Journal of Organometallic Chemistry, 273 (1984) 111–128
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

BARRELENEIRIDIUM(I) COMPLEXES. CRYSTAL STRUCTURES OF $[Ir(Me_3TFB)(\eta^6\text{-}C_6H_4Me_2)]ClO_4$ AND $[Ir(TFB)(\eta^5\text{-}PhNPh_2)]BF_4 \cdot CH_2Cl_2$ (TFB = tetrafluorobenzobarrelene)

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(Received March 20th, 1984)

Summary

A new series of cationic areneiridium(I) complexes of formula [Ir(barrelene)(arene)]$^+$ or [Ir(barrelene)(PhNRPh)]$^+$ (R = Ph or H) have been synthesized from neutral iridium complexes of the type [IrY(barrelene)]$_x$ (barrelene = Me_3TFB, Y = Cl or OMe ($x = 2$), Y = acac ($x = 1$); barrelene = TFB, Y = OMe ($x = 2$), Y = acac ($x = 1$)). The crystal structures of $[Ir(Me_3TFB)(1,4\text{-}C_6H_4Me_2)]ClO_4$ and $[Ir(TFB)(PhNPh_2)]BF_4 \cdot CH_2Cl_2$ have been determined by X-ray diffraction. They crystallize in the space groups *Pbca* and *Pna*2_1 respectively with lattice constants of 17.6947(11), 15.8072(10), 16.0019(11) Å and 9.8059(2), 20.8097(9), 14.3367(4) Å. Final *R* factors were 0.063 and 0.042 for the observed data. Both complexes show a staggered arrangement between the arene and the TFB moieties and deviation from planarity of the coordinated arene ligands. In the second complex the Ir–C and N–C distances, the C–N–C angle, the type of arene puckering, and the spectroscopic data indicate a distortion of the coordinated arene towards a η^5-coordinated iminocyclohexadienyl form.

Introduction

π-Arene-rhodium(I) and -iridium(I) complexes have attracted considerable interest in recent years [1,2] for a variety of reasons, including the lability of the π-arene bond [3–5]. In particular, some rhodium, iridium and ruthenium complexes containing BPh_4, PPh_3 or $OPPh_3$ ligands form π-arene complexes through these ligands

0022-328X/84/$03.00

[6–10]. Furthermore, some related complexes containing the phenyl ring of aniline or phenylamine ligands coordinated to rhodium or iridium atoms have been described [11,12].

We previously described several η^6-arene-diolefin-rhodium or -iridium complexes showing a general tendency for the coordinated arene to depart from planarity [13–15]. Because of the new synthetic procedures available to us, and in the light of our interest in this area, we have begun a programme of preparation and structural characterization of a family of barreleneiridium complexes.

Results and discussion

The dinuclear $[IrCl(Me_3TFB)]_2$ (I) complex was prepared by reaction of $IrCl_3 \cdot xH_2O$ with trimethyltetrafluorobenzobarrelene (Me_3TFB). However, $IrCl(TFB)_2$ was obtained when tetrafluorobenzobarrelene (TFB) was used as diolefin [15]. Both chloro complexes react with potassium hydroxide in methanol or in the presence of acetylacetone to give $[Ir(OMe)(diolefin)]_2$ (diolefin = Me_3TFB (II), TFB (III)) or Ir(acac)(diolefin) (diolefin = Me_3TFB (IV), TFB (V) [16]). Interestingly, complexes III and V react with hydrochloric acid to give the dinuclear complex $[IrCl(TFB)]_2$ (VI), inaccessible by direct reaction between $IrCl_3 \cdot xH_2O$ and TFB. Complexes I–VI are useful starting materials for the synthesis of $[Ir(diolefin)(arene)]^+$ complexes. In particular, compounds V and VI provide sources of some new arene complexes not prepared from $IrCl(TFB)_2$ [15].

The neutral complexes are yellow, except for complex III which is orange. In all cases the IR spectra show the presence of the coordinated barrelene ligand [3,15], and there are also strong bands characteristic of the coordinated chloride (ν(Ir–Cl) 265, 305 (I) and 255, 295 cm^{-1} (VI)), methoxo (ν(C–O) ca. 1050 cm^{-1}) or acetylacetonate (ν(C$\overset{\ldots}{-}$O) 1525 and 1550 cm^{-1} (IV)) groups.

A direct route for the synthesis of $[Ir(Me_3TFB)(arene)]ClO_4$ complexes is indicated in eq. 1:

$$1/2[IrCl(Me_3TFB)]_2 + AgClO_4 + \text{arene} \rightarrow [Ir(Me_3TFB)(\text{arene})]ClO_4 + AgCl \quad (1)$$

arene = C_6Me_6 (VII), 1,2,4,5-$C_6H_2Me_4$ (VIII), 1,3,5-$C_6H_3Me_3$ (IX), 1,2,4-$C_6H_3Me_3$ (X), 1,4-$C_6H_4Me_2$(XI), 1,3-$C_6H_4Me_2$ (XII), 1,2-$C_6H_4Me_2$ (XIII), C_6H_5Me (XIV), C_6H_6 (XV), 1,4-$C_6H_4(OH)_2$ (XVI), acetophenone (XVII), tetralin (XVIII), naphthalene (XIX), biphenyl (XX), indene (XXI), 9,10-dihydroanthracene (XXII)

Similar $[Ir(TFB)(arene)]BF_4$ complexes (arene = $C_6H_{6-n}Me_n$, $n = 2,3,4,6$) have been recently prepared [15] by treatment of an acetone suspension of $IrCl(TFB)_2$ with $AgBF_4$ and arene ligands under reflux. However, tetrafluorobenzobarrelene-iridium-arene complexes with lower electron densities in the ring (C_6H_5Me or C_6H_6) can be prepared by reaction of complex V with $HClO_4$, or according to eq. 1 using complex VI as starting material.

Interestingly, $[Ir(TFB)(PhNRPh)]BF_4$ or $[Ir(Me_3TFB)(PhNRPh)]ClO_4$ complexes can be prepared in the presence of excess of $NRPh_2$ by the following procedures:

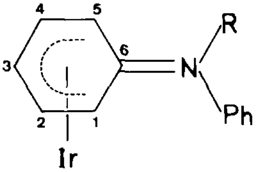
$$1/x[IrY(TFB)]_x + NRPh_2 + HBF_4 \rightarrow [Ir(TFB)(PhNRPh)]BF_4 + HY$$

R = Ph (XXV) or H (XXVI); Y = acac, $x = 1$; Y = OMe, $x = 2$

$$1/2[IrCl(Me_3TFB)]_2 + AgClO_4 + NRPh_2 \rightarrow [Ir(Me_3TFB)(PhNRPh)]ClO_4$$

R = Ph (XXVII) of H (XXVIII)

The presence of only one molecule of the amine per iridium atom suggest initially that a phenyl ring is π-coordinated to the metal. Furthermore, the presence of strong bands at 1590 (XXV), 1600 (XXVI), 1587 (XXVII) and 1598 (XXVIII) cm^{-1} assigned to ν(C=N), probably coupled to the ring C=C vibrations, suggest a significant contribution of an iminocyclohexadienyl form [11]:



(R=Ph or H)

Furthermore, the ^{13}C NMR spectrum for complex XXVIII shows the presence of two types of phenyl carbon nuclei, with a pattern very similar to that reported by Maitlis and coworkers for related dicationic η^5-aniline-iridium(III) complexes [11] (^{13}C NMR spectrum of complex XXVIII: coordinated phenyl ring: δ(ppm) 94.1, C(3); 94.0, C(2/4); 76.0, C(1/5); uncoordinated phenyl ring: δ(ppm) 137.0, C(6′) (and C(6)); 130.1, C(2′/4′); 126.6, C(3′); 123.4, C(1′/5′)). The X-ray structure of complex XXV (see below) completely substantiates this conclusion. On the other hand, a similar feature is probably present in the recently reported analogous complexes of the type $[Ir(COD)(PhNRPh)]BF_4$ [12]; the IR (R = H, ν(C=N) 1598 cm^{-1}; R = Ph, ν(C=N) 1590 cm^{-1}) and ^{13}C NMR (R = H *) spectra also support this type of bonding for the latter complexes.

The cationic arene complexes are generally white (complex XIX is yellow) and behave as 1/1 electrolytes in acetone. Their IR spectra show the absorptions due to the uncoordinated anion along with bands characteristic of coordinated barrelene and arene ligands.

Table 1 lists some relevant NMR data for $[Ir(diolefin)(arene)]^+$ complexes. As expected the resonances of protons directly bound to the arene ring are modified upon coordination. Furthermore, the chemical shift of the arene-methyl substituent moves downfield by ca. 0.45–0.3 (Me_3TFB), 0.4–0.3 (TFB) and 0.3–0.25 (COD) ppm. On the other hand the upfield displacement of the chemical shift of the vinyl protons for these iridium complexes is higher than it is for analogous rhodium derivatives [3]. In both metals, the displacement is directly related to the number of methyl groups present in the arene, and thus increases with the donor capacity of the arene. The ^1H NMR spectra of these arene-barrelene-iridium complexes in deuteroacetone ** show no formation of $[Ir(barrelene)(acetone\text{-}d_6)_x]^+$, whereas formation of the $[Ir(COD)(acetone\text{-}d_6)_x]^+$ species has been observed for the related

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* ^{13}C NMR spectrum of $[Ir(COD)(PhNHPh)]BF_4$: coordinated phenyl ring: 95.0, C(3); 94.75, C(2/4); 76.9, C(1/5); uncoordinated phenyl ring: δ (ppm) 137.0, C(6′); 130.1, C(2′/4′); 126.7, C(3′); 124.1, C(1′/5′).

** In contrast, dissociation of the coordinated arene is generally observed in analogous arene-barrelene-rhodium complexes [3].

TABLE 1

SELECTED CHEMICAL SHIFTS[a] FOR $[Ir(diolefin)(arene)]^+$ COMPLEXES

Arene	Diolefin = Me_3TFB			Diolefin = TFB			Diolefin = COD[b]		
	Vinyl protons	Coordinated arene		Vinyl protons	Coordinated arene		Vinyl protons	Coordinated arene	
		aromatic H	methyl H		aromatic H	methyl H		aromatic H	methyl H
C_6Me_6	c	–	2.56	3.30	–	2.55	3.54[d]	–	2.28[d]
1,2,4,5-$C_6H_2Me_4$	3.06	6.50	2.62	3.55	6.85	2.56	4.18	6.57	2.46
1,3,5-$C_6H_3Me_3$	3.11	6.87	2.56	3.67	6.96	2.59	4.32	6.84	2.49
1,2,4-$C_6H_3Me_3$	3.21–3.06	7.03–6.48	2.63, 2.56	3.70	6.96–6.86	2.59	4.32[d]	6.86, 6.71 6.63[d]	2.52, 2.48 2.47[d]
1,4-$C_6H_4Me_2$	3.21	6.79	2.60	3.79	6.97	2.63	4.49	6.83	2.55
1,3-$C_6H_4Me_2$	3.31	7.07–6.72	2.68	–	–	–	4.49	6.94–6.75	2.54
1,2-$C_6H_4Me_2$	3.33	7.14–6.77	2.65	3.77	6.96–6.93	2.62	4.49	6.96–6.82	2.51
C_6H_5Me	3.45	7.01	2.73	–	–	–	4.66	7.01–6.92	2.59
C_6H_6	3.59	7.14	–	–	–	–	4.83	7.07	–

[a] Spectra were measured in acetone-d_6 solution. Chemical shifts are given in δ (ppm). [b] The resonances of these complexes have been assigned by Muetterties et al. [4,5].
[c] This resonance is obscured by the H_2O signal of the deuterated solvent [d]Determined in $CDCl_3$.

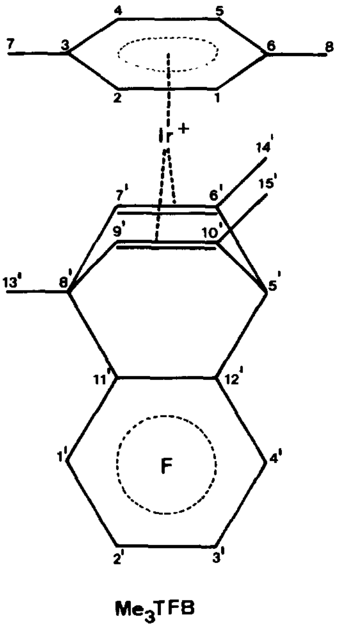
$[Ir(COD)(arene)]^+$ complexes when arene = C_6H_5Me or C_6H_6 [4]. Nevertheless, exchange experiments in deuteroacetone on the reaction:

$$[Ir(barrelene)(1,4\text{-}C_6H_4Me_2)]^+ + C_6Me_6 \rightleftarrows [Ir(barrelene)(C_6Me_6)]^+ + 1,4\text{-}C_6H_4Me_2$$

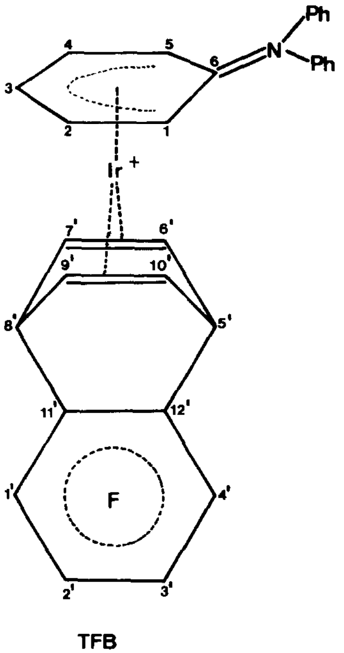
showed that, after 24 h, 30% of $[Ir(TFB)(C_6Me_6)]^+$ was formed, but less than 5% of the $[Ir(Me_3TFB)(C_6Me_6)]^+$ cation was observed under similar conditions. These results indicate that the lability of the arene–iridium bond is modified by the auxiliary diolefin in the order COD > TFB > Me_3TFB, in good agreement with previous results on analogous rhodium complexes [3].

Crystal structures

Complexes $[Ir(Me_3TFB)(1,4\text{-}C_6H_4Me_2)]ClO_4$ and $[Ir(TFB)(PhNPh_2)]BF_4 \cdot CH_2Cl_2$ (XI and XXV hereafter) show different coordination patterns.



XI



XXV

The coordination in compound XI is similar to that in the unmethylated analogue [15], with two short distances, Ir–C(5) and Ir–C(2), corresponding to the carbon atoms situated opposite to the olefin bonds, two with intermediate values (Ir–C(1) and Ir–C(4)), and the other two (Ir–C(3) and Ir–C(6)) with longer ones. In compound XXV the carbon atoms opposite to the olefinic bonds show a short distance to the Ir atom for C(2), but for C(5) the value is similar to those to C(1), C(3) and C(4), while the Ir–C(6) distance is much longer; the C(6) atom deviates significantly from the coordination set, suggesting, when considered with the spec-

TABLE 2

BOND DISTANCES (Å) AND BOND ANGLES (°)

	XI	XXV
Ir–C(1)	2.299(10)	2.286(15)
Ir–C(2)	2.250(9)	2.220(14)
Ir–C(3)	2.343(11)	2.297(15)
Ir–C(4)	2.276(9)	2.308(14)
Ir–C(5)	2.228(9)	2.287(16)
Ir–C(6)	2.346(9)	2.457(11)
Ir–C(6′)	2.165(8)	2.116(11)
Ir–C(7′)	2.128(8)	2.097(16)
Ir–C(9′)	2.135(7)	2.138(11)
Ir–C(10′)	2.166(7)	2.146(14)
C(1)–C(2)	1.430(16)	1.436(18)
C(2)–C(3)	1.414(16)	1.417(23)
C(3)–C(4)	1.421(14)	1.410(22)
C(4)–C(5)	1.396(13)	1.456(21)
C(5)–C(6)	1.398(14)	1.449(26)
C(6)–C(1)	1.412(14)	1.434(24)
C(3)–C(7)/C(6)–N	1.464(20)	1.372(15)
C(6)–C(8)/N–C(11)	1.503(17)	1.434(19)
/N–C(21)	–	1.454(18)
C(1′)–C(2′)	1.390(13)	1.364(22)
C(1′)–C(11′)	1.385(11)	1.389(18)
C(2′)–C(3′)	1.361(15)	1.353(22)
C(3′)–C(4′)	1.389(13)	1.393(20)
C(4′)–C(12′)	1.365(12)	1.383(19)
C(5′)–C(6′)	1.554(11)	1.564(25)
C(5′)–C(10′)	1.525(11)	1.454(22)
C(5′)–C(12′)	1.523(11)	1.501(20)
C(6′)–C(7′)	1.426(11)	1.397(27)
C(7′)–C(8′)	1.518(10)	1.526(23)
C(8′)–C(9′)	1.517(10)	1.499(18)
C(8′)–C(11′)	1.514(11)	1.512(20)
C(9′)–C(10′)	1.443(10)	1.439(19)
C(11′)–C(12′)	1.396(11)	1.372(21)
C(1′)–F(1′)	1.330(10)	1.368(22)
C(2′)–F(2′)	1.347(11)	1.351(15)
C(3′)–F(3′)	1.336(12)	1.347(19)
C(4′)–F(4′)	1.376(11)	1.342(17)
C(6′)–C(14′)	1.473(12)	–
C(8′)–C(13′)	1.509(12)	–
C(10′)–C(15′)	1.488(12)	–
Cl–O(1)/B–F(1)	1.405(11)	1.317(30)
Cl–O(2)/B–F(2)	1.414(10)	1.336(32)
Cl–O(3)/B–F(3)	1.374(17)	1.348(29)
Cl–O(4)/B–F(4)	1.398(19)	1.325(28)
/C(10)–Cl(1)	–	1.715(27)
/C(10)–Cl(2)	–	1.804(27)
C(6)–C(1)–C(2)	119.1(9)	118.7(14)
C(1)–C(2)–C(3)	123.0(10)	122.0(13)
C(2)–C(3)–C(4)	115.7(10)	119.2(14)
C(3)–C(4)–C(5)	121.2(9)	119.1(13)
C(4)–C(5)–C(6)	122.6(9)	120.0(13)
C(5)–C(6)–C(1)	117.7(9)	118.1(12)

TABLE 2 (continued)

	XI	XXV
C(2)–C(3)–C(7)/C(5)–C(6)–N	121.0(11)	121.3(16)
C(4)–C(3)–C(7)/C(1)–C(6)–N	123.3(11)	120.5(16)
C(5)–C(6)–C(8)/C(6)–N–C(11)	120.9(9)	120.4(12)
C(1)–C(6)–C(8)/C(6)–N–C(21)	121.4(11)	122.9(11)
/C(11)–N–C(21)	–	116.1(10)
C(11′)–C(1′)–F(1′)	123.6(7)	121.3(12)
C(2′)–C(1′)–F(1′)	116.0(7)	117.8(11)
C(2′)–C(1′)–C(11′)	120.4(8)	120.9(14)
C(1′)–C(2′)–F(2′)	119.8(9)	120.5(14)
C(1′)–C(2′)–C(3′)	121.0(8)	120.1(13)
C(3′)–C(2′)–F(2′)	119.2(8)	119.4(13)
C(2′)–C(3′)–F(3′)	120.7(9)	120.6(13)
C(4′)–C(3′)–F(3′)	120.7(9)	119.2(13)
C(3′)–C(4′)–C(12′)	121.5(8)	119.7(13)
C(12′)–C(4′)–F(4′)	120.5(8)	122.5(12)
C(10′)–C(5′)–C(12′)	108.7(6)	111.2(13)
C(6′)–C(5′)–C(12′)	109.9(6)	108.1(10)
C(6′)–C(5′)–C(10′)	98.6(6)	98.0(10)
C(5′)–C(6′)–C(7′)	109.8(6)	110.8(12)
C(6′)–C(7′)–C(8′)	116.7(7)	114.8(13)
C(7′)–C(8′)–C(11′)	108.6(6)	109.1(11)
C(7′)–C(8′)–C(9′)	96.2(6)	94.6(10)
C(9′)–C(8′)–C(11′)	107.9(6)	110.2(13)
C(8′)–C(9′)–C(10′)	115.5(6)	111.6(11)
C(5′)–C(10′)–C(9′)	110.9(6)	114.5(12)
C(1′)–C(11′)–C(8′)	127.9(7)	125.5(16)
C(8′)–C(11′)–C(12′)	113.7(7)	115.3(11)
C(1′)–C(11′)–C(12′)	118.3(7)	119.2(12)
C(5′)–C(12′)–C(11′)	114.6(7)	112.6(11)
C(4′)–C(12′)–C(11′)	120.2(8)	119.8(12)
C(4′)–C(12′)–C(5′)	125.1(7)	127.6(12)
C(2′)–C(3′)–C(4′)	118.5(9)	120.2(14)
C(3′)–C(4′)–F(4′)	118.0(8)	117.7(13)
C(5′)–C(6′)–C(14′)	120.7(7)	–
C(7′)–C(6′)–C(14′)	125.1(8)	–
C(7′)–C(8′)–C(13′)	112.1(6)	–
C(9′)–C(8′)–C(13′)	120.0(7)	–
C(11′)–C(8′)–C(13′)	117.8(7)	–
C(9′)–C(10′)–C(15′)	124.0(7)	–
C(5′)–C(10′)–C(15′)	120.3(7)	–
O(1)–Cl–O(2)/F(1)–B–F(2)	107.2(7)	115.5(24)
O(1)–Cl–O(3)/F(1)–B–F(3)	113.9(8)	112.9(20)
O(1)–Cl–O(4)/F(1)–B–F(4)	104.8(10)	108.8(20)
O(2)–Cl–O(3)/F(2)–B–F(3)	109.4(8)	99.6(20)
O(2)–Cl–O(4)/F(2)–B–F(4)	109.5(11)	109.0(21)
O(3)–Cl–O(4)/F(3)–B–F(4)	111.9(11)	110.7(19)
/Cl(1)–C(10)–Cl(2)	–	111.5(15)

troscopic data, a η^3-type for the coordination in this complex. This would involve double bonding in the C(6)–N bond [11]. Bond distances and angles in the arene ring agree with those reported for analogous complexes [15] within the experimental error, but bond angles around C(6) and N atoms (see Tables 2 and 3) suggest a sp^2

TABLE 3

SELECTED TORSION ANGLES (°)

	XI	XXV
C(6)–C(1)–C(2)–C(3)	−2.8(12)	4.1(22)
C(1)–C(2)–C(3)–C(4)	6.5(12)	5.1(22)
C(2)–C(3)–C(4)–C(5)	−2.4(11)	−1.2(21)
C(3)–C(4)–C(5)–C(6)	−5.6(12)	−11.5(21)
C(4)–C(5)–C(6)–C(1)	9.3(11)	20.4(21)
C(5)–C(6)–C(1)–C(2)	−5.1(11)	−16.6(21)
C(5′)–C(6′)–C(7′)–C(8′)	−0.3(9)	−4.2(20)
C(5′)–C(10′)–C(9′)–C(8′)	−0.2(9)	2.6(16)
C(6′)–C(5′)–C(8′)–C(7′)	−0.1(5)	−2.3(10)
C(6′)–C(5′)–C(8′)–C(9′)	−109.8(5)	−108.4(10)
C(6′)–C(5′)–C(8′)–C(11′)	125.6(6)	123.9(11)
C(10′)–C(5′)–C(8′)–C(7′)	109.5(5)	107.6(12)
C(10′)–C(5′)–C(8′)–C(9′)	−0.1(5)	1.4(9)
C(10′)–C(5′)–C(8′)–C(11′)	−124.7(5)	−126.3(12)
C(12′)–C(5′)–C(8′)–C(7′)	−126.1(5)	−125.0(12)
C(12′)–C(5′)–C(8′)–C(9′)	124.3(5)	128.8(10)
C(12′)–C(5′)–C(8′)–C(11′)	−0.3(5)	1.1(10)
C(5)–C(6)–N–C(21)	–	−11.2(21)
C(5)–C(6)–N–C(11)	–	178.6(13)
C(1)–C(6)–N–C(21)	–	164.6(13)
C(1)–C(6)–N–C(11)	–	−5.6(21)
C(6)–N–C(21)–C(22)	–	123.1(16)
C(6)–N–C(21)–C(26)	–	−60.6(19)
C(6)–N–C(11)–C(12)	–	100.3(16)
C(6)–N–C(11)–C(16)	–	−82.7(16)

character for both atoms and some double bond character for the C(6)–N bond [17]. Significant differences in the Ir–C(olefin) distances are observed in both compounds (see Table 2).

The puckering in the arene ring previously observed in this type of compound [15] is also seen in both complexes XI and XXV (see Figs. 1 and 2). Table 4 presents the puckering data [18,19]. Complex XI has the arene with a "skew" conformation, closer to the corresponding unmethylated TFB complex. In complex XXV the puckering departs from the usual conformations at $\theta \sim 90°$, flattening to a "diplanaire" [20] conformation but distorted towards an "envelope" at C(6), in such a way that the angle between the least-squares plane defined by C(1), C(2), C(3), C(4), C(5) and that through C(1), C(6), C(5) is 16.8(9)°, close to that in $[Rh(C_5Me_5)(PhNHMe)]^{2+}$ [11].

The methyl-substituted C atoms of $1,4\text{-}C_6H_4Me_2$ in complex XI and the NPh_2-substituted C atom in complex XXV, as in other $[M(diolefin)(arene)]^+$ derivatives [3,13–15], are not situated opposite to the olefinic bonds, confirming an electronic effect. The relative twist between the arene rings and the respective TFB moieties, destroying the symmetry, and measured by the angle in projection between C(5′) ··· C(8′) and C(6) ··· C(3), respectively (see Figs. 1 and 2) is, on average, −35.9 in XI and −36.0° in XXV, (it is −31.8° in [15]). The distance from the Ir atom to the

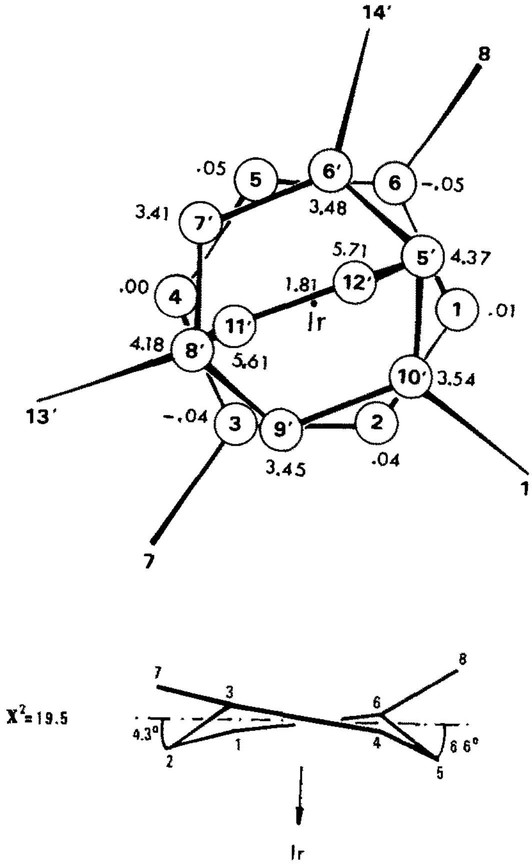


Fig. 1. Coordination of the Ir atom in compound XI as projected on to the least-squares plane through the arene ring. Atomic deviations in Å. The puckering of the arene ring is shown below.

least-squares planes through the arene rings and through the olefinic bonds are 1.805(5) and 1.667(6) Å in XI, and 1.778(8) and 1.656(7) Å in XXV, in agreement with results for other Ir complexes [15].

The geometry of the ClO_4^-, BF_4^-, TFB, CH_2Cl_2 and phenyl groups shows the usual features, in agreement with known data for structures of this type [3,15].

TABLE 4

PUCKERING OF THE ARENE RING (q_2, q_3 and Q values are in Å; ϕ_2 and θ in °)

Compound	Cremer and Pople parameters [18,19]				
	q_3	q_2	ϕ_2	θ	Q
Theoretical skew	0	Q	270	90	Q
Theoretical "diplanaire" [20]	q_3	q_2	90	112.5	Q
XI	0.084(9)	+0.011(9)	271(7)	82(6)	0.85(9)
XXV	−0.07(1)	0.14(1)	104(5)	116(5)	0.16(1)

Experimental

C, H and N analyses were carried out with a Perkin–Elmer 240-B microanalyzer. Conductivities were measured at 20 °C in ca. 4×10^{-4} *M* acetone solutions using a Philips 9501/01 conductimeter. IR spectra were recorded on a Perkin–Elmer 599 spectrophotometer over the range 4000–200 cm^{-1}, using Nujol mulls between polyethylene sheets. ^1H and ^{13}C NMR spectra were recorded on a Varian FT80 A instrument. All reactions were carried out under dry nitrogen, and the solvents were dried by standard methods and distilled before use. Analytical data are listed in Table 5.

Preparation of $[IrCl(Me_3TFB)]_2$ *(I)*

To a mixture of water (12 ml), ethanol (24 ml), and Me_3TFB (1.42 g, 5.3 mmol) was added $IrCl_3 \cdot xH_2O$ (1.87 g, 5.3 mmol). The suspension was refluxed for 24 h under nitrogen and the yellow precipitate was filtered off, washed with methanol, and air dried (Yield 77%).

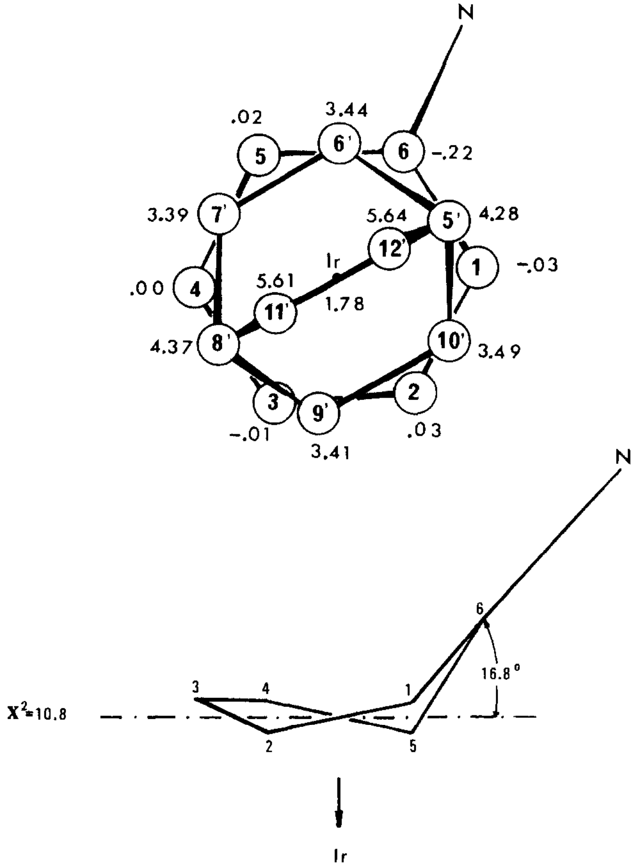


Fig. 2. Coordination of the Ir atom in compound XXV as projected on to the least-squares plane through the C(1)–C(5) atoms. Atomic deviations in Å. The puckering of the arene ring is shown below.

TABLE 5. ANALYSES, MOLAR CONDUCTIVITIES, AND YIELDS FOR THE COMPLEXES PREPARED

Complex		Analysis (Found (calcd.) (%))			Λ_M (ohm^{-1} cm^2 mol^{-1})	Yield (%)
		C	H	N		
$[IrCl(Me_3TFB)]_2$	(I)	37.0	2.8	–	–	77
		(36.3)	(2.4)			
$[Ir(OMe)(Me_3TFB)]_2$	(II)	38.9	3.1	–	–	93
		(39.1)	(3.1)			
$[Ir(OMe)(TFB)]_2$	(III)	35.3	2.3	–	–	96
		(34.8)	(2.0			
$Ir(acac)(Me_3TFB)$	(IV)	42.5	3.1	–	–	32
		(42.9)	(3.4)			
$[IrCl(TFB)]_2$	(VI)	32.5	1.5	–	–	87
		(31.8)	(1.3)			
$[Ir(Me_3TFB)(C_6Me_6)]ClO_4$	(VII)	45.7	4.3	–	142	66
		(44.9)	(4.2)			
$[Ir(Me_3TFB)(1,2,4,5\text{-}C_6H_2Me_4)]ClO_4$	(VIII)	44.0	4.1	–	138	85
		(43.3)	(3.8)			
$[Ir(Me_3TFB)(1,3,5\text{-}C_6H_3Me_3)]ClO_4$	(IX)	43.3	3.9	–	142	85
		(42.4)	(3.6)			
$[Ir(Me_3TFB)(1,2,4\text{-}C_6H_3Me_3)]ClO_4$	(X)	42.5	3.6	–	138	81
		(42.4)	(3.6)			
$[Ir(Me_3TFB)(1,4\text{-}C_6H_4Me_2)]ClO_4$	(XI)	41.1	3.3	–	136	91
		(41.5)	(3.3)			
$[Ir(Me_3TFB)(1,3\text{-}C_6H_4Me_2)]ClO_4$	(XII)	41.3	3.8	–	134	89
		(41.5)	(3.3)			
$[Ir(Me_3TFB)(1,2\text{-}C_6H_4Me_2)]ClO_4$	(XIII)	42.0	3.8	–	138	80
		(41.5)	(3.3)			
$[Ir(Me_3TFB)(C_6H_5Me)]ClO_4$	(XIV)	40.7	3.2	–	138	81
		(40.5)	(3.1)			
$[Ir(Me_3TFB)(C_6H_6)]ClO_4$	(XV)	39.5	2.9	–	140	78
		(39.5)	(2.8)			
$[Ir(Me_3TFB)(1,4\text{-}C_6H_4(OH)_2)]ClO_4$	(XVI)	37.9	3.0	–	125	74
		(37.6)	(2.7)			
$[Ir(Me_3TFB)(\text{acetophenone})]ClO_4$	(XVII)	40.2	3.1	–	118	20
		(40.6)	(3.0)			
$[Ir(Me_3TFB)(\text{tetralin})]ClO_4$	(XVIII)	43.0	3.6	–	122	71
		(43.4)	(3.5)			
$[Ir(Me_3TFB)(\text{naphthalene})]ClO_4$	(XIX)	43.1	3.3	–	109	67
		(43.6)	(2.9)			
$[Ir(Me_3TFB)(\text{biphenyl})]ClO_4$	(XX)	44.4	3.3	–	132	55
		(45.4)	(3.1)			
$[Ir(Me_3TFB)(\text{indene})]ClO_4$	(XXI)	42.5	3.3	–	135	73
		(42.6)	(3.0)			
$[Ir(Me_3TFB)(9,10\text{-dihydroanthracene})]ClO_4$	(XXII)	47.2	3.4	–	133	86
		(47.1)	(3.3)			
$[Ir(TFB)(C_6H_5Me)]ClO_4$	(XXIII)	38.2	3.0	–	122	71
		(37.4)	(2.3)			
$[Ir(TFB)(C_6H_6)]ClO_4$	(XXIV)	35.5	2.0	–	116	32
		(36.3)	(2.0)			
$[Ir(TFB)(PhNPh_2)]BF_4\cdot CH_2Cl_2$	(XXV)	45.2	2.8	1.7	120	82
		(44.5)	(3.1)	(1.6)		
$[Ir(TFB)(PhNHPh)]BF_4$	(XXVI)	43.0	2.8	2.2	117	25
		(42.7)	(2.5)	(2.1)		
$[Ir(Me_3TFB)(PhNPh_2)]ClO_4$	(XXVII)	48.7	3.6	1.8	129	89
		(49.2)	(3.4)	(1.7)		
$[Ir(Me_3TFB)(PhNHPh)]ClO_4$	(XXVIII)	44.9	3.2	2.2	118	75
		(44.5)	(3.2)	(1.9)		

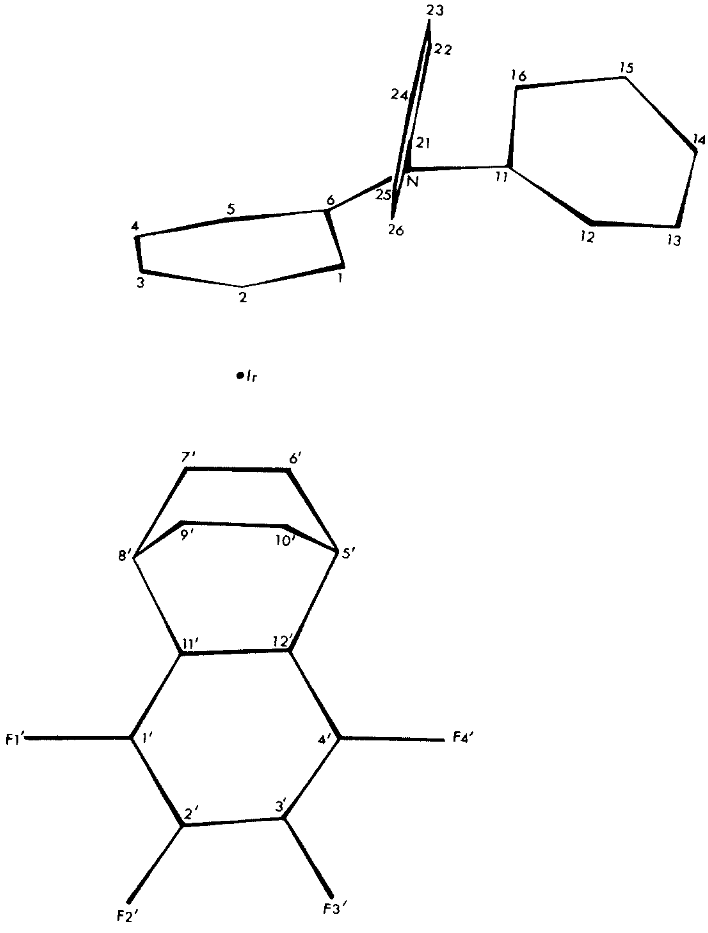


Fig. 3. A view of the cation in compound XXV showing the atom numbering.

Preparation of $[Ir(OMe)(Me_3TFB)]_2$ *(II)*

A solution of 0.52 mmol of potassium hydroxide in 4.4 ml of methanol was added to a suspension of complex I (257.3 mg, 0.26 mmol) in 20 ml of methanol. After 2 h stirring a yellow solid was formed. Addition of 12 ml of water led to complete precipitation of the complex, which was filtered off, washed with methanol/water (1/1 v), and vacuum-dried. (Yield 93%).

Preparation of $[Ir(OMe)(TFB)]_2$ *(III)*

This complex was prepared by two routes:

(i) Potassium carbonate (97.5 mg) was added to a suspension of $IrCl(TFB)_2$ [15] (309.5 mg, 0.46 mmol) in methanol (25 ml). After 2 h stirring an orange solid was formed. Addition of 12 ml of water led to complete precipitation of the complex, which was filtered off, washed with methanol/water (1/1 v), and vacuum-dried. (Yield 65%).

(ii) A solution of 0.78 mmol of potassium hydroxide in 8.5 ml of methanol was added to a suspension of $IrCl(TFB)_2$ (533.1 mg, 0.78 mmol) in 16 ml of methanol. After 2 h stirring an orange solid was formed. Addition of 12 ml of water led to complete precipitation of the orange complex, which was filtered off, washed with methanol/water (1/1 v), and vacuum-dried (Yield 96%).

Preparation of Ir(acac)(Me_3TFB) (IV)

A suspension of complex I (146.8 mg, 0.15 mmol) in 25 ml of acetone was treated with 2,4-pentanedione (30.8 μl, 0.30 mmol) and potassium hydroxide (30 mmol) in 3.2 ml of methanol. After 30 min stirring the mixture was evaporated to dryness, the residue was treated with dichloromethane (50 ml), and the resulting suspension was filtered. The yellow filtrate was vacuum-concentrated to ca. 0.5 ml and 10 ml of hexane were added. The solid was filtered off, washed with hexane, and vacuum-dried. (Yield 32%).

The analogous Ir(acac)(TFB) (V) complex [16] was similarly prepared.

Preparation of $[IrCl(TFB)]_2$ (VI)

This complex was prepared by two routes:

(i) A solution of complex V (216.3 mg, 0.42 mmol) in 40 ml of ether was stirred for 1 h with 0.42 mmol of HCl in 3.5 ml of water. The resulting solution was concentrated under reduced pressure to ca. 0.5 ml. Addition of methanol led to precipitation of a yellow solid, which was filtered off, washed with methanol, and vacuum-dried. (Yield 53%).

(ii) Addition of aqueous HCl (19.5 μl, 0.22 mmol) to a suspension of complex III (102.3 mg, 0.11 mmol) in 10 ml of ethanol gave a yellow solid. After 1 h stirring the solid formed was filtered off, washed with methanol, and vacuum-dried. (Yield 87%).

Preparation of complexes of the $[Ir(Me_3TFB)(arene)]ClO_4$ (VII–XXII)

A suspension of complex I (104.3 mg, 0.10 mmol) in 20 ml of dichloromethane was treated for 1 h with $AgClO_4$ (43.6 mg, 0.21 mmol) and a large excess of the corresponding arene C_6Me_6 (85.2 mg. 0.52 mmol); 1,2,4,5-$C_6H_2Me_4$ (68.4 mg, 0.51 mmol); 1,3,5-$C_6H_3Me_3$ (1 ml); 1,2,4-$C_6H_3Me_3$ (1 ml); 1,4-$C_6H_4Me_2$ (1 ml); 1,3-$C_6H_4Me_2$ (1 ml); 1,2-$C_6H_4Me_2$ (1 ml); C_6H_5Me (1 ml); C_6H_6 (1 ml); 1,4-$C_6H_4(OH)_2$ (57.0 mg, 0.52 mmol); acetophenone (1 ml); biphenyl (80.6 mg, 0.52 mmol); tetralin (1 ml); naphthalene (66.6 mg, 0.52 mmol); indene (0.3 ml); 9,10-dihydroanthracene (92.2 mg, 0.51 mmol)). The AgCl was removed by filtration through kieselguhr. The filtrate was concentrated under reduced pressure and the complex was precipitated with ether and recrystallized from dichloromethane/ether.

Preparation of $[Ir(TFB)(C_6H_5Me)]ClO_4$ (XXIII)

A solution of complex V (65.6 mg, 0.13 mmol) in 30 ml of ether was treated for 1 h with 2 ml of C_6H_5Me and $HClO_4$ (0.13 mmol). The formed solid was filtered off, washed with ether, and vacuum-dried.

Preparation of $[Ir(TFB)(C_6H_6)]ClO_4$ (XXIV)

A suspension of complex VI (76 mg, 0.08 mmol) in 20 ml of dichloromethane was stirred for 1 h with $AgClO_4$ (34.7 mg, 0.16 mmol) and 2 ml of C_6H_6. The formed AgCl was removed by filtration through kieselguhr. The filtrate was concentrated under reduced pressure and the complex was precipitated with ether and recrystallized from dichloromethane/ether.

(Continued on p. 126)

TABLE 6

CRYSTAL ANALYSIS PARAMETERS AT ROOM TEMPERATURE

Crystal data		
Formula	$[Ir(Me_3TFB)(1,4\text{-}C_6H_4Me_2)]ClO_4$	$[Ir(TFB)(PhNPh_2)]BF_4 \cdot CH_2Cl_2$
Crystal habit	Colorless, prismatic	Colorless, prismatic
Crystal size (mm)	0.22 × 0.31 × 0 36	0.06 × 0 19 × 0 34
Symmetry	Orthorhombic, *Pbca*	Orthorhombic *Pna*2_1
Unit cell determination least-squares fit to θ(Cu) < 45 °	88 reflexions	67 reflexions
Unit cell dimensions (Å)	17 6947(11), 15 8072(10), 16.0019(11)	9.8059(2), 20 8097(9), 14.3367(4)
Packing: V (Å^3), Z	4475.8(3), 8	2925 5(2), 4
D (g cm^{-3}), M, $F(000)$	1.851, 623 989, 2384	1 897, 835 453, 1616
Experimental data		
Radiation and technique	Cu-K_α, PW 1100 Philips Diffractometer Bisecting geometry	Cu-K_α PW 1100 Philips Diffractometer Bisecting geometry
Monochromator	Graphite-oriented	Graphite-oriented
Collection mode	$\omega/2\theta$, 1 × 1° det. apertures, θ < 65, 1 min/reflec, scan width of 1 3°	$\omega/2\theta$, 1 × 1 deg det. apertures, θ < 65 1 min/reflec, scan width of 1 4°
Total independent data	3801	2593

Observed data $I < 2\sigma(I)$	3389	2514
Stability	Two reflexions every 80 min no variation	Two reflexions every 90 min. no variation
μ(cm^{-1}). Min-max transmission factors	130.01, 0.061–0.150	110.83, 0.140–0.514
Solution and refinement		
Solution mode	Patterson, X-Ray 76 System [21] Vax 11/750	Patterson, X-Ray 76 System [21] Vax 11/750
Refinement mode	Least-squares on F's, observed reflexions only. 4 blocks in the final cycles.	Least-squares on F's, observed reflexions only. 2 blocks in the final cycles.
Final shift/error	0.22	0.31
Parameters:		
no. of variables	386	488
degrees of freedom	3003	2026
ratio of freedom	8.8	5.2
Weighting scheme	Empirical as to give no trends in $\langle W\Delta^2 \rangle$ vs. $\langle F_o \rangle$ or $\langle \sin\theta/\lambda \rangle$.	Empirical as to give no trends in $\langle W\Delta^2 \rangle$ vs. $\langle F_o \rangle$ or $\langle \sin\theta/\lambda \rangle$
Max. thermal values (Å^2)	U_{33} (O(2)) 0.25(2)	U_{22} (F(21)) 0.30(3)
Final ΔF-peaks	2.0 e Å^{-3} near the Ir atom	1.5 e Å^{-3} near the Ir atom
Final R, R_w	0.063, 0.069	0.042, 0.052
Atomic factors	International Tables for X-Ray Crystallography [22]	International Tables for X-Ray Crystallography [22]

TABLE 7

FINAL ATOMIC COORDINATES FOR $[Ir(Me_3TFB)(1,4\text{-}C_6H_4Me_2)]ClO_4$

Atom	*x/a*	*y/b*	*z/c*
Ir	0.16422(2)	0.01552(2)	0.15960(2)
C(1′)	0.1770(5)	−0.1783(5)	0.4260(5)
C(2′)	0.1249(6)	−0.2010(6)	0.4870(5)
C(3′)	0.0549(6)	−0.1654(6)	0.4892(6)
C(4′)	0.0361(5)	−0.1064(6)	0.4283(6)
C(5′)	0.0683(4)	−0.0251(4)	0.2943(5)
C(6′)	0.1312(5)	0.0431(5)	0.2870(5)
C(7′)	0.2035(5)	0.0033(5)	0.2847(5)
C(8′)	0.2045(4)	−0.0933(4)	0.2899(5)
C(9′)	0.1577(4)	−0.1085(5)	0.2119(5)
C(10′)	0.0830(4)	−0.0718(5)	0.2125(5)
C(11′)	0.1579(4)	−0.1203(5)	0.3646(5)
C(12′)	0.0857(4)	−0.0846(5)	0.3667(5)
C(13′)	0.2833(5)	−0.1288(6)	0.2818(6)
C(14′)	0.1171(6)	0.1308(6)	0.3138(7)
C(15′)	0.0188(6)	−0.1041(7)	0.1618(6)
F(1)	0.2442(3)	−0.2156(3)	0.4309(4)
F(2)	0.1438(4)	−0.2584(5)	0.5456(4)
F(3)	0.0045(4)	−0.1886(6)	0.5470(4)
F(4)	−0.0349(3)	−0.0710(4)	0.4309(4)
C(1)	0.1128(6)	0.0777(7)	0.0428(6)
C(2)	0.1551(6)	0.0043(8)	0.0198(6)
C(3)	0.2332(6)	−0.0045(7)	0.0362(6)
C(4)	0.2663(5)	0.0606(6)	0.0853(5)
C(5)	0.2239(6)	0.1299(6)	0.1122(7)
C(6)	0.1492(6)	0.1434(6)	0.0871(6)
C(7)	0.2749(9)	−0.0791(11)	0.0077(9)
C(8)	0.1084(10)	0.2235(8)	0.1097(13)
Cl	0.3951(1)	0.1459(1)	0.2905(2)
O(1)	0.4427(6)	0.2151(7)	0.2743(10)
O(2)	0.3201(5)	0.1770(8)	0.2925(12)
O(3)	0.4003(6)	0.0822(10)	0.2323(11)
O(4)	0.4158(13)	0.1183(13)	0.3703(11)

Preparation of $[Ir(TFB)(PhNPh_2)]BF_4 \cdot CH_2Cl_2$ *(XXV)*

This complex was prepared by two routes:

(i) A solution of complex V (52.5 mg, 0.10 mmol) in 10 ml of ether was treated for 34 h with NPh_3 (74.7 mg, 0.30 mmol) and HBF_4 (0.10 mmol). The solid formed was recrystallized from dichloromethane/ether. (Yield 35%).

(ii) A solution of complex III (105.2 mg, 0.12 mmol) in 10 ml of dichloromethane was treated for 90 min with NPh_3 (86.1 mg, 0.35 mmol) in 10 ml of dichloromethane and HBF_4 (0.24 mmol). The resulting solution was vacuum-concentrated to ca. 10 ml and the complex was precipitated with 40 ml of ether then recrystallized from dichloromethane/ether. (Yield 82%).

Preparation of $[Ir(TFB)(PhNHPh)]BF_4$ *(XXVI)*

A solution of complex V (85.9 mg, 0.12 mmol) in 20 ml of ether was treated for 17 h with $NHPh_2$ (64.1 mg, 0.38 mmol) in 5 ml of ether and HBF_4 (0.12 mmol). The solid formed was recrystallized from dichloromethane/ether.

TABLE 8

FINAL ATOMIC COORDINATES FOR $[Ir(TFB)(PhNPh_2)]BF_4 \cdot CH_2Cl_2$

Atom	*x/a*	*y/b*	*z/c*
Ir	0.22776(4)	0.02274(2)	0.2500(–)
C(1′)	0.2872(14)	−0.2275(6)	0.2406(18)
C(2′)	0.3682(16)	−0.2708(6)	0.2858(10)
C(3′)	0.4561(16)	−0.2505(7)	0.3523(11)
C(4′)	0.4678(14)	−0.1853(7)	0.3727(9)
C(5′)	0.3779(17)	−0.0702(7)	0.3428(9)
C(6′)	0.4032(12)	−0.0364(5)	0.2468(16)
C(7′)	0.3089(25)	−0.0572(6)	0.1804(10)
C(8′)	0.2127(13)	−0.1101(7)	0.2137(10)
C(9′)	0.1443(11)	−0.0689(5)	0.2856(9)
C(10′)	0.2382(15)	−0.0491(6)	0.3572(10)
C(11′)	0.2952(12)	−0.1625(6)	0.2605(15)
C(12′)	0.3848(12)	−0.1415(6)	0.3276(9)
F(1′)	0.1984(11)	−0.2505(4)	0.1750(7)
F(2′)	0.3603(12)	−0.3341(4)	0.2656(8)
F(3′)	0.5352(12)	−0.2929(5)	0.3983(8)
F(4′)	0.5564(9)	−0.1679(4)	0.4393(7)
C(1)	0.2138(13)	0.1224(7)	0.3163(11)
C(2)	0.0805(13)	0.0967(7)	0.2982(12)
C(3)	0.0374(16)	0.0799(6)	0.2070(12)
C(4)	0.1313(16)	0.0837(6)	0.1328(9)
C(5)	0.2699(15)	0.1059(7)	0.1499(12)
C(6)	0.3023(12)	0.1352(5)	0.2388(15)
N	0.4188(9)	0.1708(4)	0.2508(11)
C(11)	0.4474(14)	0.2005(6)	0.3388(9)
C(12)	0.5384(16)	0.1713(7)	0.3982(11)
C(13)	0.5651(20)	0.2026(12)	0.4844(11)
C(14)	0.5106(19)	0.2604(9)	0.5056(12)
C(15)	0.4261(22)	0.2872(8)	0.4457(14)
C(16)	0.3887(17)	0.2586(7)	0.3601(12)
C(21)	0.5282(13)	0.1725(6)	0.1824(9)
C(22)	0.5656(20)	0.2312(7)	0.1475(12)
C(23)	0.6768(28)	0.2336(11)	0.0868(14)
C(24)	0.7458(18)	0.1775(11)	0.0617(13)
C(25)	0.7058(18)	0.1194(11)	0.0983(13)
C(26)	0.5955(16)	0.1177(8)	0.1586(12)
C(10)	0.2371(27)	0.5829(13)	0.1073(19)
CL(1)	0.1129(5)	0.5481(3)	0.0400(3)
CL(2)	0.4056(5)	0.5626(3)	0.0662(4)
B	0.2689(24)	0.4949(11)	0.3999(14)
F(1)	0.2302(27)	0.4940(18)	0.3120(16)
F(2)	0.3084(28)	0.4384(10)	0.4349(19)
F(3)	0.3838(16)	0.5291(9)	0.4139(12)
F(4)	0.1677(16)	0.5178(9)	0.4514(13)

Preparation of complexes of the type [Ir(Me_3TFB)(PhNRPh)]ClO_4 (R = Ph, H) (XXVII–XXVIII)

A suspension of complex I (104.1 mg, 0.10 mmol) in 20 ml of dichloromethane was treated for 1 h with a large excess of the corresponding $NRPh_2$ ligand (R = H (88.8 mg, 0.52 mmol); R = Ph (134.9 mg, 0.55 mmol)) and $AgClO_4$ (43.5 mg, 0.21 mmol). The AgCl was removed by filtration through kieselguhr. The filtrate was concentrated under reduced pressure and the complex was precipitated with ether and recrystallized from dichloromethane/ether.

X-Ray analysis

Compound XXV (Fig. 3) has a CH_2Cl_2 molecule of crystallization. The main features of the analysis are shown in Table 6. Table 7 and 8 present the atomic coordinates. Lists of structure factors, thermal parameters and hydrogen positions can be obtained from the authors on request.

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