Aminolysis of iridium thiophene compounds

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Dedicated to Professor Rosalinda Contreras, friend and colleague, on the ocassion of her 60th birthday in recognition of her oustanding contribution to the main group chemistry

Abstract

The dicationic iridium 2,5-dimethylthiophene Cp*Ir[SC(Me)CHCHC(Me)][BF$_4$]$_2$ (**6**) reacts with secondary cyclic and acyclic amines to give salts with formula [Cp*Ir[SC(Me)CHCH(Me)C=NR$_2$][BF4][R$_2$ = piperidyl, (**12**); pyrrolidyl, (**13**); morpholyl, (**14**); piperazyl, (**15**); R = diethyl (**16**) and methyl, benzyl (**17**)]. The coordinated thiophene compound undergoes C-S cleavage to give the corresponding iminium-thiolate derivatives. The hydrolysis of the iminium salts affords the acylthiolate Cp*Ir[SC(Me)CHCH(Me)C=O] (**7**).

The characterization of **12-17** is established in solution through ^{1}H, ^{11}B, ^{13}C and ^{19}F NMR, and compounds **12-14** are also studied in the solid state by X-ray diffraction. The crystalline structures, as well as the studies in solution for compounds **12-17**, show only one thermodynamic product, which was obtained from previous isomerization of the kinetic species; meanwhile compound **16** was obtained in mixture with **7** and the corresponding quaternary salt.

**Keywords:** Thiophene, iridium, nucleophilic addition, aminothiols

Introduction

Dicationic ruthenium compounds [(arene)Ru(thiophene)]$^{2+}$ containing thiophene, 2-methylthiophene, 2,5-dimethylthiophene and 1,2,3,4-tetramethylthiophenes react with ammonia to give salts of the formula [(arene)Ru(SC$_4$R$_4$NH$_2$)]X (arene = C$_6$Me$_6$ or cymene; R = H, Me; X = BF$_4$, PF$_6$ or OTf). The coordinated thiophene, as well as the substituted 2- and 2,5-methyl derivatives undergo C-S cleavage in order to give the corresponding iminium thiolate derivatives.[1]

Additional stereochemical insights into the ammonolysis reaction are obtained by studies on the 2,5-dimethylthiophene ruthenium compound [(cymene)Ru(2,5-Me$_2$C$_4$H$_2$S)]$^{2+}$ (**1**) where there

is evidence of a kinetic **2** and thermodynamic **3** isomers (Scheme1a). The isomerization occurs under very mild conditions and there is no evidence of racemization. The kinetic isomer can be rearranged to the thermodynamic one upon standing, even at solid state, at 30 °C.[1]

Solutions of [(cymene)Ru{η^4-SC(Me)CHCHC(Me)NH$_2$}]OTf (**2**) react with aqueous KOH in order to give the kinetic isomer of the corresponding acylthiolate [(cymene)Ru{η^4-SC(Me)CHCHCO(Me)}] (**4**), Scheme 1a. The ammonolysis of 1,2,3,4-tetramethylthiopene complexes proceeds rather differently from the cases of the less substituted thiophenes.[1]

Base hydrolysis of dicationic (cymene)Ru(II) and Cp*Ir(III) with the coordinated 2,5-dimethyl-thiophene, which has also been studied, results in the generation of the corresponding acylthiolate derivatives [(cymene)Ru{η^4-SC(Me)CHCHCOMe}] (**4**)[2] and [Cp*Ir{η^4-SC(Me)CHCHCOMe}] (**7**),[3,4] respectively. The acylthiolate derivatives react to afford more complex polinuclear compounds: dinuclear (**5**) in the case of ruthenium,[2] (Scheme 1a) and dinuclear (**9**, **10**) and tetranuclear (**8**) in the case of iridium[3] compounds, (Scheme 1b).
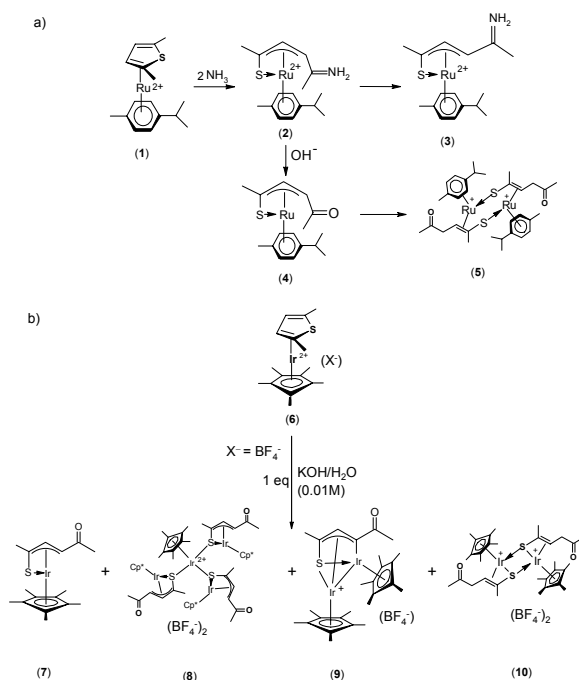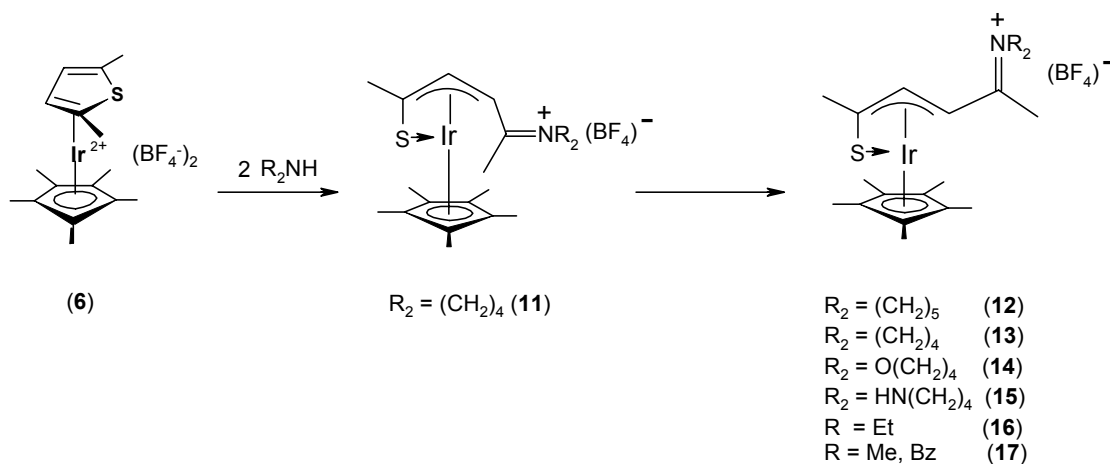

Scheme 1

Thus in order to expand our knowledge concerning the behavior of compound **6**, we decided to perform a thorough investigation of the chemical properties of this compound in the presence of secondary amines.

Results and Discussion

The addition of secondary amines to [Cp*Ir(2,5-dimethyl-thiophene)][BF$_4$] (**6**) resulted in a rapid color change from white to yellow, orange or red, for compounds [Cp*Ir{SC(Me)CHCH(Me)C=NR$_2$}]BF$_4$ [R$_2$ = piperidyl (**12**); pyrrolidyl (**13**); morpholyl (**14**); piperazyl (**15**)], which were obtained after stirring 18 h at room temperature, Scheme 2.

(**6**)   R$_2$ = (CH$_2$)$_4$ (**11**)

R$_2$ = (CH$_2$)$_5$ (**12**)
R$_2$ = (CH$_2$)$_4$ (**13**)
R$_2$ = O(CH$_2$)$_4$ (**14**)
R$_2$ = HN(CH$_2$)$_4$ (**15**)
R = Et   (**16**)
R = Me, Bz   (**17**)

Scheme 2

The reaction was so well behaved for cyclic amines, it gave the iminium salts in good yields; meanwhile diethylamine, which is an acyclic derivative, showed that there was a competition between the formation of compound [Cp*Ir{SC(Me)CHCH(Me)C=N(Et)$_2$}]BF$_4$ (**16**) and its hydrolysis to afford the acylthiolate compound [Cp*Ir{SC(Me)CHCH(Me)C=O}] (**7**), as well as its corresponding quaternary salt [NH$_2$(Et)$_2$]BF$_4$. Diisopropylamine and dicyclohexylamine showed the formation of compound **7** along with the corresponding quaternary salt [NH$_2$(R)$_2$]BF$_4$ [R = CHMe$_2$; C$_6$H$_{11}$)] without evidence of the iminium salt. Finally, the chiral methylbenzylamine lead to the exclusive formation of compound [Cp*Ir{SC(Me)CHCH(Me)C=N(Me)(Bz)}]BF$_4$ (**17**); however, several attempts to isolate it were unsuccessful and there was only ^{1}H and ^{13}C NMR spectroscopic evidence of its presence (Tables 1 and 2).

There was no reaction between compound **6** and diphenylamine, both of which were recovered, and there was no evidence of the iminium salt under the conditions described in the experimental section (*vide infra*) in the case of ephedrine, pyridine and aniline. Particularly, ephedrine was not a selective reaction.

Table 1. ^{1}H, ^{11}B and ^{19}F NMR of compounds **12-17**[a]

Compound	S-C-*Me*	C*H*$_A$	C*H*$_B$	N=C*Me*	N*R*	Cp*	^{11}B & ^{19}F NMR	Color M p (°C) Yield (%)
12	2.33 (s)	6.11(d, 6.0)	2.62 (d, 6.0)	2.29 (s)	4.10 (m, 2H) 3.80 (m, 4H) 3.45 (m, 2H) 1.80 (m, 2H)	1.95 (s)	-1.68[b] -153.1[c]	Orange 178-180[d] 83.7
13[e]	2.33 (s)	6.06 (d, 6.2)	2.47 (d, 6.2)	2.31 (s)	3.80 (t, 2H, 6.5) 3.42 (s, br, 2H) 3.20 (m, 2H) 2.05 (m, 2H)	1.92 (s)	-1.79[b] -153.3[c]	Orange 154-156 93.4
14	2.32 (s)	6.20 (d, 6.0)	2.68 (d, 6.0)	2.31 (s)	3.90 (m, 4H) 3.70 (m, 2H) 3.50 (m, 2H)	1.97 (s)	-1.67[b] -153.3[c]	Red 176-179 86.7
15	2.31 (s)	5.95 (d, 6.2)	2.56 (d, 5.9)	2.29 (s)	3.94(m, 2H) 3.55(m, 2H) 3.06 (m, 4H)	1.92 (s)	-1.38[b] -151.8[c]	Orange 140-143[d] 51.3
15[e]	2.33 (s)	5.97 (d, 6.2)	2.64 (d, 5.9)	2.59 (s)	3.87(m, 2H) 3.60 (m, 2H) 3.05 (m, 4H)	1.94 (s)	-1.35[b] -152.4[c]	_____
16	2.33 (s)	6.12 (d, 6.1)	2.62 (d, 6.1)	2.31 (s)	3.80 (m, 2H) 3.55 (m, 2H) 1.40 (m, 6H)	1.95 (s)	-1.53[b] -151.9[c]	Orange 178-179[d] 47.8
17[f]	2.05 (s)	6.20(d, 5.9)	2.75 (d, 6.4)	2.24 (s)	1.77 (d, 6.9, 3H); 4.10(m, 1H); 4.50(m, 1H); 6.92-7.55 (m)	1.60 (s)	-1.94[b] -146.9[c]	Not isolated

(a) In ppm, J (Hz), CD_3NO_2; (b) ^{11}B; (c) ^{19}F; (d) Decompose; (e) In $CDCl_3$; (f) In C_6D_6.

When a stoichiometric ratio of reactants was used, the reaction, monitored qualitatively by ^{1}H NMR, showed that no considerable conversion to products took place. Hence, it is clear that an excess of ligand is always necessary. The role of the basicity of the amine is not quite clear because piperidine and morpholine afford quite similar results. Apparently, steric effects may also prevent the nucleophilic addition reactions, as observed from the diphenylamine.

Table 2. ^{13}C NMR,[a] mass spectra and elemental analysis of compounds **12-17**

Compound	S-C	CH$_A$	CH$_B$	C=N	NR	Cp* Cq	Cp* Me	S-Me	C-Me	HRMS m/z [M-BF$_4$]$^+$ or Elemental Analysis
12	98.6	79.7	50.6	181.8	53.1 52.0 26.8 25.9 23.2	92.9	8.8	23.8	17.3	C$_{21}$H$_{33}$S$_1$Ir$_1$N$_1$: 524.19629. Found: 524.19490 (error = -1.61 ppm)
13	99.0	78.8	51.7	180.9	53.4 52.6 25.2 24.2	92.5	9.9	24.7	19.1	C$_{20}$H$_{31}$S$_1$Ir$_1$N$_1$: 510.18064. Found: 510.18128 (error = 2.31 ppm)
14	99.6	79.8	51.1	183.4	66.4 65.8 51.6 50.4	93.0	8.8	23.8	17.4	C$_{20}$H$_{31}$S$_1$Ir$_1$N$_1$O$_1$BF$_4$: 612.54 theo/(found): C: 39.22 (39.20) H: 5.10 (4.99)
15	98.6	79.5	50.5	181.7	53.1 51.9 46.1 45.5	92.6	8.5	23.5	17.0	C$_{20}$H$_{32}$S$_1$Ir$_1$N$_2$: 525.19154. Found: 525.19114 (error = 0.28 ppm)
15[b]	99.0	77.5	53.4	181.7	53.4 51.7 46.8 46.0	92.6	9.7	24.6	17.9	
16	99.3	77.6	51.0	183.0	49.5 48.7 13.2 10.3	92.4	9.6	24.5	18.0	C$_{20}$H$_{33}$S$_1$Ir$_1$N$_1$BF$_4$: 598.56 theo/(found): C: 40.13 (40.08) H: 5.56 (5.79)
17[c]	99.6	79.0	49.9	184.8	22.5 58.2 140.7(i) 137.8(o) 129.6(p) 128.6(m)	92.2	9.2	24.5	20.4	Not isolated

a) In ppm, CD$_3$NO$_2$; b) In CDCl$_3$; c) In C$_6$D$_6$.

The addition and C-S cleavage processes occur regiospecifically at the (Me)S-C linkage. The presence of only one isomer for derivatives **12-17** was established by ^{1}H and ^{13}C NMR which showed only one set of Cp* signals. However, the reaction was monitored through ^{1}H NMR for

compound **6** in presence of pyrrolidine, in a 1:2 ratio. This showed the formation of the kinetic product as the *anti* conformer **11** [^{1}H NMR (CD$_3$NO$_2$) δ: 5.62 (d, 4.7 Hz, CH$_A$); 3.60 (br, CH$_B$); 2.34 (s, Me) 2.00 (s, Cp*)] which easily went to the corresponding *syn* thermodynamic one **13** [^{1}H NMR (CD$_3$NO$_2$) δ: 6.06 (d, 6.2 Hz, CH$_A$); 2.47 (d, 6.2 Hz, CH$_B$); 2.33 (s, Me) 1.92 (s, Cp*), Table 1] (Scheme 2). Additional to the ^{1}H and ^{13}C NMR spectra of **12-17**, HETCOR and APT experiments were performed to support the corresponding assignment. The ^{11}B and ^{19}F NMR confirmed the presence of the BF$_4$ counterion in all cases.

The iminum carbon is demonstrably electrophilic, because it is susceptible to base hydrolysis attack, as observed for ruthenium analogue species.[1] Partial recyclization of the thiophene ligand proceeds in the thermodynamic compound **12** in presence of triflic acid. It is known that the kinetic isomers of the ruthenium analogues are rapidly transformed after treatment with protic sources.[1] The iridium compound **13** showed faster interconversion between kinetic and thermodynamic products, which did not allow to compare the reactivity of the kinetic isomer with the ruthenium analogue.

Attempts to remove the Cp*Ir fragment from compound **13** were carried out in presence of (n-Bu$_4$)NCl or MeOTf unsuccessfully, which suggest the high stability of the η^3-allyl-Ir bond. Addition of D$_2$O to compound **12** did not show any change even after a week; meanwhile an equimolar water solution of compound **13** and H$_2$O/KOH (0.03M) afforded quantitatively the acylthiolate **7**. Compounds **12-14** melted, **13** and **14** without decomposition, and crystallized from nitromethane/diethyl ether as single crystals, except **13** which crystallized from CHCl$_3$ at room temperature. The crystallographic studies were carried out at room temperature and the assignment of these species as an iminium derivative is supported by the bond distances and angles at C4. The C=N distances of **12**, **13** and **14** are 1.313(6), 1.306(12) and 1.308(10) Å, respectively, which is appropiate for a double bond, whereas bonds between nitrogen and the carbon atoms of the corresponding cyclic amines are longer N-C7 1.491(6), N-C11 1.494(7) **12**; N-C7 1.464(12), N-C10 1.441(16) **13**; and N-C7 1.479(11), N-C10 1.477(10) **14** Å. The molecular structures are presented in Figures 1-3, respectively. Table 3 includes the corresponding crystal data and Tables 4 and 5 selected bond lengths and bond angles, respectively.

The structure of these iminium salts in the solid state revealed a sandwich structure wherein the thiophene ligand is cleaved. These iminium centers are conjugated via a π-bonding network with the rest of the allylthiolate, where the highest delocalization was observed for compound **12**, and similar behavior has been reported for the aminolysis of dicationic ruthenium thiophene compounds.[1]

The distances of Ir(1)-S(1) and S(1)-C(1) are decreasing in the following order: **12** > **14** > **13** and **14** > **12** > **13**, respectively. The piperidine and morpholine fragments showed a chair conformation and the pyrrolidine, an envelope one.

Table 3. X-ray data collection parameters for compounds **12-14**

Compound	12	13	14
formula	$C_{21}H_{33}BF_4IrNS$	$C_{21}H_{32}BCl_3F_4IrNS$	$C_{20}H_{31}BF_4IrNOS$
fw	610.55	715.90	612.53
Cryst syst	Monoclinic	Triclinic	Triclinic
Space Group	P2/c	P-1	P-1
a (Å)	13.450(3)	9.6363(10)	8.3432(2)
b (Å)	7.877(3)	12.0380(10)	11.4873(3)
c (Å)	21.840(3)	12.6614(10)	12.5263(4)
α (º)	90	67.321(10)	95.8270(10)
β (º)	91.34(2)	74.241(10)	108.9380(1)
γ (º)	90	85.072(10)	97.3640(10)
V (Å^3)	2313.2(11)	1304.0(2)	1113.00(5)
Z	4	2	2
D_{calc} (g cm^{-3})	1.753	1.823	1.828
Temp (K)	270(2)	293(2)	298(2)
Diffractometer	Enraf Nonius CAD4	Enraf-Nonius CAD4	Kappa CCD
2θ scan range (º)	5.18 to 51.92°	5.32 to 52.48	5.84 to 55.08
Index ranges	$-16 \leq h \leq 16$	$-11 \leq h \leq 11$	$-10 \leq h \leq 10$
	$0 \leq k \leq 9$	$-13 \leq k \leq 14$	$-12 \leq k \leq 14$
	$0 \leq l \leq 26$	$0 \leq l \leq 15$	$-16 \leq l \leq 14$
no. of reflns collcd	4527	2932	10670
no. of indpt reflns	4527	2932	5058
no. of indpt obsd	3635 (F>4σ(F))	2932 (F>4σ(F))	4204 (F>4σ(F))
Final R_1	0.0282	0.0391	0.0560
Final wR_2	0.0801	0.1037	0.1253
GOOF	1.081	1.056	1.070

Table 4. Selected bond lengths (Å) for compounds **12-14**

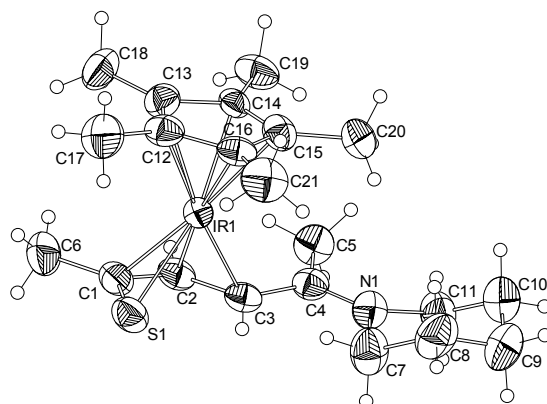| Compound	12		13	14
Ir(1)-S(1)	2.4066(15)		2.372(3)	2.393(2)
Ir(1)-C(1)	2.173(5)		2.146(7)	2.158(8)
Ir(1)-C(2)	2.137(4)		2.138(7)	2.145(7)
Ir(1)-C(3)	2.182(5)		2.178(9)	2.191(8)
S(1)-C(1)	1.750(5)		1.734(11)	1.755(9)
C(1)-C(2)	1.417(7)		1.422(14)	1.404(11)
C(2)-C(3)	1.423(7)		1.465(13)	1.457(11)
C(3)-C(4)	1.438(7)		1.426(14)	1.436(11)
C(4)-N(1)	1.313(6)		1.306(12)	1.308(10)
C(4)-C(5)	1.488(7)		1.474(17)	1.502(12)
C(1)-C(6)	1.500(7)		1.480(14)	1.505(11)
N(1)-C(7)	1.491(6)		1.464(12)	1.479(11)
C(7)-C(8)	1.537(8)		1.51(2)	1.507(14)
C(9)-C(10)	1.493(11)		1.525(15)	1.517(13)
C(8)-C(9)	1.514(9)		1.496(18)	
C(10)-C(11)	1.501(9)			
N(1)-C(11)	1.494(7)	N(1)-C(10)	1.441(16)	1.477(10)
Ir(1)-C(12)	2.179(5)	Ir(1)-C(11)	2.169(9)	2.158(8)
C(8)-O(1)				1.423(11)
C(9)-O(1)				1.415(11)

Figure 1. ORTEP drawing of the cationic portion of compound **12**.

Table 5. Selected bond angles (deg) for compounds **12-14**

Compound	2	13	14
C(1)-Ir(1)-S(1)	44.57(13)	44.8(3)	45.0(2)
C(2)-Ir(1)-C(1)	38.39(19)	38.8(4)	38.1(3)
C(2)-Ir(1)-S(1)	72.69(14)	73.1(3)	73.2(2)
C(3)-Ir(1)-S(1)	77.59(15)	77.2(3))	77.4(2)
Ir(1)-S(1)-C(1)	60.63(16)	60.7(3)	60.4(3)
C(1)-C(2)-C(3)	117.7(4)	115.6(10)	116.0(7)
C(2)-C(3)-C(4)	124.0(5)	121.2(12)	123.2(7)
C(3)-C(4)-C(5)	120.3(5)	124.2(9)	119.5(7)
C(4)-N(1)-C(7)	121.0(4)	124.4(10)	123.8(7)
N(1)-C(4)-C(3)	120.8(4)	116.1(10)	121.3(7)
C(2)-C(1)-S(1)	116.7(4)	116.7(7)	117.8(6)
C(2)-C(1)-Ir(1)	69.4(3)	70.3(4)	70.4(4)
S(1)-C(1)-Ir(1)	74.80(18)	74.5(3)	74.6(3)
C(1)-C(2)-Ir(1)	72.2(3)	70.9(4)	71.5(5)
C(4)-N(1)-C(11)	122.8(5)		
C(11)-N(1)-C(7)	115.2(5)		
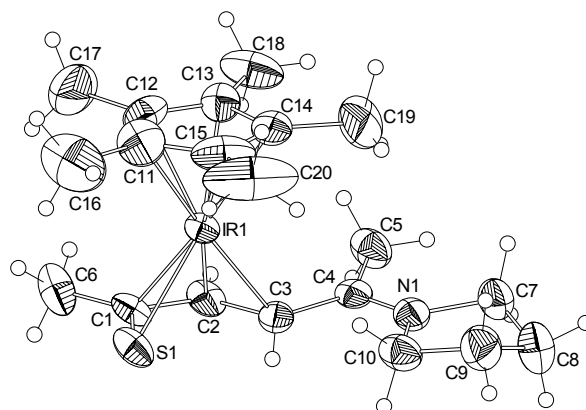
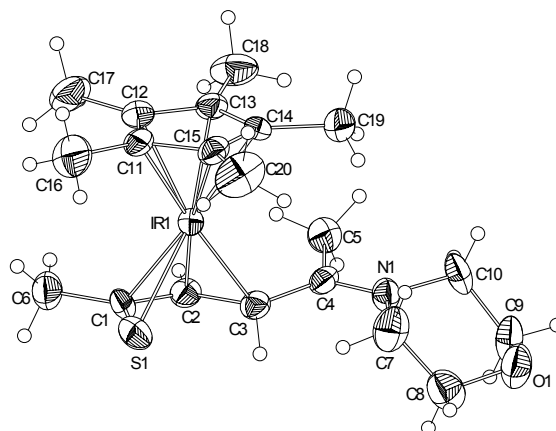**Figure 2.** ORTEP drawing of the cationic portion of compound **13**.

Figure 3. ORTEP drawing of the cationic portion of compound **14**.

The IR spectra of **12-16** shows a strong band, assigned to the $\nu_{C=N}$, at around (cm^{-1}):1578, **12**; 1594, **13**; 1571, **14**; 1574, **15** and 1590, **16**.

Experimental Section

General Procedures. All reactions were carried out with exclusion of air using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under nitrogen prior to use. The starting material Cp*Ir(2,5-dimethyl-η^5-thiophene)][BF$_4$]$_2$ (**6**) was prepared by the published method.[5]

In the ^{1}H and ^{13}C, ^{11}B and ^{19}F NMR spectra, chemical shifts are expressed in ppm downfield from Me$_4$Si, BF$_3 \cdot$OEt$_2$ and CF$_3$COOH, respectively. Coupling constants, J, are given in Hertz.

Preparation of Compounds [Cp*Ir{SC(Me)CHCH(Me)C=NR$_2$}]BF$_4$ [R$_2$ = piperidyl (12); R$_2$ = pyrrolidyl (13); R$_2$ = morpholyl (14); R$_2$ = piperazyl (15); R = diethyl (16); R = methyl, benzyl (17). General procedure

The addition of an excess of the amine (2 equiv) in ~1-2 mL of CH$_3$NO$_2$ to a solution of compound **6** (150 mg, 0.245 mmol) in CH$_3$NO$_2$ (30 mL) was stirred at room temperature for 18 h. Immediately after the addition of the amine, a strong change in color was observed (*vide infra*). The solvent was evaporated and the product was extracted with ~30 mL of CH$_2$Cl$_2$, the volume was reduced to ~10 mL and precipitated with Et$_2$O (~60 mL). The corresponding solids of **12** and **14** were recrystallized from CH$_3$NO$_2$ /Et$_2$O, at -10 °C, to afford powders or single crystals. Compound **13** was recrystallized from CHCl$_3$ at room temperature. See Table 1 and 2 for data related to melting point, elemental analyses, yield, mass spectra and NMR spectroscopy. The different compounds were:

R$_2$ = piperidyl (12). The orange solution afforded orange crystals.

R$_2$ = pyrrolidyl(13). The orange solution afforded red crystals.

R$_2$ = morpholyl (14). The orange-dark solution afforded cherry-red crystals.

R$_2$ = piperazyl (15). The orange-red solution afforded an orange-red solid of **15** along with an unknown orange compound in a 6:4 ratio, respectively.

R = diethyl (16). The yellow-brown solution afforded a brown-orange solid, which after recrystallization with Et$_2$O gave an insoluble white powder corresponding to the quaternary salt [NH$_2$(Et)$_2$]BF$_4$ in 47.8% yield (related to the amine),[6] [^{1}H NMR (CDCl$_3$) δ: 6.8(s,br); 3.14(m); 1.35(m). ^{13}C NMR (CDCl$_3$) δ: 44.0 (CH$_2$) and 11.2 (Me)]; meanwhile in the soluble fraction of the remaining solid, the acylthiolate iridium compound **7** was isolated in 44.9% yield (related to compound **6**).[3,4] A chromatographic column of alumina was carried out for separation of both cationic compounds in CH$_2$Cl$_2$; the quaternary salt stayed at the top of the column and compound **6** was eluted with CH$_2$Cl$_2$/acetone to afford an orange oil which after recrystallization in CHCl$_3$/Et$_2$O gave an orange solid.

R = methyl, benzyl (17). In our hands, it was not possible to isolate this product. However, according with ^{1}H and ^{13}C NMR spectroscopy this is the only product formed during the reaction. Attempts to isolate **17** led only to unidentified decomposition products.

R = diisopropyl The yellow-green solution afforded a yellow solid which after purification afforded the quaternary salt of [NH$_2$(CHMe)$_2$]BF$_4$ in 52.3% yield (related to the amine) [^{1}H NMR (acetone-d$_6$) δ: 7.1 (s, br); 3.71 (septuplete); 1.40(d, 6.7 Hz). ^{13}C NMR δ: 48.4 (CH); 18.4 (Me). ^{11}B NMR δ: -1. 62. ^{19}F NMR δ: - 146.8] and compound **7**, (59%) (related to compound **6**). Both products were isolated from several recystallizations of CH$_2$Cl$_2$/Et$_2$O and Et$_2$O, respectively.

R = dicyclohexyl The amber solution afforded a yellow-oily solid which after purification afforded the quaternary salt of [NH$_2$(C$_6$H$_{11}$)$_2$]BF$_4$ (54%) (related to the amine). [^{1}H NMR (CDCl$_3$) δ: 6.4 (s, br); 3.11 (m); 1.21-2.07 (m). ^{13}C NMR δ: 54.8 (CH); 29.15, 24.59 (CH$_2$); ^{11}B NMR δ: -1. 67; ^{19}F NMR δ: - 146.7] and compound **7** (56%) (related to compound **6**).

Supplementary Information Available

Crystal data, tables of atom coordinates and tempertaure factors, bond lengths, bond angles, anisotropic temperature factors, torsion angles and labeled ORTEP diagrams (43 pages). CCDC 659916, 659915 and 659914 contain the supplementary crystallographic data for **12**, **13** and **14**.

Acknowledgements

References

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