*Inorg. Chem.* **2007**, *46*, 7800–7809


# Selective Low-Temperature Syntheses of Facial and Meridional Tris-cyclometalated Iridium(III) Complexes

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Received March 7, 2007

We have developed a selective low-temperature synthesis of fac and mer tris-cyclometalated Ir(III) complexes. The chloro-bridged dimers $[Ir(C\hat{}N)_2Cl]_2$ (C^N = cyclometalating ligand) are cleaved in coordinating solvents like acetonitrile to give neutral $Ir(C\hat{}N)_2(NCCH_3)Cl$ species which in turn are reacted with $AgPF_6$ to give hexafluorophosphate salts of the bis-acetonitrile species $[Ir(C\hat{}N)_2(NCCH_3)_2]PF_6$ for C^N = 2,2′-thienylpyridine (thpy) and 2-phenylpyridine (ppy). These bis-acetonitrile complexes are excellent starting materials for the synthesis of tris-Ir(III) complexes. The complexes of the general formula *fac*-$Ir(C\hat{}N)_3$ were synthesized with the ligands thpy and ppy at 100 °C in *o*-dichlorobenzene from the corresponding $[Ir(C\hat{}N)_2(NCCH_3)_2]PF_6$ complexes. The reaction of $[Ir(C\hat{}N)_2(NCCH_3)_2]$-$PF_6$ with thpy at room temperature did not give the expected tris complex but instead gave $[Ir(thpy)_2(N,S\text{-}thpy)]PF_6$, with the third chelating ligand complexed through the sulfur atom of the thiophene ring. $[Ir(thpy)_2Cl]_2$, $[Ir(ppy)_2Cl]_2$, $Ir(thpy)_2(NCCH_3)Cl$, $[Ir(thpy)_2(NCCH_3)_2]PF_6$, $[Ir(ppy)_2(NCCH_3)_2]PF_6$, and $[Ir(thpy)_2(N,S\text{-}thpy)]PF_6$ were structurally characterized by X-ray crystallography. Additionally, hydroxy-bridged dimers, $[Ir(C\hat{}N)_2(OH)]_2$, were synthesized as starting materials for the selective synthesis of *mer*-$Ir(C\hat{}N)_3$ complexes at 100 °C in *o*-dichlorobenzene. A mechanism is proposed that may account for the selectivity observed in the formation of the *mer*-$Ir(C\hat{}N)_3$ and *fac*-$Ir(C\hat{}N)_3$ isomers in previous studies and the studies presented here.

## Introduction

The cyclometalated complexes of metal ions have received a great deal of attention in recent years due in part to their rich photophysical properties. Although $d^8$ metal ions such as Pt(II),[1−7] Pd(II),[8−11] and Au(III)[12−17] have been examined, the emphasis has been on $d^6$ tris-cyclometalated complexes. Ir(III) tris-cyclometalated ligand complexes in particular have received increased attention, as they are isoelectronic analogues of the highly emissive diimine coordination compounds of Ru(II) and Os(II). Tris-Ir(III) complexes of cyclometalating ligands exhibit long lifetimes and high emission quantum yields, desirable luminescence properties. These photophysical properties have led to the investigation of these molecules for applications such as photocatalysts,[18] singlet oxygen sensitizers,[19] oxygen sensors,[20] and possibly

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10.1021/ic700440c CCC: $37.00 
Published on Web 08/14/2007

the most widely studied application, organic light emitting diodes (OLEDs).[21−30] These Ir(III) molecules can be incorporated into the layered structure of OLEDs as phosphorescent dopants. The increased spin−orbit coupling provided by Ir(III) promotes mixing of the singlet and triplet excited states and increases the theoretical limit of efficiency beyond the 25% predicted for organic molecules that emit by fluorescence.

Homoleptic cyclometalated complexes of $d^6$ metal centers like Ir(III) can adopt two configurations, facial (fac) or meridional (mer). The fac and mer isomers of cyclometalated Ir(III) complexes have markedly different photophysical properties.[31] Typically, the fac isomers have order of magnitude longer lifetimes and quantum efficiencies than the mer isomers at room temperature, making them much better for OLEDs and other applications. With this in mind a general, uncomplicated, and selective synthetic route to the fac isomers has been an area of interest in the past few years. Several groups have investigated the synthesis of fac isomers of tris-cyclometalated Ir(III) complexes, but in most cases harsh reaction conditions were utilized.[22,31−37] At the onset of our research, all reported routes to fac isomers used the high temperatures (200+ °C) afforded by refluxing glycerol, or melt reactions employing excess ligand as the solvent.[31−37] The mer isomers of these cyclometalated complexes have been reported as kinetic products in glycerol at lower temperatures (120−150 °C) that inhibit the formation of fac isomers.[22,31] A selective low-temperature route that eliminates the use of glycerol or ligands as solvents and avoids the formation of mer isomers could result in the more straightforward isolation of the desired fac products. Recently a procedure that utilized silver triflate as a reagent in 2-ethoxyethanol at 95 °C was reported to give low yields of the fac isomer of a heteroleptic complex.[20] Relatively high yields of mer isomers have also been reported by treatment of the dimer with a silver salt and triethylamine as a base.[20,38] Herein we report low-temperature routes for the preparation of *fac*-Ir(thpy)$_3$ and *fac*-Ir(ppy)$_3$ at 100 °C with improved yields and no evidence of formation of the mer isomers of these complexes. Additionally, we report the selective preparation of *mer*-Ir(thpy)$_3$ and *mer*-Ir(ppy)$_3$ at 100 °C. The mechanistic implications of these synthetic reactions are also discussed.

## Experimental Section

**General Considerations.** All synthetic procedures involving $IrCl_3 \cdot 3H_2O$ and other Ir(III) species were performed under an inert $N_2$ atmosphere. NMR spectra were recorded on Varian Unity (300 MHz) or Varian Inova (300 MHz) instruments. High-resolution mass spectrometry was carried out on a Bruker BioTOF II or Bruker microTOF$_Q$ mass spectrometer.

The ligand 2-phenylpyridine (ppy) was purchased from Aldrich Chemical Co., and 2,2′-thienylpyridine (thpy) was synthesized according to a published procedure utilizing a Grignard coupling.[39] Cyclometalated Ir(III) $\mu$-chloro-bridged dimers, $(C\hat{}N)_2Ir(\mu\text{-}Cl)_2Ir(C\hat{}N)_2$, (abbreviated as $[Ir(C\hat{}N)_2Cl]_2$) were synthesized via a slight modification of the method reported by Nonoyama;[40] $IrCl_3 \cdot 3H_2O$ (Pressure Chemical Co.) was refluxed with 2−2.5 equiv of cyclometalating ligand in a 3:1 mixture of 2-methoxyethanol and water, where 2-methoxyethanol (Aldrich) was used in place of 2-ethoxyethanol. Single crystals of both $[Ir(thpy)_2Cl]_2$ (**1a**) and $[Ir(ppy)_2Cl]_2$ (**1b**) were grown from slow evaporation of dichloromethane solutions. *mer*-Ir(ppy)$_3$ was prepared by a slight modification of a method previously reported.[20] Compound **1b** was refluxed in acetone with silver triflate (Aldrich); upon filtration, ppy and triethylamine (Aldrich) were added and the solution was again refluxed.

**Ir(thpy)$_2$(NCCH$_3$)Cl (2a).** Compound **1a** was dissolved in acetonitrile; slow evaporation in air gave orange X-ray quality crystals. Examination by $^1$H NMR of **1a** in $CD_3CN$ gave evidence for formation of a new asymmetric complex that still contains trans nitrogen atoms consistent with the cleavage of the dimer in solution to give **2a**. Subsequent X-ray crystallography confirmed the structure of **2a** as a bis(thpy) Ir(III) complex with one chloride and one acetonitrile ligand.

**[Ir(thpy)$_2$(NCCH$_3$)$_2$]PF$_6$ (3a).** Compound **1a** (0.3010 g, 0.2746 mmol) in 150 mL of acetonitrile was heated to dissolve all of the chloro-bridged dimer. A 50 mL acetonitrile solution of $AgPF_6$ (0.1505 g, 0.5953 mmol) was added to the Ir solution. Heating this mixture in the dark to 60−70 °C for 2 h resulted in a gray precipitate. The reaction mixture was filtered over a Celite pad to separate a yellow solution from the gray AgCl precipitate. The solution was concentrated in vacuo, and diethyl ether was added to give a yellow precipitate that was collected by filtration. A second crop was obtained in a similar manner by removing the solvents


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from the filtrate then redissolving in a minimal amount of acetonitrile and precipitating with diethyl ether. The solids were dried under vacuum to give 0.3616 g (89% yield) of product. X-ray quality crystals were grown by slow evaporation of a $CH_2Cl_2$ solution. $^1$H NMR ($CD_2Cl_2$): $\delta$ 8.85 (dd, 2 H, $J$ = 0.6−0.9, 5.3 Hz), 7.85 (ddd, 2 H, $J$ = 1.2−1.5, 7.7, 7.7 Hz), 7.58 (d, 2 H, $J$ = 7.8 Hz), 7.25 (d, 2 H, $J$ = 4.8 Hz), 7.23 (ddd, 2 H, $J$ = 1.5, 6.0, 7.5 Hz), 6.05 (d, 2 H, $J$ = 4.8), 2.37 (s, 6 H). HRESIMS ($M^+$): calcd for $C_{22}H_{18}IrN_4S_2$, 593.0573; found, 593.0580.

**[Ir(thpy)$_2$(OH)]$_2$ (4a).** Compound **3a** (0.0502 g, 0.0679 mmol) was dissolved in 15 mL of methanol. The addition of solid NaOH (0.0070 g, 0.1750 mmol) resulted in an immediate color change from light orange to dark red-orange and precipitation of a solid. The reaction was allowed to stir for 18 h. The solid was collected by filtration and rinsed with MeOH to remove any residual starting material (2 × 10 mL). The red-orange solid was dried under vacuum to yield 0.0329 g (92% yield) of product. $^1$H NMR ($CD_2Cl_2$): $\delta$ 8.26 (dd, 4 H, $J$ = 0.6−0.9, 5.7 Hz), 7.52 (m, 8 H), 7.09 (d, 4 H, $J$ = 4.8 Hz), 6.51 (ddd, 4 H, $J$ = 1.2, 6.2, 6.2 Hz), 5.89 (d, 4 H, 4.5 Hz). HRESIMS ($M^+ - OH^-$): calcd for $C_{36}H_{25}Ir_2N_4OS_4$, 1039.0118; found, 1039.0143.

**[Ir(thpy)$_2$(N,S-thpy)]PF$_6$ (5a).** Compound **3a** (0.0500 g, 0.0676 mmol) was dissolved in 10 mL acetone and purged with $N_2$ for 20 min. Thpy (0.0129 g, 0.0800 mmol) was added, and the reaction was stirred for 72 h. The acetone was removed by rotary evaporation to give an oily yellow-brown solid. This solid was redissolved in a small amount of acetone and precipitated with diethyl ether to give a yellow-brown solid that was collected by filtration. This procedure was repeated to give two more crops. The solids were dried under vacuum to give a total of 0.0357 g (65% yield) of product. X-ray quality crystals were grown by slow evaporation of an acetone solution. $^1$H NMR ($CD_2Cl_2$): $\delta$ 8.09 (m, 2 H), 7.95 (ddd, 1 H, $J$ = 0.6−0.9, 1.5, 6.0 Hz), 7.79 (ddd, 1 H, $J$ = 1.5, 7.3−7.5, 8.1 Hz), 7.74 (ddd, 1 H, $J$ = 1.5, 7.2, 8.1 Hz), 7.67 (ddd, 1 H, $J$ = 0.9−1.2, 1.1, 5.7 Hz), 7.62 (ddd, 1 H, $J$ = 0.6−1.1, 1.35−1.5, 8.3 Hz), 7.58 (dd, 1 H, $J$ = 0.9, 3.6), 7.55 (ddd, 1 H, $J$ = 0.6−0.9, 1.5, 8.3 Hz), 7.43 (d, 1 H, $J$ = 4.8 Hz), 7.39 (dd, 1 H, $J$ = 3.3−3.6, 5.1), 7.38 (d, 1 H, $J$ = 5.1 Hz), 7.34 (ddd, 1 H, $J$ = 0.6−0.9, 1.4, 6.0 Hz), 7.31 (ddd, 1 H, $J$ = 2.7, 5.7−6, 6.3 Hz), 7.28 (dd, 1 H, $J$ = 0.9, 5.1 Hz), 7.01 (ddd, 1 H, $J$ = 1.5−1.8, 5.7−5.9, 7.5 Hz), 6.92 (ddd, 1 H, $J$ = 1.2−1.5, 5.9−6.0, 7.4 Hz), 6.21 (d, 1 H, $J$ = 4.8 Hz), 6.11 (d, 1 H, $J$ = 4.8 Hz). HRESIMS ($M^+$): calcd for $C_{27}H_{19}IrN_3S_3$, 672.0342; found, 672.0314.

***fac*-Ir(thpy)$_3$ (6a).** Compound **3a** (0.0501 g, 0.0677 mmol) and thpy (0.0122 g, 0.0757 mmol) were combined in 5 mL of *o*-dichlorobenzene and heated at ∼100 °C under $N_2$ for 116 h. The reaction solution was chromatographed on a silica gel column packed with hexanes to first elute *o*-dichlorobenzene with hexanes. Switching to 1:1 dichloromethane/hexanes eluted the product, **6a**, as a bright orange band in 55−65% yield. The $^1$H NMR spectrum was consistent with previously reported values.[32]

**[Ir(ppy)$_2$(NCCH$_3$)$_2$]PF$_6$ (3b).** Compound **1b** (0.2006 g, 0.1871 mmol) in 75 mL of acetonitrile was heated to dissolve all of the chloro-bridged dimer. A 50 mL acetonitrile solution of $AgPF_6$ (0.1034 g, 0.4089 mmol) was added to the Ir solution. This mixture was stirred in the dark for 2 h, resulting in a gray precipitate. The reaction mixture was filtered over a Celite pad to separate a yellow solution from the gray AgCl precipitate. The solution was concentrated in vacuo, and benzene was added. The solution was cooled to freezing in the refrigerator. Upon melting, solid was present and was collected by vacuum filtration. A second crop was obtained in a similar manner by removing the solvents from the filtrate then redissolving in a minimal amount of acetonitrile and precipitating with diethyl ether. The solids were dried under vacuum to give 0.2341 g (86% yield) of the bright yellow solid. X-ray quality crystals were grown from an acetonitrile solution. $^1$H NMR ($CD_2Cl_2$): $\delta$ 9.00 (ddd, 2 H, $J$ = 1.2, 1.2, 5.9 Hz), 7.97 (m, 4 H), 7.59 (dd, $J$ = 0.9, 7.8 Hz), 7.42 (ddd, 2 H, $J$ = 3.2, 5.8, 5.8 Hz), 6.93 (ddd, 2 H, $J$ = 1.2, 7.5, 7.5 Hz), 6.76 (ddd, 2 H, $J$ = 1.2, 7.5, 7.5 Hz), 6.09 (dd, 2 H, $J$ = 0.75, 7.7 Hz), 2.32 (s, 6 H). HRESIMS ($M^+$): calcd for $C_{26}H_{22}IrN_4$, 581.1445; found, 581.1458.

**[Ir(ppy)$_2$(OH)]$_2$ (4b).** Compound **3b** was produced in situ by dissolving **1b** (0.0521 g, 0.0486 mmol) in 25 mL of acetonitrile and treating with $AgPF_6$ (0.0350 g, 0.l384 mmol). After being stirred for 1.5 h, the solution was filtered over Celite to remove AgCl and the solvent was removed by rotary evaporation. The remaining solid was dissolved in 20 mL of MeOH, and upon addition of solid NaOH (0.0315 g, 0.7875 mmol) the color changed from yellow to brown and a solid precipitated. After the reaction mixture was stirred an additional 24 h, the solid was collected by filtration and rinsed with methanol. The orange-brown solid was dried under vacuum to yield 0.0347 g (69% yield). The $^1$H NMR spectrum in acetone-$d_6$ was consistent with previously reported values.[41] The spectrum was also recorded in dichloromethane-$d_2$. $^1$H NMR ($CD_2Cl_2$): $\delta$ 8.48 (dd, 4 H, $J$ = 0.9, 6.0 Hz), 7.87 (dd, 4 H, $J$ = 0.6, 8.4 Hz), 7.64 (ddd, 4 H, $J$ = 1.5, 7.5, 8.1 Hz), 7.55 (dd, 4 H, $J$ = 1.2, 7.8 Hz), 6.75 (ddd, 4 H, $J$ = 0.9−1.2, 7.5, 7.5 Hz), 6.68 (ddd, 4 H, $J$ = 1.2−1.5, 5.9, 7.3 Hz), 6.54 (ddd, 4 H, $J$ = 1.2−1.5, 7.4, 7.4 Hz), 5.87 (dd, 4 H, $J$ = 1.2, 7.5 Hz).

***fac*-Ir(ppy)$_3$ (6b).** Compound **3b** (0.0503 g, 0.0691 mmol) and ppy (0.0110 mL, 0.0770 mmol) were combined in 5 mL of *o*-dichlorobenzene and heated to ∼100 °C under a nitrogen atmosphere for 120 h. The reaction solution was chromatographed on a silica gel column packed with hexanes to first elute *o*-dichlorobenzene with hexanes. Switching to dichloromethane eluted the product, **6b**, as a bright yellow band in 55−65% yield. The $^1$H NMR spectrum was consistent with previously reported values.[31]

**NMR Tube Reaction of 1a with 4,4′-Di-*tert*-butyl-2,2′-bipyridine (bpy*).** Compound **1a** (0.0032 g, 0.0029 mmol) and bpy* (0.0015 g, 0.0056 mmol) were combined in an NMR tube in dichloromethane-$d_2$. After 4 days a mixture of **1a**, bpy*, and predominantly the product [Ir(thpy)$_2$(bpy*)]$^+$ were present; examination after 20 days showed complete conversion of the starting materials to [Ir(thpy)$_2$(bpy*)]$^+$.

**NMR Tube Reaction of 3a with bpy*.** Compound **3a** (0.0051 g, 0.0069 mmol) and bpy* (0.0023 g, 0.0086 mmol) were combined in an NMR tube in acetone-$d_6$. After 1 h the reaction had gone to completion at room temperature to form [Ir(thpy)$_2$(bpy*)]$^+$.

**NMR Tube Reactions of 5a with Deuterated Solvents.** The lability of the N,S-bound ligand was investigated by dissolving compound **5a** in several deuterated solvents. When **5a** is dissolved in acetonitrile-$d_3$, methanol-$d_4$, or dimethylsulfoxide-$d_6$, peaks for the free ligand (thpy) and new bis-solvento complexes are present. When dissolved in tetrahydrofuran-$d_4$, dichloromethane-$d_2$, tetrachloroethane-$d_2$, or *o*-dichlorobenzene-$d_4$ **5a** does not immediately undergo substitution of the N,S-bound ligand.

**NMR Tube Reaction of 4a with thpy in *o*-Dichlorobenzene-$d_4$.** Compound **4a** (0.0053 g, 0.0050 mmol) and thpy (0.0017 g, 0.0105 mmol) were combined in an NMR tube with *o*-dichlorobenzene-$d_4$ and monitored at room temperature. After 2 days 60% conversion to *mer*-Ir(thpy)$_3$ was observed. After 7 days the conversion to the mer isomer was ∼70%. After 42 days at room temperature the peaks for *mer*-Ir(thpy)$_3$ were still the only product peaks and the conversion was ∼90%. The reaction was driven to

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**Table 1.** Crystallographic Data and Refinement Parameters

| compound | **1a** | **2a** | **3a** | **5a** | **1b** | **3b** |
|---|---|---|---|---|---|---|
| empirical formula | $C_{37}H_{26}Cl_4Ir_2N_4S_4$ | $C_{20}H_{15}ClIrN_3S_2$ | $C_{23}H_{20}Cl_2F_6IrN_4PS_2$ | $C_{27}H_{19}F_6IrN_3PS_3$ | $C_{44}H_{32}Cl_2Ir_2N_4$ | $C_{26}H_{22}F_6IrN_4P$ |
| cryst color, morphology | brown/red, block | orange, block | yellow, block | orange, block | yellow, plate | yellow, rod |
| cryst syst | monoclinic | monoclinic | triclinic | hexagonal | monoclinic | triclinic |
| space group | *C*2/*c* | $P2_1/n$ | $P\bar{1}$ | $R\bar{3}C$ | $P2_1/n$ | $P\bar{1}$ |
| *a*, Å | 15.165(2) | 10.4378(19) | 8.4639(13) | 20.8082(18) | 9.2872(6) | 8.8704(12) |
| *b*, Å | 21.011(3) | 15.831(3) | 13.114(2) | 20.8082 | 11.9810(8) | 18.131(3) |
| *c*, Å | 11.8879(18) | 12.053(2) | 13.816(2) | 71.402(7) | 16.7420(11) | 25.655(4) |
| α, deg | 90 | 90 | 98.724(2) | 90 | 90 | 93.993(2) |
| *β*, deg | 102.626(2)° | 102.938(3) | 105.480(2) | 90 | 99.6740(10) | 96.938(2) |
| *γ*, deg | 90 | 90 | 102.992(2) | 120 | 90 | 93.926(2) |
| vol, Å$^3$ | 3696.4(10) | 1941.1(6) | 1403.1(4) | 26774(3) | 1836.4(2) | 4073.6(10) |
| *Z* | 4 | 4 | 2 | 36 | 2 | 6 |
| fw, g mol$^{-1}$ | 1181.06 | 589.12 | 824.62 | 818.80 | 1072.04 | 727.65 |
| density (calcd), g cm$^{-3}$ | 2.122 | 2.016 | 1.952 | 1.828 | 1.939 | 1.780 |
| temp, K | 173(2) | 173(2) | 173(2) | 173(2) | 173(2) | 173(2) |
| abs coeff, mm$^{-1}$ | 7.744 | 7.241 | 5.216 | 4.813 | 7.423 | 5.039 |
| *F*(000) | 2248 | 1128 | 796 | 14256 | 1024 | 2112 |
| *θ* range, deg | 1.68−25.07 | 2.16−25.04 | 1.57−25.08 | 1.27−25.05 | 2.10−25.04 | 0.80−25.08 |
| index ranges | $-18 \le h \le 18$<br>$-24 \le k \le 24$<br>$-14 \le l \le 14$ | $-12 \le h \le 12$<br>$-18 \le k \le 18$<br>$-14 \le l \le 14$ | $-10 \le h \le 10$<br>$-15 \le k \le 15$<br>$-16 \le l \le 16$ | $-24 \le h \le 13$<br>$-8 \le k \le 24$<br>$-84 \le l \le 84$ | $-8 \le h \le 11$<br>$-14 \le k \le 11$<br>$-19 \le l \le 19$ | $-10 \le h \le 10$<br>$-21 \le k \le 21$<br>$-30 \le l \le 30$ |
| reflns collected | 17 995 | 14 146 | 12 046 | 27 208 | 10 061 | 40 103 |
| independent reflns | 3288 ($R_{int}$ = 0.0385) | 3438 ($R_{int}$ = 0.0277) | 4952 ($R_{int}$ = 0.0417) | 5286 ($R_{int}$ = 0.0771) | 3242 ($R_{int}$ = 0.0263) | 14 435 ($R_{int}$ = 0.0639) |
| weighting factors[a] *a*,*b* | 0.0242, 22.4128 | 0.0159, 2.2129 | 0.0542, 4.7535 | 0.0519, 107.4903 | 0.0180, 4.5009 | 0.0391, 2.5426 |
| max, min transmission | 1.000000, 0.782776 | 0.63000, 0.41346 | 0.353600, 0.227302 | 0.790000, 0.461158 | 0.500000, 0.391887 | 0.830000, 0.677500 |
| data/restraints/params | 3288/3/239 | 3438/0/245 | 4952/0/352 | 5286/95/481 | 3242/364/386 | 14 435/516/1052 |
| R1, wR2 [$I > 2\sigma(I)$] | 0.0212, 0.0539 | 0.0206, 0.0417 | 0.0374, 0.0975 | 0.0486, 0.1102 | 0.0259, 0.0526 | 0.0503, 0.0922 |
| R1, wR2 (all data) | 0.0242, 0.0555 | 0.0257, 0.0430 | 0.0418, 0.1014 | 0.0791, 0.1199 | 0.0325, 0.0548 | 0.0849, 0.1005 |
| GOF | 1.038 | 1.075 | 1.056 | 1.060 | 1.060 | 1.027 |
| largest diff. peak, hole, eÅ$^{-3}$ | 1.317, −1.054 | 0.660, −0.528 | 2.402, −1.451 | 1.289, −1.091 | 0.948, −0.823 | 1.120, −1.182 |

[a] $w = [\sigma^2(F_o^2) + (aP)^2 + (bP)]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$.

completion by heating at 90 °C. Continued heating of the mer product for an additional 12 days resulted in a trace amount (<1%) amount of fac isomer.

**NMR Tube Reaction of 5a in *o*-Dichlorobenzene-$d_4$.** Compound **5a** was combined with *o*-dichlorobenzene-$d_4$ in an NMR tube, heated at 90−100 °C, and monitored by NMR over 6 days. **6a** was formed quickly; a significant amount was present after only 6 h. After 141 h the reaction was essentially complete with the ratio of **6a**/**5a** being 2:1.

**NMR Tube Reaction of 5a in Tetrachloroethane-$d_2$.** Compound **5a** was combined with tetrachloroethane-$d_2$ in an NMR tube, monitored at room temperature for 13 days, and then heated at 60 °C and later 80 °C. At room temperature the reaction forms **1a** and upon heating to 60 °C the production of **1a** is increased and no new products are formed. Increasing the temperature to 80 °C results in the formation of **6a** after 30 h. The precipitation of **6a** prevented the final quantitative analysis of the reaction at completion by NMR.

**Reaction of 3a with thpy.** Compound **3a** (0.0250 g, 0.0338 mmol) and thpy (0.00640 g, 0.0397 mmol) were combined with dichloromethane (5 mL) and toluene (35 mL) and heated to reflux under a nitrogen atmosphere for 192 h. **6a** was formed in 36% isolated yield.

**NMR Tube Reaction of 3b with ppy.** Compound **3b** (0.005 g, 0.00687 mmol) and ppy (0.001 mL, 0.00700 mmol) were combined in an NMR tube with *o*-dichlorobenzene-$d_4$ and heated at 80 °C. **6b** was formed after 1 h with the consumption of **3b** being complete after 66 h. There was no evidence of the mer isomer in the reaction.

**NMR Tube Reaction of 4b with ppy.** Compound **4b** (0.0010 g, 0.0010 mmol) and ppy were combined in an NMR tube with *o*-dichlorobenzene-$d_4$. After 42 h at room temperature no reaction was observed, due in part to the limited solubility of **4b**. The NMR tube was then heated at 105 °C, allowing **4b** to dissolve. After 22 h of heat 70% conversion to *mer*-Ir(ppy)$_3$ was observed, and the reaction was complete after 216 h with no evidence of the fac isomer **6b**. Additional heating of the mer product for 120 h at 105 °C showed no conversion to the fac isomer.

**Attempted NMR Tube Isomerization of *mer*-Ir(ppy)$_3$ to *fac*-Ir(ppy)$_3$.** *mer*-Ir(ppy)$_3$ was combined with *o*-dichlorobenzene-$d_4$ and monitored at room temperature; after 4 days, no reaction was observed. The tube was then heated at 100 °C for 10 days; again, no formation of **6b** was detected.

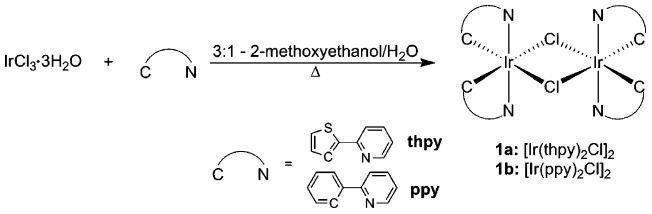
**Single-Crystal X-ray Crystallography.** Single crystals were attached to glass capillary fibers. **1a**, **3a**, and **5a** were mounted on a Bruker SMART Platform CCD diffractometer, while **1b**, **2a**, and **3b** were mounted on a Siemens SMART Platform CCD diffractometer for data collection at 173(2) K using a graphite monochromator and Mo Kα radiation ($\lambda$ = 0.71073 Å). An initial set of cell constants was calculated from reflections harvested from three sets of 20 frames such that orthogonal wedges of reciprocal space were surveyed. Final cell constants were determined from a minimum of 944 strong reflections from the actual data collection. Data were collected to the extent of 1.5 hemispheres to a resolution of 0.84 Å with the exception of **1a**, which was surveyed to a resolution of 0.77 Å. Three major sections of frames were collected with 0.30° steps in $\omega$. The intensity data were corrected for absorption and

**Table 2.** Selected Bond Lengths (Å) for the Reported Structures

| | 1a | 2a | 3a | 5a | 1b | 3b | $[Ir(tpy)_2Cl]_2$[b] |
|---|---|---|---|---|---|---|---|
| Ir−N1 | 2.043(4) | 2.054(3) | 2.069(5) | 2.072(6) | 2.053(12)[a] | 2.052(7)[a] | 2.09(1) |
| Ir−N2 | 2.058(4) | 2.063(3) | 2.071(6) | 2.070(7) | 2.052(12)[a] | | 2.09(1) |
| Ir−C7 | 1.976(4) | 1.999(4) | 2.000(6) | 2.030(9) | 1.890(12)[a] | 2.004(8)[a] | 2.02(2) |
| Ir−C16 (C18)[c] | 1.984(4) | 2.003(4) | 2.013(6) | 1.991(9) | 2.111(12)[a] | | 2.03(2) |
| Ir−Cl1 | 2.547(9) | 2.4730(10)[d] | | | 2.5116(12)[a] | | 2.57(1) |
| Ir−Cl2 | 2.466(9) | | | | | | 2.50(1) |
| Ir−N3 | | 2.117(3) | 2.102(5) | 2.144(22)[a,e] | | 2.131(7)[a] | |
| Ir−N4 | | | 2.125(5) | | | | |
| Ir−S3 | | | | 2.551(7)[a] | | | |

[a] Values averaged due to disorder or multiple molecules in asymmetric unit. [b] $T = 296$ K, see ref 45. [c] C18 analogous carbon in ppy. [d] Chloride. [e] Pyridine.

**Scheme 1.** Synthesis of Chloro-Bridged Dimers




decay using SADABS.[42,43] Space groups were determined on the basis of systematic absences and intensity statistics. Direct-methods solutions provided the positions of most of the non-hydrogen atoms. Full-matrix least-squares/difference Fourier cycles were performed to locate the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were placed in idealized positions and refined as riding atoms with relative isotropic displacement parameters. All calculations were performed with the SHELXTL suite of programs.[44] Details of the refinement, as well as selected bond lengths, are given in Tables 1 and 2.

## Results and Discussion

**Synthesis of *fac*-Ir(C^N)$_3$ and Intermediate Complexes.** Iridium(III) chloride has been shown to react with a variety of cyclometalating ligands to give chloride-bridged dimers in refluxing 2-ethoxyethanol.[40] In our hands, replacement of 2-ethoxyethanol with 2-methoxyethanol appears to have no deleterious effect on the formation of **1a** and **1b**; both are formed in 60−80% yields (Scheme 1).

The chloro-bridged dimers **1a** and **1b** are solvated in strongly coordinating solvents such as acetonitrile, dimethylformamide, and dimethylsulfoxide to give mononuclear complexes such as **2a** and **2b** (Scheme 2).[41] This dimeric cleavage and the tendency for solvent molecules such as acetonitrile to occupy open coordination sites were used to synthesize the bis-acetonitrile complexes **3a** and **3b** by reaction with $Ag^+$ to remove $Cl^-$. The acetonitrile ligands of complexes **3a** and **3b** are labile; these complexes readily undergo substitution reactions at room temperature to give complexes such as **4a**, **4b**, and **5a**, as shown in Scheme 2. Additionally, these bis-acetonitrile complexes undergo cyclometalation reactions at relatively low temperature to make the highly desired fac isomers of Ir(thpy)$_3$ and Ir(ppy)$_3$. Complexes **4a** and **4b** also undergo cyclometalation reactions at low temperature but instead give the mer isomers of Ir(thpy)$_3$ and Ir(ppy)$_3$. The presence of the basic hydroxide site of **4a** and **4b** provides a convenient route to mer isomers without the addition of an external base. Synthesis of the intermediate bis-acetonitrile complexes **3a** and **3b** eliminates many variables including the harsh reaction conditions involved in previous synthetic reaction schemes to fac isomers.

**NMR Characterization.** The $^1$H NMR spectra in $CD_2Cl_2$ solutions of the thpy and ppy dimers, **1a** and **1b** (six and eight resonances, respectively), are consistent with those previously reported. These data are consistent with symmetrical complexes with $C_2$ symmetry in which both cyclometalated ligands are equivalent; the nitrogen atoms of the pyridyl rings are mutally trans as are those in the previously determined structure of $[Ir(tpy)_2Cl]_2$ (tpy = 2-(*p*-tolyl)-pyridine).[45] In coordinating solvents such as acetonitrile, the dimeric structure is lost, as is evidenced by the more complicated nature of the $^1$H NMR spectra of the complexes in these solvents.[41]

Removal of the remaining $Cl^-$ with $Ag^+$ in acetonitrile gave the cationic bis-acetonitrile complexes (**3a** and **3b**) that were characterized via $^1$H NMR as well with six and eight peaks in the aromatic region, respectively. The mild reaction conditions preserve the original orientation of the cyclometalating ligands with trans nitrogen atoms and cis acetonitrile ligands giving complexes of $C_2$ symmetry. The lowest field resonance in both **3a** (8.85 ppm) and **3b** (9.00 ppm) is assigned to the proton ortho to the nitrogen in the pyridyl ring. This proton is positioned over the C≡N of the acetonitrile ligands in a region of deshielded electron density compared to the other ligand protons.[46] Interestingly, the increased shielding effect from the circulation of the electrons of the triple bond in comparison to that of the bridging chlorine atoms in the dimers can be observed by the shift to lower ppm of these ortho protons in **3a** and **3b**.

In the case of the reaction of **3a** in acetone with thpy, a non-cyclometalated sulfur-bonded complex **5a** was isolated; **5a** yielded a very complicated $^1$H NMR spectrum indicative of a molecule with $C_1$ or $C_i$ symmetry. Integration of the peaks in the aromatic region indicated a total of 19 protons,

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(43) Sheldrick, G. *SADABS*, v.2.03; Bruker AXS, Madison, WI, 2002.
(44) *SHELXL*, v.6.1; Bruker AXS, Madison, WI, 2001.
(45) Garces, F. O.; Dedeian, K.; Keder, N. L.; Watts, R. J. *Acta Crystallogr., Sect. C* **1993**, *49*, 1117.
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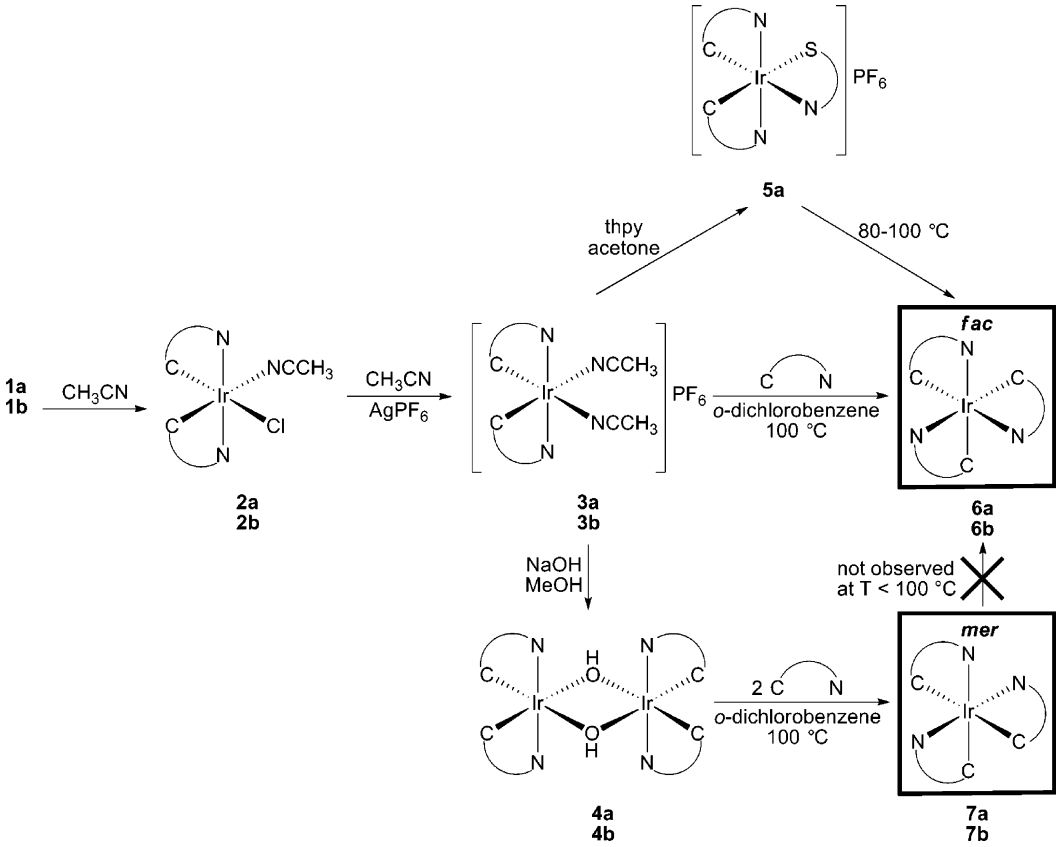
**Scheme 2.** Low-Temperature Synthetic Scheme to fac and mer Cyclometalated Ir(III) Complexes, as Well as Other Intermediate Compounds




indicating that the new product was not *mer*-Ir(thpy)$_3$ which would exhibit 18 aromatic proton resonances. The presence of 19 resonances and the peak patterns observed suggested that the complex instead consisted of two cyclometalated thpy ligands and one thpy ligand bound through the nitrogen and sulfur atom. Ligation through the sulfur of the thpy ligand gives a complex of $C_1$ symmetry with an extra proton displayed in the aromatic region as compared to that of *mer*-Ir(thpy)$_3$. Confirmation of **5a** as a cationic species was confirmed by the presence of a peak for a $PF_6^-$ counterion in a $^{31}$P NMR spectrum of the compound. Assignment of the $^1$H NMR spectrum of **5a** was difficult due to the sheer number of resonances in the aromatic region, some of which were overlapping; however, careful examination of the coupling between peaks and a COSY NMR spectrum allowed the determination of which protons were associated with a given ring system and allowed the complete simulation[47] and full assignment of the spectrum (see Supporting Information).

**X-ray Crystallography.** Somewhat surprisingly in view of the interest in this area, the X-ray structures of the chloro-bridged starting materials used in this study have not been previously determined. However, [Ir(tpy)$_2$Cl]$_2$ and two other dimers containing substituted cyclometalating ligands have been characterized by X-ray crystallography. Single crystals of the chloro-bridged dimers, **1a** and **1b**, were grown from dichloromethane, and the resulting structural data are used here for comparison of bond lengths with the newly synthesized complexes. In both **1a** and **1b** the nitrogen atoms were confirmed to be mutually trans to each other in the mer chelate arrangement; the arrangement of the ligands is such that rearrangement at the metal center must occur for *fac*-Ir(C^N)$_3$ complexes to be formed upon reaction with a third cyclometalating ligand. **1a** crystallized as a dichloromethane solvate in the space group *C*2/*c* (Figure 1). **1a** crystallized on a 2-fold axis that lies between the chlorine atoms; thus, the asymmetric unit consists of half of the molecule. The co-crystallized dichloromethane molecule also lies on a 2-fold axis and is disordered in a 50:50 ratio over this symmetry element. **1b** crystallized in the space group $P2_1/n$ with the asymmetric unit lying on an inversion center. The ppy rings are also disordered to give both the $\Lambda$ and $\Delta$ orientations in a 50:50 ratio in the asymmetric unit. The absolute structure of the molecule therefore cannot be determined. Dimeric units of $\Lambda\Delta$ and $\Delta\Lambda$ stereochemistry or $\Lambda\Lambda$ and $\Delta\Delta$ stereochemistry could occupy the same space with 50% occupancies; however, we believe that it is more likely an arrangement of $\Lambda\Lambda$ and $\Delta\Delta$ isomers because the structures of **1a** and [Ir(tpy)$_2$Cl]$_2$ contain discrete molecules of $\Lambda\Lambda$ and $\Delta\Delta$ symmetry which alternate throughout the cell. The Ir−C, Ir−N, and Ir−Cl bond lengths for these complexes are given in Table 2 along with previously determined values for [Ir(tpy)$_2$Cl]$_2$.[45] As is the case in [Ir(tpy)$_2$Cl]$_2$, the Ir−C bonds lengths in **1a** (1.976(4) and 1.984(4) Å) are shorter than the Ir−N bonds (2.043(4) and 2.058(4) Å). The individual bond lengths observed in **1b** vary much

(47) Marat, K. *Spinworks*, v.2.3; University of Manitoba: Winnipeg, Canada, 2004.

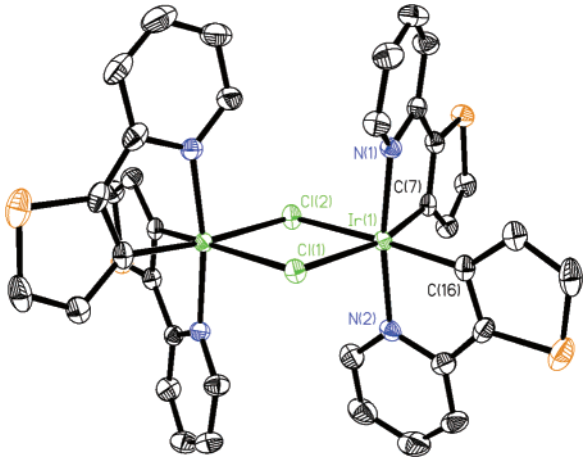



**Figure 1.** Thermal ellipsoid plot of **1a**. The dichloromethane solvent molecule removed for clarity.

more than those of **1a** or $[Ir(tpy)_2Cl]_2$, possibly due to the occupational disorder that is observed in this structure. Average values of the Ir−C (2.000(12) Å) and Ir−N (2.053(12) Å) bond lengths in this structure correlate well with those previously mentioned.

Thermal ellipsoid plots of the pseudo-octahedral geometry of **2a**, **3a**, and **3b** are shown in Figure 2. The crystallographic data for these structures, along with those for **1a** and **1b**, are given in Table 2. Discussion of the disorder of these and the following structures, as well as atomic coordinates, bond lengths, and angles for each complex, are available in the Supporting Information. The structure of **2a** consists of Ir(III) coordinated to two thpy ligands which maintain the mer chelate arrangement adopted in the dichloro-bridged dimers with cis cyclometalating carbons and trans nitrogens. One chloride and one ligating acetonitrile molecule complete the octahedral coordination sphere to give a neutral molecule.

Again observed in the structure of **3a** is the *cis*-C,C and *trans*-N,N chelation geometry of the thpy ligands. Two bound acetonitrile molecules occupy the remaining coordination sites. The Ir−C distances observed for **3a** (2.000(6) and 2.013(6) Å) are slightly longer than those observed for **1a** (1.976(4) and 1.984(4) Å), perhaps due to the better $\sigma$-donating and $\pi$-accepting nature of the acetonitrile ligands in comparison to $Cl^-$. Additionally, the trans influence of the cyclometalating carbon atoms on the Ir−N acetonitrile bonds is observed by comparing these bond lengths (2.102(5) and 2.125(5) Å) to those in structures of $Ru(bpy)_2(NCCH_3)_2^{2+}$ salts where bpy = 2,2′-bipyridine (2.032−2.044 Å).[48,49] The negatively charged thiophene moiety has a stronger trans influence than that of the lone-pair-donating pyridyl group, resulting in lengthening of the trans nitrile bonds.

The structure of **5a** consists of Ir(III) surrounded by two thpy ligands bound in the typical cyclometalating fashion with the *cis*-C,C and *trans*-N,N chelation, as well as a third thpy ligand bound through the N of the pyridyl ring and the S of the thiophene ring. Thiophene has been shown previously to weakly coordinate Ir(III),[50−54] as well as other transition metals,[55−59] through the sulfur atom. The weak nature of the coordination of the sulfur-bound ligand is evident by its facile replacement by solvent molecules when **5a** is in the presence of coordinating solvents such as acetonitrile, methanol, and dimethylsulfoxide. In the crystal structure this third ligand is occupationally disordered by 180° at the Ir atom so that the pyridine ring and thiophene exchange places. The disordered components were resolved to give a 73.3:26.7 ratio of occupancy. The S-bound thpy ligand is not flat, as is typically seen for cyclometalating ligands (Figure 3). The S adopts the $sp^3$ trigonal pyramidal geometry typically seen for atoms with two bonds and two lone pairs, one of which is coordinated, resulting in the thiophene ring being tilted out of the equatorial plane. The Ir−N distances for the trans nitrogen atoms (2.072(6) and 2.070(7) Å) are similar to those previously observed while the Ir−N bond of the S-bound ligand trans to the phenyl carbon (2.108(13)/2.180(30) Å) is considerably longer due to the stronger trans influence of the thienyl as compared to pyridyl moiety. The Ir−C bond trans to the pyridyl group is longer than Ir−C bonds previously observed as pyridine is a better $\sigma$-donor than previously examined ligands. The Ir−S bond lengths of the two disorder components are very long (2.430(3) and 2.672(11) Å), as would be expected for a weakly coordinated atom.

The structure of **3b** contained three crystallographically independent molecules in the asymmetric unit. The Ir−C bond length averaged over each of the three independent molecules (2.004(8) Å) is again shorter than the average Ir−N bond distance (2.052(7) Å). Due to the high estimated standard deviations of the bond distances of the **1b**, no conclusions can be made about the trans influence of acetonitrile on the basis of these structures. However, the distances obtained from the structure of **3b** correlate very well with those of **3a**. Not surprisingly the average length of the Ir−N bonds to the acetonitrile ligands (2.131(7) Å)

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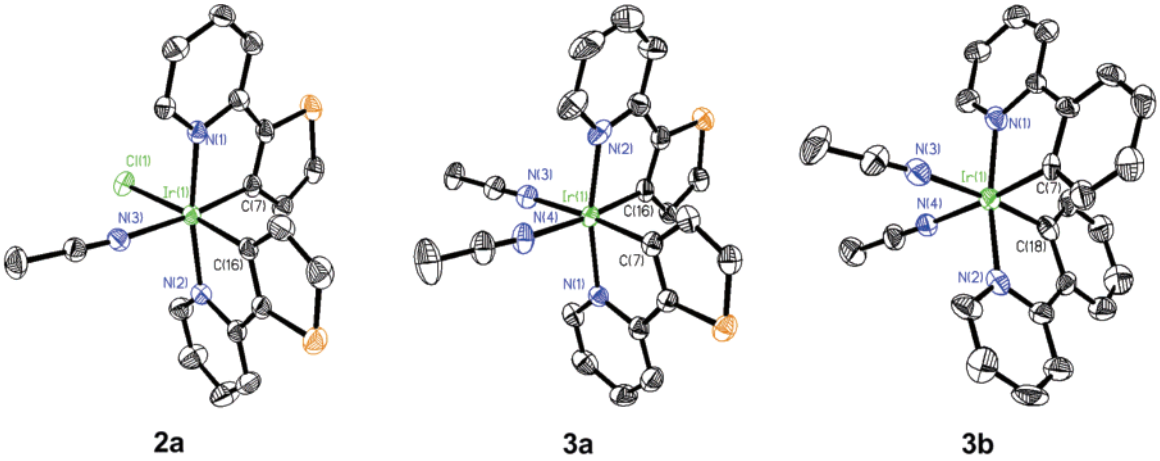


**Figure 2.** Thermal ellipsoid plots of **2a**, **3a**, and **3b**, respectively. Hydrogen atoms and $PF_6$ counterions are omitted for clarity.

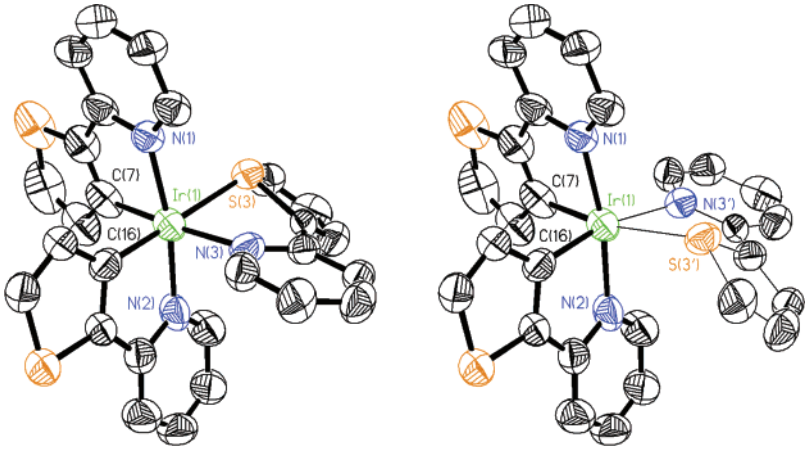


**Figure 3.** Thermal ellipsoid plots showing the two disorder components of **5a**. Hydrogen atoms and $PF_6$ counterions and protons are omitted for clarity.

are longer than those of acetonitrile bonds trans to pyridyl rings, as previously discussed with **3a**.

**Mechanistic Considerations and Discussion.** When we began this work, our goal was to synthesize *fac*-Ir(C^N)$_3$ complexes with high selectivity at low temperatures. In this regard we were successful, although several other groups have been active and published very interesting synthetic studies as well. The traditional syntheses of *fac*-Ir(C^N)$_3$ complexes use high temperature, for example, reactions in refluxing glycerol.[31−37] At lower temperatures (120−150 °C), otherwise similar reactions give the less-emissive mer isomers, which are subsequently isomerized to fac to avoid low yields and/or contamination.[22,31] A significant kinetic barrier in these reactions is the breakage of the final Ir−Cl bond as evidenced by (1) the relative ease that the chloro-bridged dimers cleave in polar solvents to give neutral mono-solvento complexes followed by (2) the requirement of $Ag^+$ ion reactions to induce the second solvent molecule into the Ir(III) coordination sphere. Several reactions that we have carried out attest to the much higher reactivity of these bis-solvento complexes with regard to both ligand substitution and cyclometalation. Among these are the rapid formation of **5a** from **3a** in acetone and the more rapid reaction of **3a** than **1a** with bpy* in acetone to form the mixed cyclometalating ligand *mer*-Ir(C^N)$_2$(bpy*)$PF_6$ compounds. More recently, a fac isomer of a mixed ligand complex has been made at 95 °C, but in low yield.[20] In all of these cases a consistent mechanistic explanation for the conditions needed for the synthesis and interconversion of the fac and mer geometry products is absent. Particularly intriguing is the question of how the mer geometry in the chloro-bridged starting materials is converted into the tris fac products. All of our experiments suggest that the tris mer complex is not an intermediate along the "low temperature" reaction path to the tris fac product. For example a reaction of *mer*-Ir(ppy)$_3$ at 100 °C in *o*-dichlorobenzene-$d_4$ for 10 days gives *no conversion* to **6b**; however, the reaction of **3b** [*mer*-Ir(ppy)$_2$(NCCH$_3$)$_2$]$^+$ with an additional equivalent of ppy at 100 °C gives exclusively **6b** after 5 days in 60% isolated yield. Another example is the low-temperature rearrangement of the tris-S-bonded complex **5a** which when heated to only 100 °C gives *fac*-Ir(thpy)$_3$ and no *mer*-Ir(thpy)$_3$. Clearly, the production of *mer*-Ir(ppy)$_3$ and *mer*-Ir(thpy)$_3$ in these low-temperature reactions without added base is inhibited while the isomerization of one of the C^N ligands of [*mer*-Ir(C^N)$_2$(NCCH$_3$)$_2$]$^+$ and addition of C^N to give the fac product is facilitated.

In addition to the observed absence of a low-temperature

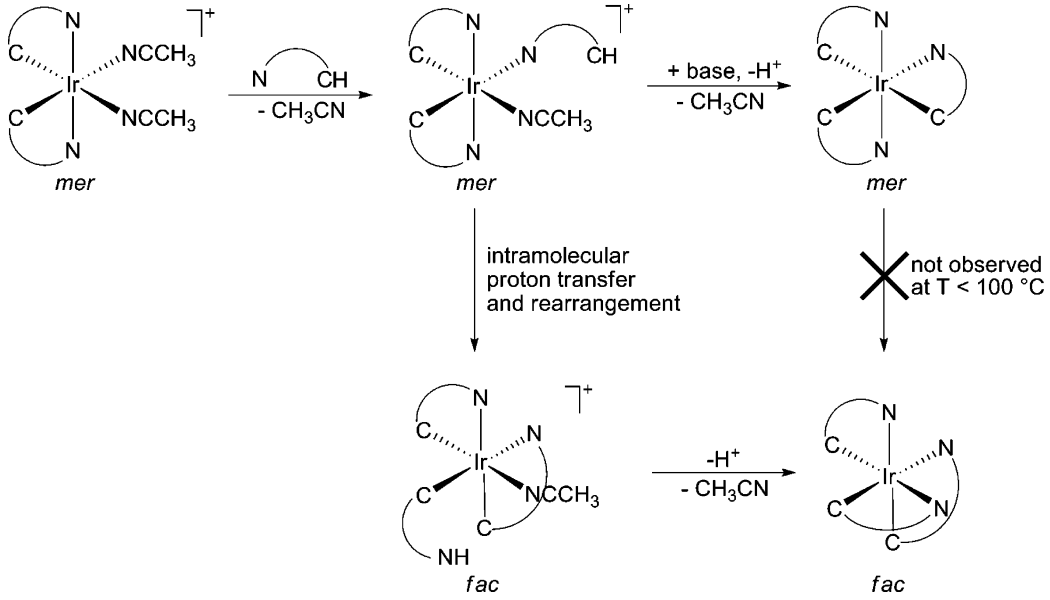


**Figure 4.** Proposed mechanism for the formation of mer and fac isomers.

isomerization reaction of mer to fac, we have observed that the tris mer products can be selectively synthesized at low temperature by the addition of a base to aid in deprotonation of the third ligand. We propose that at low temperature the addition of a base is necessary to obtain the mer isomer when starting with the chloro-bridged dimers or bis-acetonitrile complexes; however, when heating hydroxide-bridged dimers **4a** and **4b** in *o*-dichlorobenzene-$d_4$, which have a "built-in base" in the hydroxide moiety, to ~100 °C we observe formation of only tris mer species with *no formation* of fac isomers. These results, along with the above studies of the synthesis of the fac isomers, are consistent with the need for an added base for the production of the mer species.

On the basis of our studies and literature reports, we propose a mechanism that is consistent with the formation of both mer and fac isomers. The mechanism features common intermediates of the form $[Ir(C\text{^}N)_2(-N\text{^}C)L]^+$ where $-N\text{^}C$ represents a monodentate cyclometalating ligand attached only through N, and L is either a solvent molecule (e.g., acetonitrile), chloride, or a second ligating atom (other than C) from the entering N^C ligand (such as the S in the case of N^C = thpy). The scheme in Figure 4 drawn for the specific case of L = acetonitrile and N^C = ppy shows the reactions of the $[Ir(C\text{^}N)_2(-N\text{^}C)L]^+$ intermediate which form mer and fac, respectively.

The proposed mechanism starts with the replacement of one acetonitrile ligand with the nitrogen end of the incoming bidentate ligand to form the intermediate common to both the mer and fac tris complex mechanisms. In the presence of a sufficient concentration of added base (or in the case of reaction with **4a** and **4b**, the hydroxide ligand L) the carbon end of the ligand is deprotonated and coordinates with removal of the second acetonitrile. *The determination of the sequence of these steps is beyond the scope of our present studies.* The net result of this path is the fomation of the mer tris isomer. If an added base or a basic ligand site is *not* present, the formation of the fac isomer is completed by a sequence of steps that includes decomplexation of one of the mutually trans nitrogens of the intermediate, proton transfer from the carbon of the incoming ligand, coordination of this carbon to Ir, and then replacement of the remaining acetonitrile by the nitrogen released in the isomerization step. Again, the exact sequence of these steps is not known. Even though the basicity of the carbon is much higher than the nitrogen end of the cyclometalating ligand, the unimolecular nature of the transfer and the presumed exergonic energy balance afforded by the change in coordination geometry at Ir could offer sufficient lowering of the transition-state energies of the overall process. In the traditional high-temperature synthetic scheme, the replacement of acetonitrile in most of the intermediate species by chloride is expected to considerably slow the ligand substitution steps and perhaps make the direct formation of fac energetically unfeasible until very high temperatures are available to directly isomerize the mer isomer.

## Conclusions

Selective low-temperature syntheses of fac and mer tris-cyclometalated Ir(III) complexes have been developed. Fac isomers of the cyclometalating ligands thpy and ppy are selectively formed at 100 °C. The use of bis-acetonitrile complexes as the source of Ir(III) eliminates the activation of Ir−Cl bonds in the rate-limiting step. In *o*-dichlorobenzene and the absence of added base, internal proton transfer and isomerization provides a selective low-temperature route for the preparation of the fac isomers after removal of the solvent by flash column chromatography. We suggest that C−H bond activation via proton removal by an added base is the rate-limiting step in the formation of mer tris complexes. Our use of hydroxy-bridged dimers provides a "built-in base" that aids deprotonation of the cyclometalating carbon and allows selective formation of the mer isomers of thpy and ppy at 100 °C. We believe that these syntheses will prove to be generally useful for the production of the fac and mer

isomers of other C^N ligands and heteroleptic complexes with two different cyclometalating ligands.

**Acknowledgment.** This work was supported by the Center for Analytical Process Chemistry at the University of Washington, the Initiative for Renewable Energy and the Environment at the University of Minnesota, and the Materials Research Science and Engineering Center at the University of Minnesota. The authors thank Dr. Victor G. Young Jr. and William W. Brennessel of the University of Minnesota X-ray crystallography laboratory for assistance with some of the crystal structures and Galen Sedo who solved the structure of **1a** as part of the CHEM 5755 class.

**Supporting Information Available:** Atomic coordinates, bond lengths, and angles in cif format; $^1$H NMR spectra, $^1$H NMR simulation of **5a**, and details of disorder resolution of the structures of **1a**, **1b, 3b**, and **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC700440C