After 72 h refluxing the mixture was concentrated to ca. 10 ml. The precipitated white solid was filtered off, washed with methanol and vacuum-dried.

Preparation of complexes of the type Ir(SnCl$_3$)(TFB)L$_2$ (XIII–XVIII)

A solution of 0.07 mmol of IrCl(TFB)L$_2$ (IV–IX) in 25 ml of acetone was treated with $SnCl_2 \cdot 2H_2O$ (15.3 mg, 0.07 mmol) for 10 min. The resulting solution was vacuum-concentrated to ca. 0.5 ml. Slow addition of hexane led to precipitation of the required complexes, which were filtered off, washed with hexane and vacuum-dried.

The deep blue complex Ir(SnCl$_3$)(COD)(phen) was prepared analogously, starting from [Ir(COD)(phen)]Cl [11]. Yield: 18%. Analysis Found: C, 32.99; H, 3.14; N, 3.51. $C_{20}H_{20}Cl_3N_2IrSn$ calcd.: C, 34.04; H, 2.86; N, 3.97%. ν(Sn–Cl) 285,300 cm^{-1}.

Preparation of complexes of the type Ir(SnCl$_3$)(TFB)(PPh$_3$)L (XIX,XX)

Addition of $SnCl_2 \cdot 2H_2O$ (12.4 mg, 0.05 mmol) to solutions of 0.05 mmol of IrCl(TFB)(PPh$_3$)L (X,XI) in 10 ml of methanol led to instantaneous precipitation of yellow solids. After 30 min stirring, the solids were filtered off, washed with methanol and vacuum-dried.

Preparation of Ir(OClO$_3$)(TFB)$_2$ (XXI)

To a suspension of IrCl(TFB)$_2$ (724.6 mg, 1.06 mmol) in 50 ml of acetone was added a stoichiometric amount of $AgClO_4$ (221.0 mg, 1.06 mmol). With exclusion of light, the mixture was stirred for 1 h. The formed AgCl was removed by filtration through anhydrous $MgSO_4$, which was washed with 500 ml of acetone. The yellow filtrate was vacuum-concentrated. Addition of dichloromethane led to precipitation of a yellow solid, which was filtered off, washed with dichloromethane and vacuum-dried.

Preparation of Ir(acac)(TFB) (XXII)

A suspension of IrCl(TFB)$_2$ (2.0 g, 2.96 mmol) in 50 ml of acetone was treated with Tl(acac) (899.9 mg, 2.96 mmol) for 3 h under nitrogen and protected from light. The formed TlCl was filtered off through kieselguhr. The yellow filtrate was vacuum-concentrated to ca. 3 ml. Addition of 10 ml of methanol led to precipitation of a yellow solid, which was filtered off, washed with methanol and vacuum-dried.

Preparation of Ir(oq)(TFB) (XXIII)

Sodium hydroxide (0.40 mmol) in 4.4 ml of methanol was added to a solution of 8-hydroxyquinoline (29.0 mg, 0.20 mmol) in 10 ml of methanol. After addition of IrCl(TFB)$_2$ (136.0 mg, 0.20 mmol) and 2 h stirring in an inert atmosphere, the precipitated dark-red solid was filtered off, subsequently washed with water and with 3 × 2 ml of methanol and finally vacuum-dried.

Preparation of Ir(oq)(TFB)(PPh$_3$) (XXIV)

In an inert atmosphere, PPh$_3$ (23.1 mg, 0.09 mmol) was added to a solution of Ir(oq)(TFB) (49.6 mg, 0.09 mmol) in 15 ml of dichloromethane. After 30 min stirring the solution was concentrated under reduced pressure. Addition of hexane caused the precipitation of an orange-coloured solid, which was filtered off, washed with hexane and vacuum-dried.

Preparation of complexes of the type [Ir(TFB)L$_2$]ClO$_4$ (XXV–XXX)

These complexes were obtained by two different routes:

(a) (XXV–XXVIII). Under nitrogen, a suspension of $Ir(OClO_3)(TFB)_2$ (50 mg, 0.07 mmol) in 20 ml of dichloromethane was treated for 30 min with the appropriate ligand ((PPh_3, 36.8 mg (0.14 mmol); 1,10-phen · H_2O, 13.3 mg (0.07 mmol), or 0.2 ml of 2-Mepy or quin). The resulting solutions were concentrated under reduced pressure to ca. 0.5 ml. Addition of ether led to the precipitation of the corresponding solids, which were filtered off, washed with ether and vacuum-dried.

(b) (XXIX–XXX). Under nitrogen and protected from daylight, a solution of $IrCl(TFB)L_2$ (V–VI) (0.13 mmol) in 20 ml of dichloromethane was treated for 30 min with $AgClO_4$ (25.4 mg, 0.13 mmol) in 5 ml of acetone. The formed AgCl was removed by filtration through kieselguhr. The filtrate was vacuum-concentrated to ca. 0.5 ml. Addition of ether led to precipitation of the appropriate solid, which was filtered off, washed with ether and vacuum-dried.

Preparation of complexes of the type $[Ir(TFB)L_2]BF_4$ (XXXI–XXXVI)

These complexes were obtained by two different routes:

(a) (XXXI–XXXIII). Under nitrogen and protected from daylight, a suspension of $IrCl(TFB)_2$ (104.2 mg, 0.15 mmol) in 25 ml of acetone or dichloromethane was treated for 30 min with the corresponding ligand (1,10-phen · H_2O; 29.7 mg (0.15 mmol) or 2-Mepy or quin: 0.2 ml) and with $AgBF_4$ (29.8 mg, 0.15 mmol) in 5 ml of acetone. The precipitated AgCl was removed by filtration through kieselguhr. The filtrate was vacuum-concentrated to ca. 0.5 ml and ether was added to precipitate the required complex, which was filtered off, washed with ether and vacuum-dried.

(b) (XXXIV–XXXVI). Under nitrogen a solution of Ir(acac)(TFB) (50.5 mg, 0.10 mmol) in 5 ml of dichloromethane was treated for 30 min with the required ligand (0.29 mmol) and with HBF_4 (0.10 mmol) in 25 ml of ether. The formed solid was filtered off, washed with ether and vacuum-dried.

Preparation of complexes of the type $[Ir(TFB)_2L]ClO_4$ (XXXVII–XLII)

Under nitrogen a suspension of $Ir(OClO_3)(TFB)_2$ (53.1 mg, 0.07 mmol) in 10 ml of dichloromethane was treated for 30 min with 0.07 mmol of the ligand L. Addition of 20 ml of ether led to precipitation of a white solid, which was filtered off, washed with ether and vacuum-dried.

Preparation of $[Ir(TFB)_2(MeCN)]BF_4$ (XLIII)

Under nitrogen and protected from daylight, $AgBF_4$ (22.0 mg, 0.11 mmol) was stirred for 30 min with a suspension of $IrCl(TFB)_2$ (77.0 mg, 0.11 mmol) in 25 ml of acetonitrile. After removing the formed AgCl by filtration through kieselguhr, the filtrate was vacuum-concentrated. Addition of ether rendered a white precipitate, which was filtered off, washed with ether and vacuum-dried.

Preparation of complexes of the type $[Ir(TFB)L(PPh_3)]A$ ($A = ClO_4$ or BF_4) (XLIV–XLVIII)

Under nitrogen, a solution of 0.1 mmol of $[Ir(TFB)L_2]A$ (XXIX,XXX,XXXII, XXXIII or XXXV) in 20 ml of dichloromethane was treated with PPh_3 (26.3 mg, 0.10 mmol) and stirred for 30 min (L = 2-Mepy, quin or 4-MeObzn) or, 18 h (L = $AsPh_3$ or $SbPh_3$). After vacuum-concentration to ca. 0.5 ml the addition of ether led to the precipitation of a solid, which was filtered off, washed with ether and vacuum-dried.

Preparation of complexes of the type [Ir(TFB)(phen)L]A ($A = ClO_4$ or BF_4) (XLIX–LII)

Under nitrogen, a suspension of 0.1 mmol of [Ir(TFB)(phen)]A (XXVI, XXXI) in 20 ml of dichloromethane was treated for 30 min with 0.1 mmol of L. After vacuum-concentration to ca. 0.5 ml, ether was added to precipitate the complex, which was filtered off, washed with ether and vacuum-dried.

Preparation of [Ir(TFB)(CO)$_3$]ClO$_4$ (LIII)

Bubbling of CO through a suspension of $Ir(OClO)_3)(TFB)_2$ (115 mg, 0.17 mmol) in 25 ml of dichloromethane led to solution of the complex and to precipitation of a white solid, which was filtered off, washed with ether and vacuum-dried. (ν(CO) 2145(s), 2095(s,br) cm^{-1}, Nujol).

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