Inorg. Chem. **2008**, *47*, 6681−6691

Probing the *mer*- to *fac*-Isomerization of Tris-Cyclometallated Homo- and Heteroleptic $(C,N)_3$ Iridium(III) Complexes

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Received January 28, 2008

We have developed techniques which allow for covalent tethering, via a "hetero" cyclometallating ligand, of heteroleptic tris-cyclometallated iridium(III) complexes to polymeric supports (for application in light-emitting diode technologies). This involved the selective synthesis and thorough characterization of heteroleptic $[Ir(C,N)_2(C',N')]$ tris-cyclometallated iridium(III) complexes. Furthermore, the synthesis and characterization of heteroleptic $[Ir(C,N)_2OR]$ complexes is presented. Under standard thermal conditions for the synthesis of the *facial* (*fac*) isomer of tris-cyclometallated complexes, it was not possible to synthesize pure heteroleptic complexes of the form $[Ir(C,N)_2(C',N')]$. Instead, a mixture of homo- and heteroleptic complexes was acquired. It was found that a stepwise procedure involving the synthesis of a pure *meridonial* (*mer*) isomer followed by photochemical isomerization of this *mer* to the *fac* isomer was necessary to synthesize pure *fac*-$[Ir(C,N)_2(C',N')]$ complexes. Under thermal isomerization conditions, the conversion of *mer*-$[Ir(C,N)_2(C',N')]$ to *fac*-$[Ir(C,N)_2(C',N')]$ was also not a clean reaction, with again a mixture of homo- and heteroleptic complexes acquired. An investigation into the thermal *mer* to *fac* isomerization of both homo- and heteroleptic tris-cyclometallated complexes is presented. It was found that the process is an alcohol-catalyzed reaction with the formation of an iridium alkoxide $[Ir(C,N)_2OR]$ intermediate in the isomerization process. This catalyzed reaction can be carried out between 50 and 100 °C, the first such example of low-temperature *mer*−*fac* thermal isomerization. We have synthesized analogous complexes and have shown that they do indeed react so as to give *fac*-tris-cyclometallated products. A detailed explanation of the intermediates (and all of their stereoisomers, in particular when systems of the generic formula $[M(a,b)_2(a',b')]$ are synthesized) formed in the *mer* to *fac* isomerization process is presented, including how the formed intermediates react further, and the stereoisomeric products they yield.

Introduction

Since the initial discovery by Watts and co-workers that *facial*-tris[2-pyridinyl-κN-phenyl-κC^2]iridium (*fac*-[Ir(ppy)$_3$]) complexes display emission quantum yields as high as 0.4, tremendous effort has been invested into developing similar compounds for use in organic light emitting diodes (OLEDs).[1] The photophysical properties of bis- and tris-cyclometallated iridium(III) complexes are very interesting for several applications. The most impressive of these is their application in combination with phosphorescent dopants, which leads to even higher quantum efficiencies with electrophosphoresence.[2] Other applications include chemiluminescent devices,[3] molecular oxygen sensors,[4] and templates in oxalate-based chiral magnets.[5]

Present work in this field has been directed toward augmenting ligand electronics so as to adjust energy levels in tris-C,N-cyclometallated iridium(III) ($[Ir(C,N)_3]$) complexes and thus to improve quantum efficiencies and cover the whole spectrum of color. This has resulted in a huge range of aromatic cyclometallating ligands being tested and used in homoligated complexes.[6] Tris-cyclometallated iridium complexes tend to show higher quantum yields and

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10.1021/ic800169n CCC: $40.75
Published on Web 06/28/2008

internal quantum efficiencies than their bis-cyclometallated analogues. However, bis-cyclometallated complexes are still very valuable photochemically, and thus a huge range of charged heteroleptic $[Ir(C,N)_2L][X]$ complexes, where L is a neutral chelating diamine or diphosphine ligand, have also been developed.[7] Neutral heteroleptic $[Ir(C,N)_2(E,E')]$ complexes exist with the heteroligand (E,E′) as a monoanionic acetate (O,O′) or picolinate (N,O).[8] Very few reports have shown the selective synthesis of heteroleptic $[Ir(C,N)_2(C',N')]$ complexes.[9]

$[Ir(C,N)_3]$-type complexes have two stereochemical forms: meridonial (*mer*) and facial (*fac*). The *mer* isomers possess three nitrogens around the equator of the molecule with two nitrogens trans to each other and the third nitrogen trans to an aromatic carbon. In the *fac*-isomer all nitrogen atoms are trans to a carbon atom. Previous work has shown the differences between the photophysical[10] and stereochemical[11] properties of the *mer* and *fac* isomeric forms of the complexes. Generally the *fac* isomer has an order of magnitude longer emission lifetime (τ) than the *mer*. Similarly, the quantum yield of emission (Φ) in the *fac* tends to be an order of magnitude greater than that of the *mer* isomer. Conversion of *mer* to *fac* isomers is possible using both thermal and photochemical techniques.

We are interested in developing heteroleptic $[Ir(C,N)_2(C',N')]$ complexes, because this can provide an entry to tris-cyclometallated Ir(III) complexes tethered to dendritic and polymeric supports. Eventually, we would like to develop OLED devices based on supported iridium complexes. Binding of cyclometallated Ir(III) complexes to dendritic,[12] linear polymeric,[13] and biochemical supports[14] has shown some very promising results for the future development of photochemical devices.

In this report, we present our initial results toward the synthesis of heteroleptic $[Ir(C,N)_2(C',N')]$ complexes.[15] The synthesis of these complexes has thrown up some stumbling blocks. It was found that using standard thermal techniques it is not possible to synthesize pure *fac* heteroleptic complexes, due to ligand scrambling. We devised a stepwise procedure which involves the reaction of $[Ir(ppy)_2Cl]$ with a heteroarene ligand, 4-methylphenyl-2-pyridine (Htolpy), yielding a heteroleptic *mer* isomer, followed by conversion of this *mer* to the corresponding *fac* isomer using photochemical techniques. Furthermore, we also applied this technique to synthesize mixed ligand functionalized species for immobilization on polymeric supports.[16] This has allowed us to analyze the photophysical effects of the support on the complex.[17] We also investigated why, when using standard thermal *mer* to *fac* isomerization techniques, a clean reaction is not observed. The mechanism involved in the thermodynamic *mer* to *fac* isomerization of tris-cyclometallated iridium complexes was studied, and a number of analogues of possible intermediates were synthesized. From these investigations, we have developed novel methods to synthesize both homo- and heteroleptic tris-cyclometallated *fac*-

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(17) The properties of the polymer-supported complexes can be easily altered, by both tethering to a support and altering the phobicity of the copolymer/codendron.

type complexes, including at lower temperatures. This report contains a detailed discussion on the various stereochemical forms of heteroleptic tris-cyclometallated iridium complexes.

Experimental Section

General Information. Standard Schlenk procedures under N_2 were carried out throughout. Reactions were carried out in the absence of light, unless otherwise stated. Reagents were used as supplied from Acros BV or Sigma-Aldrich, unless otherwise stated. The synthesis of **3** and **4** was carried out according to literature procedures (see Scheme 1).[1c,d] The synthesis of **5** and **6** was carried out according to the Thompson method.[11] ^{1}H and ^{13}C solution NMR was carried out on a Varian Inova 300 spectrometer or a Varian Oxford AS400. Elemental analyses were performed by Dornis and Kolbe, Mikroanalytisches Laboratorium, Mülheim a. d. Ruhr, Germany. Mass spectrometry (MS) measurements were carried out on an Applied Biosystems Voyager DE-STR matrix-assisted laser desorption ionization−time of flight (MALDI−TOF) MS.

Photophysics. UV−vis absorption analysis was performed on a Varian CARY 50 Scan UV−visible spectrophotometer in CH_2Cl_2. Emission measurements were carried out on a SPEX FLUOROLOG 1680 0.22m Spectrometer in acetonitrile. *fac*-[Ir(ppy)$_3$] in 2-MeTHF was used as a reference ($\Phi = 0.4$).

Electrochemistry. CV measurements were carried out on an EG&G Princeton Applied Research Potentiostat Model 263A. Experiments were carried out at room temperature (20 °C). A platinum disk working electrode was polished with alumina on felt before use. A platinum wire was used as the counter electrode. A silver wire was used as a pseudo-/quasi-reference electrode. Tetrabutylammonium hexafluorophosphate (0.1 M) in MeCN was used as the electrolyte. The scan rate was 0.1 V/s. The silver reference electrode was calibrated using the ferrocene/ferrocenium (Fc/Fc^+) redox couple as an internal standard. The oxidation potential of Fc/Fc^+ was found to be 0.51 V against the silver reference electrode.

***mer*-Ir(tpy)(ppy)$_2$: *mer*-[mono(4-Methyl-(2-pyridinyl-κN)phenyl-κC^2)-bis((2-pyridinyl-κN)phenyl-κC^2)]iridium(III), *mer*-7-*homo-N-trans*.** Bis((2-pyridinyl-κN)phenyl-κC)iridium(III) chloride (0.2045 g, 0.381 mmol) was placed in glycerol (2 mL). To this was added K_2CO_3 (0.525 g, 10 equiv, 3.8 mmol) and 4-methylphenyl-2-pyridine (0.25 mL, 4 equiv, 1.5 mmol). The resulting suspension was heated, under inert conditions, in an oil bath, to 150 °C for 40 h. This resulted in a dark brown solution. After the solution was cooled to room temperature, deionized water was added, and the mixture was vigorously mixed until a dark precipitate was observed. The dark precipitate was filtered and washed with water twice and subsequently with ethanol twice. The precipitate was then purified using column chromatography with dichloromethane as the eluent (yield 84%). The final product was bright orange in color and was a fine powder. ^{1}H NMR (300 MHz, d_6-DMSO): δ 2.00 (s, 3H, CH_3), 6.44 (d, 1H, CH), 6.59 (d, 1H, CH), 6.71 (s, 1H, CH), 6.75−7.05 (m, 8H,CH's), 7.50−7.75 (m, 7H, CH's), 7.87 (2 × d, 2H, CH's), 7.91 (2 × d, 2H, CH's), 8.15 (d, 1H, CH). ^{13}C NMR (75 MHz, d_6-DMSO): δ 22.29, 119.2, 119.4, 119.8, 119.9, 121.5, 122.7, 123.1, 123.2, 123.3, 124.8, 125.0, 125.2, 129.8, 130.2, 130.7, 132.7, 135.5, 137.2, 138.1, 138.5, 138.8, 143.0, 143.4, 145.4, 148.1, 150.8, 153.0, 160.0, 167.7, 168.3, 170.4, 175.5, 177.7. *m*/*z* 669.03 g/mol. $C_{34}H_{26}IrN_3$ calcd.: C, 61.06; H, 3.92; N, 6.28. Found: C, 61.11; H, 3.96; N, 6.11.

***fac*-Ir(tpy)(ppy)$_2$: *fac*-[mono(4-Methyl-((2-pyridinyl-κN)phenyl-κC^2)-bis((2-pyridinyl-κN)phenyl-κC^2)]iridium(III), *fac*-7.** Mer-[Ir(tpy)(ppy)$_2$] (0.2 g, 0.3 mmol) was dissolved in spectrometric-grade MeCN (500 mL). The solution was stirred in the presence of a medium pressure 150 W mercury lamp for 4 days. Column chromatography, using dichloromethane as the eluent, yielded the desired product in quantitative yield as a bright yellow powder. ^{1}H NMR (300 MHz, d_6-DMSO): δ 1.97 (s, 3H, CH_3), 6.48 (s, 1H, CH), 6.60 (d, 1H, CH), 6.67−6.70 (m, 4H, CH's), 6.75−6.80 (m, 2H, CH's), 7.02−7.11 (m, 3H, CH's), 7.40−7.47 (m, 3H, CH's), 7.61 (d, 1H, CH), 7.70−7.80 (m, 5H, CH's), 8.04 (d, 1H, CH), 8.10 (2 × d, 2H, CH's). ^{13}C NMR (75 MHz, d_6-DMSO): δ 21.491, 118.7, 119.0, 119.1, 119.4, 119.5, 120.6, 120.7, 122.1, 122.1, 122.7, 122.9, 124.1, 124.2, 129.0, 129.0, 136.2, 136.3, 136.7, 136.8, 136.9, 137.9, 141.3, 143.7, 143.8, 146.6, 146.7, 146.8, 160.8, 160.85, 160.9, 165.58, 165.6, 165.61. *m*/*z* 669.03 g/mol. $C_{34}H_{26}IrN_3$ calcd.: C, 61.06; H, 3.92; N, 6.28. Found: C, 60.98; H, 4.06; N, 6.20.

***mer*-Ir(tpy)$_2$(ppy): *mer*-[bis(4-Methyl-(2-pyridinyl-κN)phenyl-κC^2)-mono((2-pyridinyl-κN)phenyl-κC^2)]iridium(III), *mer*-8-*homo-N-trans*.** Bis(4-methyl-(2-pyridinyl-κN)phenyl-κC^2)iridium-(III) chloride (0.405 g, 0.718 mmol) was placed in glycerol (10 mL). To this was added K_2CO_3 (1.0 g, 10 equiv, 7.2 mmol) and 2-phenylpyridine (0.45 mL, 4 equiv, 2.87 mmol). The resulting suspension was heated, under inert conditions, in an oil bath, to 150 °C for 24 h. This resulted in a dark brown solution. After the solution was cooled to room temperature, deionized water was added, and the mixture was vigorously mixed until a dark precipitate was observed. The dark precipitate was filtered and washed with water twice and subsequently with ethanol twice. The precipitate was then purified using column chromatography with dichloromethane as the eluent (yield 46%). The final product was bright orange in color and was a fine powder. ^{1}H NMR (300 MHz, d_6-DMSO): δ 2.02 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 6.08 (s, 1H, CH), 6.23 (s, 1H, CH), 6.62 (d, 1H, CH), 6.71 (2 × d, 2H, CH's), 6.80−6.90 (m, 4H,CH's), 7.10 (t, 1H, CH), 7.48 (d, 1H, CH), 7.60−7.70 (m, 4H, CH's), 7.77−7.84 (m, 3H, CH's), 7.91−7.99 (m, 3H, CH's), 8.14 (d, 1H, CH). ^{13}C NMR (75 MHz, d_6-DMSO): δ 21.7, 118.2, 118.6, 119.3, 120.2, 121.0, 121.4, 121.75, 122.2, 122.5, 124.1, 124.3, 124.5, 129.9, 131.3, 133.7, 134.3, 135.7, 136.7, 137.8, 139.6, 139.9, 140.0, 142.5, 145.7, 147.9, 151.4, 153.1, 159.9, 167.9, 168.5, 170.6, 175.4, 177.8. *m*/*z* 683.19 g/mol. Elem anal. for $C_{35}H_{28}IrN_3$, calcd.: C, 61.56; H, 4.13; N, 6.15. Found: C, 61.51; H, 4.12; N, 6.10.

***fac*-Ir(tpy)$_2$(ppy): *fac*-[bis(4-Methyl-(2-pyridinyl-κN)phenyl-κC^2)-mono((2-pyridinyl-κN)phenyl-κC^2)]iridium(III), *fac*-8.** *Mer*-[Ir(tpy)$_2$(ppy)] (0.1038 g, 0.15 mmol) was dissolved in spectrometric grade MeCN (600 mL). The solution was stirred in the presence of a medium-pressure 150 W mercury lamp for 4 days. Column chromatography, using dichloromethane as the eluent, yielded the desired product in quantitative yield as a bright yellow powder. ^{1}H NMR (300 MHz, d_6-DMSO): δ 1.95 (s, 3H, CH_3), 1.96 (s, 3H, CH_3), 6.45 (s, 1H, CH), 6.49 (s, 1H, CH), 6.59 (2x d, 2H, CH's), 6.67 (2 × d, 2H, CH's), 6.77 (m, 1H, CH), 7.02 (m, 2H, CH's), 7.07 (t, 1H, CH), 7.35−7.40 (m, 3H, CH's), 7.60 (2 × d, 2H, CH's), 7.74 (m, 4H, CH's), 8.02 (t, 2H, CH), 8.08 (d, 1H, CH). ^{13}C NMR (75 MHz, d_6-DMSO): δ 22.2, 22.4, 119.2, 119.3, 119.4, 119.7, 120.2, 121.5, 121.6, 122.8, 123.4, 124.7, 124.8, 124.9, 129.8, 137.0, 137.4 137.52, 137.55, 137.58, 137.60, 137.7, 138.5, 138.55, 138.60, 141.90, 141.93, 144.4, 147.2, 147.3, 147.4, 161.7, 161.8, 166.3, 166.4. *m*/*z* 683.19 g/mol. Elem anal. for $C_{35}H_{28}IrN_3$, calcd.: C, 61.56; H, 4.13; N, 6.15. Found: C, 61.47; H, 4.15; N, 6.11.

***mer*-Ir(ppy)$_2$OPh: *mer*-[bis((2-Pyridinyl-κN)phenyl-κC^2)-monophenoxo]iridium(III), 9.** Freshly distilled, degassed phenol (0.8532 g, 0.009 mol) was added to a thoroughly degassed THF (20 mL) solution with lump Na (0.2 g, 9 mmol). This was stirred at room temperature until all Na had reacted (H_2 evolution!). The system

was kept under N_2, and bis((2-pyridinyl-κN)phenyl-κC^2)iridium(III) chloride (0.2 g, 4 mmol) was added with continuous stirring. The resulting yellow solution was stirred at the same temperature for 24 h, after which it had become red. The solution was filtered to remove Na salts. The solvent was removed from the filtrate, and EtOH was added, precipitating a dark orange powder. Yield: 48%. ^{1}H NMR (300 MHz, d_6-DMSO): δ 5.22 (d, 2H, CH), 5.64, (d, 2H, CH), 6.01 (t, 1H, *OPh*CH), 6.17 (t, 2H, CH), 6.28 (t, 2H, CH), 6.64 (t, 2H, CH), 6.83 (t, 2H, CH), 7.68 (d, 2H, CH), 7.84 (t, 2H, CH), 8.23 (d, 2H, CH), 8.77 (d, 2H, CH). ^{13}C NMR (75 MHz, d_6-DMSO) δ = 113.0, 119.8, 120.7, 122.7, 123.1, 123.5, 124.4, 125.3, 127.6, 128.4, 129.3, 129.4, 138.0, 143.5, 145.3. Elem anal. $C_{28}H_{21}IrON_2$, calcd.: C, 56.65; H, 3.57; N, 4.72. Found: C, 56.79; H, 3.69; N, 4.75.

mer-Ir(ppy)$_2$OMe: *mer*-[bis((2-Pyridinyl-κN)phenyl-κC2)-monomethoxo]iridium(III), 10. Lump Na (0.23 g, 10 mmol) was added to dry, deoxygenated methanol (40 mL) and dry, degassed THF (10 mL). Once all of the Na had dissolved, bis(2-pyridinyl-κN)phenyl-κC2)iridium(III) chloride (0.38 g, 0.7 mmol) was added to the solution. The resulting mixture was stirred at reflux for 2 h, showing a color change from yellow to bright orange. After cooling, the precipitated bright red powder was filtered and recrystallized using a large volume of dichloromethane and hexanes. The final compound was highly insoluble in all organic solvents.

X-Ray Crystal Structure Determinations. Reflections were measured on a Nonius Kappa CCD diffractometer with rotating anode (graphite monochromator, $\lambda = 0.71073$ Å) up to a resolution of $(\sin\theta/\lambda)_{max} = 0.65$ Å^{-1}. The structures were solved with Direct Methods (SIR-97[18]) and refined with SHELXL-97[19] against the F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were introduced in calculated positions and refined with a riding model. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[20] Further details are given in Table 1.

***mer*-7-*homo*-N-*trans*.** The crystal structure contains large voids (1756 Å^3/unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the program PLATON,[20] resulting in 590 electrons/unit cell.

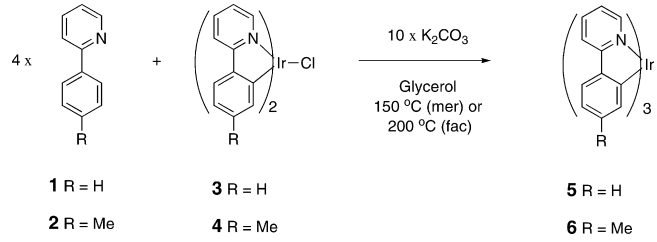
***mer*-8-*homo*-N-*trans*.** The crystal structure contains large voids (708 Å^3/unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the program PLATON,[20] resulting in 163 electrons/unit cell. Atoms N2 and C18 were constrained to the same coordinates and displacement parameters (occupancy 0.5).

Results and Discussion

1. Synthesis and Characterization of Heteroleptic Complexes [Ir(C,N)$_2$(C′,N′)]; *mer*-Isomers of 7 and 8. *All experiments in the following section were carried out in the absence of light.*

The synthesis of [Ir(C,N)$_2$Cl] complexes **3** and **4** was carried out according to literature procedures.[1c,d] Tris-cyclometallated complexes **5** and **6** were synthesized using reaction techniques developed by Thompson.[11] The *fac* isomer of **5** (from **1** and **3**) and **6** (from **2** and **4**) was synthesized when temperatures above 200 °C were used. At temperatures of approximately 150 °C, the *mer* isomer was formed (Scheme 1).

Scheme 1. The Thompson Method for the Synthesis of Homoleptic Tris-Cyclometallated Iridium(III) Complexes[11]



1 R = H
2 R = Me
3 R = H
4 R = Me
5 R = H
6 R = Me

Table 1. Details of the X-Ray Crystal Structure Determinations

	mer-**7**-*homo*-N-*trans*	*mer*-**8**-*homo*-N-*trans*
formula	$C_{34}H_{26}IrN_3$ + disordered solvent	$C_{35}H_{28}IrN_3$ + disordered solvent
fw	668.78[a]	682.80[a]
cryst color	yellow	yellow
cryst size [mm^3]	0.12 × 0.09 × 0.06	0.45 × 0.24 × 0.21
temp [K]	150	110
cryst syst	monoclinic	trigonal
space group	*C*2/*c* (no. 15)	$R\bar{3}c$ (no. 167)
a [Å]	25.0705(1)	20.02588(1)
b [Å]	35.7759(2)	20.02588(1)
c [Å]	17.6973(1)	36.14264(2)
β [deg]	133.3535(2)	
V [Å^3]	11541.81(11)	12552.593(11)
Z	16	18
Dx [g/cm^3]	1.539[a]	1.626[a]
μ [mm^{-1}]	4.653[a]	4.815[a]
abs. corr. method	multiscan	multiscan
abs. corr. range	0.65−0.75	0.07−0.37
reflns (meas./unique)	122103/13252	51277/3176
param/restraints	685/0	178/0
R1/wR2 [$I > 2\sigma(I)$]	0.0296/0.0685	0.0229/0.0496
R1/wR2 [all reflns.]	0.0453/0.0732	0.0299/0.0514
S	1.050	1.088
ρmin/max [e/Å^3]	−1.47/2.12	−0.77/1.62

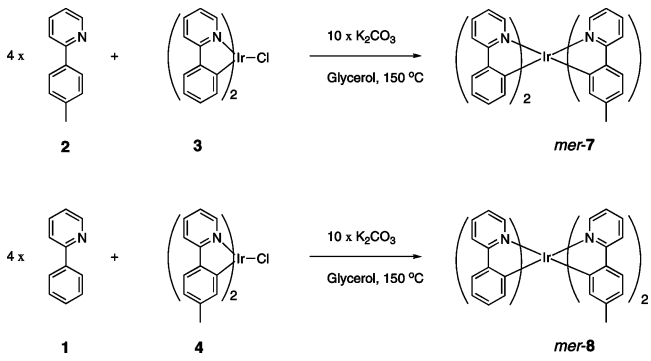
[a] Derived parameters do not contain the contribution of the disordered solvent.

The reaction of **2** with **3** (and likewise **1** with **4**) using Thompson conditions for the synthesis of *fac* isomers did not proceed cleanly (Figure S1, Supporting Information). ^{1}H NMR of the isolated products showed the presence of a mixture of several similar complexes. UV−vis absorption spectroscopy suggested that these were *fac*-type products. MALDI−TOF mass analysis, however, showed that scrambling of the ligands had occurred, and in fact, a mixture of four different complexes (*fac*-**5**−**8**) had been synthesized (Figure S1, Supporting Information). Separation of the individual complexes from this *fac*-**5**−**8** mixture was attempted but, in our hands, was not possible.

The reaction of **2** with **3** (and likewise **1** with **4**) using the Thompson reaction conditions for the synthesis of *mer* isomers, gave only one product, a *mer* isomer of **7** or **8**, respectively (Scheme 2). ^{1}H and ^{13}C NMR of the acquired *mer*-**7** and *mer*-**8** gave conclusive proof that the desired products were obtained. UV−vis absorption spectroscopy results corroborated that a *mer* isomer had indeed been synthesized and was isolated as a pure product (see the

(18) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115–119.
(19) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.
(20) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.

Scheme 2. Heteroleptic *mer* Complex Synthesis



Supporting Information for all UV−vis spectra: Figure S4 and Table S2). In homoligated complexes ([Ir(C,N)$_3$] **5** and **6**), the *mer* and *fac* isomers have dissimilar UV−vis absorption spectra, with the *mer* isomer showing one significant absorption at 272 nm, whereas the *fac* isomer shows three strong absorptions at 245, 283, and 376 nm. The synthesized heteroligated *mer* isomers, *mer*-**7** and *mer*-**8**, have a UV−vis absorption spectrum distinctly similar to those observed for the *mer* isomers of **5** and **6**.

2. Molecular Geometries of Acquired *mer*-7 and *mer*-8 in the Solid State. Single crystals of *mer*-**7**, suitable for X-ray diffraction, were acquired from slow evaporation of a dichloromethane solution. The crystal system was monoclinic with the centrosymmetric space group *C*2/*c* and two independent molecules in the asymmetric unit.[21] The molecular structure of both independent molecules confirmed that a *mer* isomer had indeed been isolated (Figure 1).[22] It is also noteworthy that the homoligands have retained their position relative to each other. The C$_2$-*trans*-(N) (the molecule is C$_2$ symmetrical with N's lying trans to each other) configured octahedral dimeric starting material **3** has two ppy ligands with nitrogens aligned trans to each other while the ortho carbons lie mutually cis to each other and trans to the bridging halides.[23] In the acquired *mer*-**7**, the carbons of the homoligands bound to iridium are now trans to the heteroligand. The N's of the homoligands lie trans to one another. Therefore, we call it *mer*-**7**-*homo*-N-*trans*[15] (there are two other geometrical isomers of *mer*-**7**, this is discussed in the following section).[24] It should be noted that 15% of the unit cell is filled with disordered solvent molecules (see Experimental Section). The small differences in the residues can be clearly seen in the fit diagram in Figure 1.

Single crystals suitable for X-ray analysis of *mer*-**8** were acquired by slow evaporation of an ethanol/dichloromethane solution. The system was trigonal with space group $R\bar{3}c$.[25] The molecular structure confirmed that a *mer* isomer had indeed been isolated (Figure 2, homoligand N's trans to each other).[26] The complex is assigned the name *mer*-**8**-*homo*-N-*trans* because the nitrogen atoms of the homoligands (tolpy) are arranged trans to each other.

3. Stereochemical Aspects of Heteroleptic [Ir(C,N)$_2$(C′,N′)] Complexes. The complexes *mer*-**7**- and *mer*-**8**-*homo*-N-*trans* are geometrical isomers under the general headings *mer*-**7** and *mer*-**8**, respectively. There are three possible geometrical isomers of both *mer*-**7** and *mer*-**8** which are depicted in Figure 3. The *homo*-N-*trans* isomer is the acquired product from the reaction of C$_2$-*trans* starting material **3**. Each of the depicted geometrical isomers also has two enantiomers/helimers, Λ and Δ. We have found no reports commenting on any other isomer than *homo*-N-*trans*-type isomers in bis-cyclometallated (C,N) iridium(III) complexes.

It is timely at this point to discuss why the formation of only the *mer-homo*-N-*trans* isomers is observed in the synthesis of *mer*-**7** and *mer*-**8**. Complexes of the type **3** or **4** are believed to be dimeric octahedral C$_2$-*trans*-N isomers (see the Supporting Information for detailed discussion). The molecular geometry of **4** in the solid state was previously reported showing a dimeric complex with C$_2$-*trans*-N geometry.[23] Previous reports point toward the likelihood that the dimer is in equilibrium with a monomer in a noncoordinating solution.[27] All of these observations point to only N-*trans*-type compounds, and absolutely no isomerization to other isomers is observed (for a detailed discussion on **3** and the intermediates in the synthesis of **3** and similar systems, see the Supporting Information).

The *trans-N* configuration of **3** holds when other ligands, either monodentate or bidentate monoanionic ones, are substituted for the halide, for example, cyanide[7c] and acac[27a] complexes. We have also observed that no C$_2$-*trans*-N to C$_1$ or C$_2$-*trans*-C (likewise tbp-*trans*-N to tbp-*cis*- or tbp-*trans*-C) isomerization of these complexes occurs even under relatively extreme conditions.[28] No ligand scrambling or the formation of non-homo-N-*trans* products was observed in the synthesis of *mer*-**7**-homo-N-*trans*, suggesting that homoligands remain bound, in the *trans*-N fashion, to the iridium center, throughout the reaction.

(21) See the Experimental Section.

(22) The three cyclometallating ligands are aligned in an octahedral configuration around the iridium centre. The C−C and C−N bond lengths and angles are within normal ranges expected for *mer*-tris-cyclometallated iridium(III) complexes. (a) Garces, F. O.; Dedeian, K.; Keder, N. L.; Watts, R. J *Acta Crystallogr.* **1993**, *C49*, 1117–1120. (b) See ref 11. The monoanionic heteroligand, 2-(4-methylphenyl)pyridine (tolpy), has longer Ir−N bond distances (2.142(5) and 2.136(3) Å, respectively) compared to those of the homoligands (2-(phenyl)pyridine, ppy) which have their nitrogens aligned trans to each other (2.047(3) and 2.032(3) Å, respectively, Supporting Information, Table S1). This can be explained by the different trans influence both on carbon and on nitrogen. However, subtle effects, for example, the role of the tolyl-CH$_3$ group, could also be influencing the Ir−N or Ir−C bond distances.

(23) (a) Schmid, B.; Garces, F. O.; Watts, R. J. *Inorg. Chem.* **1994**, *33*, 9–14. (b) Douglas, B. E.; Saito, Y. *ACS Symp. Ser.* **1980**, *119*, 338.

(24) Due to the centrosymmetry of the space group, the crystal is a racemic mixture of both Λ and Δ stereoisomers.

(25) See the Experimental Section.

(26) The three cyclometallating ligands are aligned in an octahedral configuration around the iridium center. As with the previous crystal structure, the C−C and C−N bond lengths and angles are within normal ranges expected for *mer*-tris-cyclometallated iridium(III) complexes.

(27) (a) Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzaq, F.; Kwong, R.; Tsyba, I.; Bortz, M.; Mui, B.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2001**, *40*, 1704–1711. (b) See ref 1c.

(28) This is related to the slow rate of isomerization of Ir(III), and the disfavor of such systems to undergo Berry pseudorotation. Deeming, A. J.; Proud, P. J.; Dawes, H. M.; Hursthouse, M. B.; *J. Chem. Soc., Dalton Trans.* **1986**, 2545−2549.

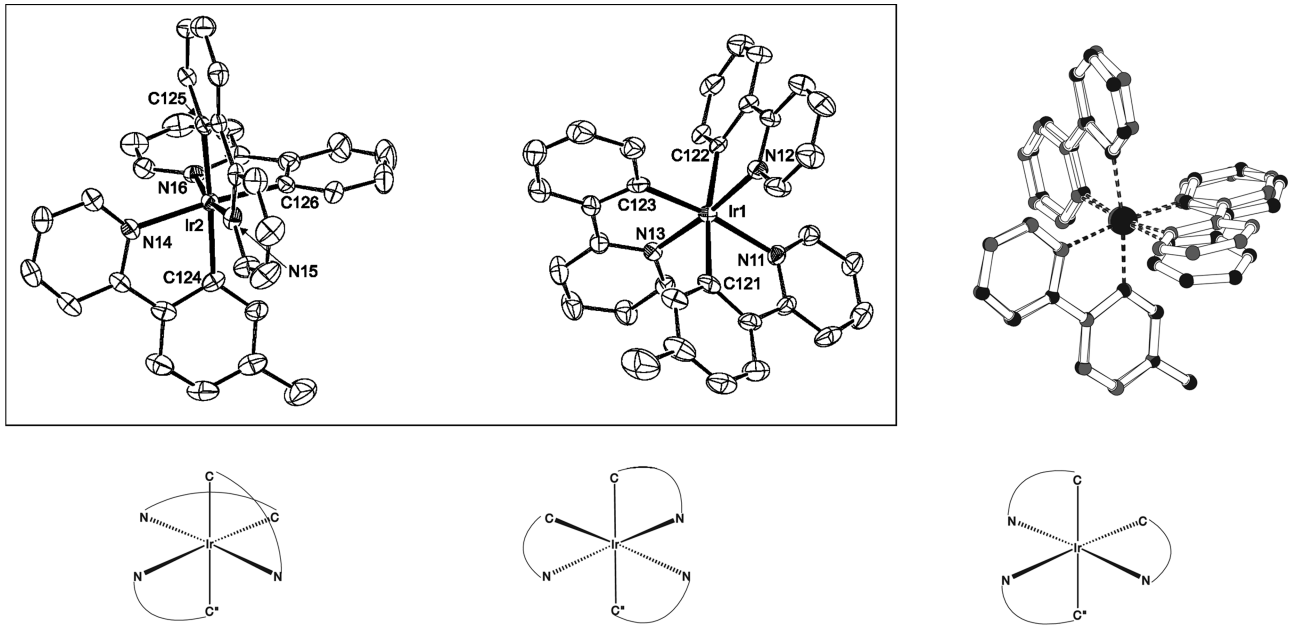


Figure 1. (left) Displacement ellipsoid plot (50% probability level) of the two independent molecules of *mer*-**7**-*homo*-N-*trans* in the crystal structure. View along the crystallographic *a*,*c* diagonal. Hydrogen atoms and disordered solvent molecules have been omitted for clarity. (right) Quaternion fit overlay plot of residue 1 and the inverted residue 2.

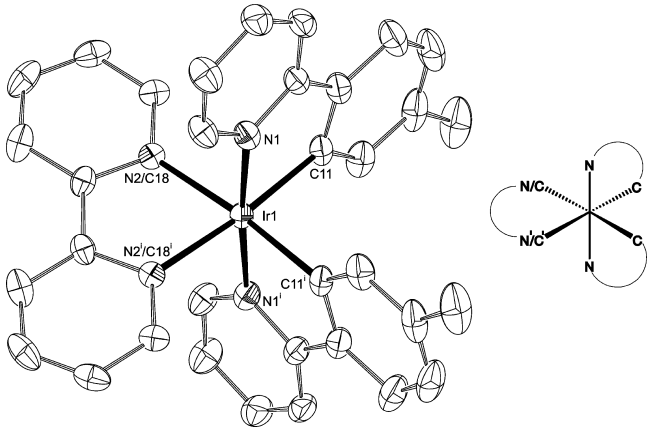


Figure 2. Displacement ellipsoid plot (50% probability level) of the *mer*-**8**-*homo*-N-*trans* isomer in the crystal. Hydrogen atoms and disordered solvent molecules have been omitted for clarity. Symmetry operation *i*: 1/3 + *x* − *y*, 2/3 − *y*, 1/6 − *z*.

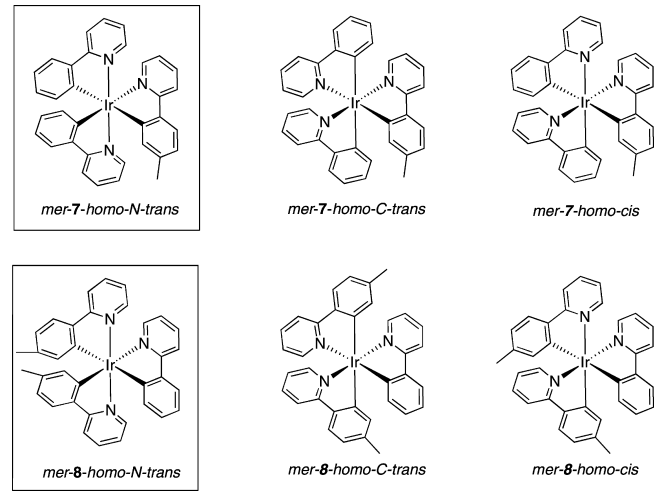


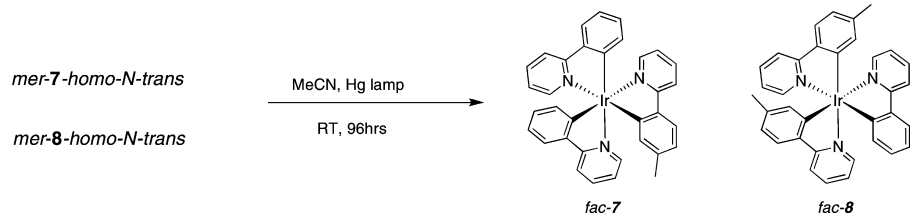
Figure 3. Geometrical isomers of *mer*-**7** and *mer*-**8** (the highlighted compounds are the synthesized species).

Because the homoligands remain *trans*-N in the synthesis of *mer*-**7**-homo-N-*trans*, we assume they play no role in the reaction, and their geometry never changes with respect to each other during the cyclometalation reaction. If there was any geometrical positional ligand exchange, different geometrical isomers would definitely be expected.[29]

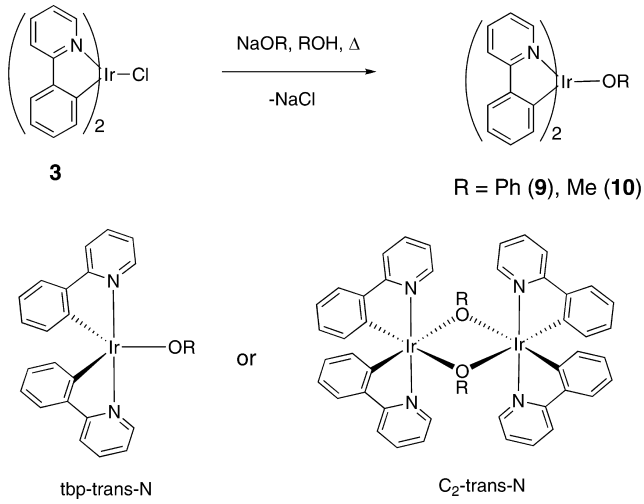
4. Synthesis and Characterization of Heteroleptic Complexes [Ir(C,N)$_2$(C′,N′)]; *fac*-Isomers of 7 and 8 Obtained by *mer*-to *fac*-Isomerization. *All experiments in the following section were carried out in the absence of natural light.*

The acquired complexes *mer*-**7**- and *mer*-**8**-homo-N-*trans* could be quantitatively converted to *fac*-**7** and *fac*-**8** photochemically, *without* scrambling of the ligands, by stirring the complexes in deoxygenated acetonitrile at room temperature over 4 days with a medium-pressure 150 W Hg UV lamp submersed in the reaction solution (Scheme 3). Similar synthetic techniques with analogous systems were published during the time this work was carried out.[30] The ^{1}H and ^{13}C NMR spectra of *fac*-**7** and -**8** showed a slight shift in the resonance ppm of all aromatic and tolyl C*H*'s in comparison with *mer*-**7**- and *mer*-**8**-homo-N-*trans*. UV absorption spectra showed three distinct absorptions at 245/247 nm, 285/286 nm, and 376/376 nm, respectively (see the Supporting Information, Figure S4), similar to that of *fac*-**5**/**6**. *Fac*-**7** and -**8** have only one geometrical isomer. They both have two enantiomers/helimers, Λ and Δ. The attained *fac*-**7** and -**8** are racemic mixtures. Crystals suitable for X-ray diffraction of *fac*-**8** were acquired. However, the CH_3 groups could not be localized on a specific ligand. Partially populated tolyl−CH_3 positions of all three ligands were observed (CIF file available in the Supporting Information).

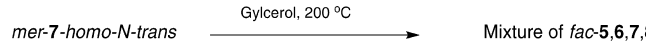
Scheme 3. Photochemical Conversion of *mer*-**7**- and *mer*-**8**-*homo-N-trans* to *fac*-**7** and *fac*-**8**



Scheme 4. Synthesis of Alkoxide Iridium Complexes and Possible Isomers of Alkoxide Complexes



Scheme 5. Attempted Thermodynamic Conversion of *mer*-**7**-*homo-N-trans* to *fac*-**7**



5. Synthesis and Characterization of Heteroleptic [Ir(C,N)$_2$(alkoxide)] Complexes. *All experiments in the following section were carried out in the absence of light.*

We believe iridium alkoxide complexes to be intermediates in the thermal *mer*-to-*fac*isomerization. To this date, all reports on thermal isomerization (also see later in this report) have been carried out in alcoholic solvents. We have therefore synthesized iridium alkoxide [Ir(C,N)$_2$OR] complexes and studied their reaction with cyclometallating ligands. Complex **3** was added to a solution of NaOPh in large excess. A color change was observed after heating, from yellow to dark orange. A single isomer of **9** was isolated after 24 h. We observed a symmetrical ^{1}H NMR spectrum (Scheme 4). Two isomers are possible for **9**: either a dimeric structure comprising octahedral hexacoordinate iridium centers in a C$_2$-*trans*-N configuration or a monomeric structure with a five-coordinate iridium center with both nitrogens trans to each other in the case of an ideal tbp structure (tbp-*trans*-N; see Scheme 4). In both structures, a symmetrical ^{1}H NMR spectrum is expected (11 aromatic H resonances, 8 ppy, and 3 phenolate) which indeed has been observed for **9**. The alternative dimeric asymmetrical C$_1$ complex would show a nonsymmetrical ^{1}H NMR spectrum, which is obviously not the case. Only the dimeric C$_2$-*cis* complex would also show a symmetrical ^{1}H NMR spectrum. However, we believe it unlikely that the C$_2$-*trans*-N complex **3** would yield a C$_2$-*cis* complex without any signs of a C_1 complex. Moreover, previous reports of the synthesis of the analogous hydroxyl and solvento- complexes stated that the complex was a dimeric C$_2$-*trans*-N isomer.[23a] Complex **10** was synthesized in a similar manner; however, it showed very low solubility in all organic solvents and thus was not characterized using NMR techniques.

Heating of complex **9** in phenolic solution at reflux showed no change in the constitution of the complex; the complex stayed in the C$_2$-*trans*-N/tbp-*trans*-N configuration. To study whether complexes **9** and **10** could be the starting point for the synthesis of tris-cyclometallated [Ir(C,N)$_3$] complexes, they were separately dissolved in 1,2-dichlorobenzene (*mer*−*fac* isomerization does not occur in this solvent, bp 180 °C) with 1 equiv of Hppy and heated to reflux (in darkness). After 24 h, the reactions were stopped. With both complexes **9** and **10**, ^{1}H NMR and UV−vis spectroscopy both showed the presence of [tris((2-pyridinyl-κN)phenyl-κC^2)]iridium(III) complex **5**. In the case of **9**, more than 50% was *fac*-**5**. Similarly, complexes **9** and **10** were reacted with Htolpy. The formation of tris-cyclometallated products was also observed, however, *with* scrambling of the ligands. These are the only examples of nonphotochemical *fac*-product formation in hydroxyl-free solvents. Obviously, 1 equiv of ROH is released during this reaction, which could then promote *mer*-to-*fac* isomerization of any formed *mer* species (see later in this report).

6. Investigation of Thermal *mer*-to-*fac* Isomerization. *All experiments in the following section were carried out in the absence of light.*

Earlier studies have shown that heating of *mer*-[Ir(ppy)$_3$] in glycerol at 200 °C for 24 h yields *fac*-[Ir(ppy)$_3$].[11] Heating of either *mer*-**7**- or -**8**-homo-N-*trans* in glycerol at 200 °C for 24 h did not yield pure *fac*-**7** or -**8**, respectively, but instead a mixture of complexes **5**−**8** (Scheme 5). UV−vis absorption suggested that *fac*-type isomers were present. MALDI−TOF mass analysis showed a similar pattern of the *fac*-**5**−**8** mixture, as is depicted in Figure S1, Supporting Information. This would indicate that scrambling of the ligands has occurred during isomerization.

A number of conditions of the thermodynamic *mer*-to-*fac* isomerization were investigated:

(a) To investigate intermolecular interactions, isomerizations under thermal conditions were carried out, while varying the dilution of *mer*-**7**-homo-N-*trans* in glycerol. At every dilution, *mer*-to-*fac* isomerization was observed with ligand scrambling. By ^{1}H NMR/MALDI−TOF, there was no

(29) Springer, C. S. *J. Am. Chem. Soc.* **1973**, *95*, 1459–1467.
(30) Dedeian, K.; Shi, J.; Shepherd, N.; Forsythe, E.; Morton, D. C. *Inorg. Chem.* **2005**, *44*, 4445–4447.

observable difference in the intensity of the various peaks corresponding to compounds **5**−**8** when using different dilutions. Therefore, the process of ligand scrambling is *not* concentration-dependent.

(b) Upon gradual heating of a solution of *mer*-**7**-homo-N-*trans* in glycerol, from 150 to 200 °C, no *mer*-to-*fac* isomerization occurred below 191 °C. Furthermore, ligand scrambling products **5**, **6**, and **8** were not observed below 191 °C.

(c) *mer*-to-*fac* isomerization was a faster process in the absence of a base. When a base (K_2CO_3) was present, the process was an order of magnitude slower. In both cases, ligand scrambling was observed.

(d) From experiments involving the heating of *fac*-**7** for 24 h in glycerol at either 150 °C or at 200 °C (with and without K_2CO_3 present), pure *fac*-**7** was recovered quantitatively. Neither *mer* products nor ligand scrambling products were observed in this set of experiments.

(e) A range of solvents was then tested. In refluxing decane (174 °C), *mer*-**7**-homo-N-*trans* did not dissolve or isomerize to *fac* product(s), nor was ligand scrambling observed. Moreover, with *mer*-**7**-homo-N-*trans* dissolved in refluxing 1,2-dichlorobenzene (180 °C) or benzonitrile (191 °C), respectively, *no* isomerization or ligand scrambling was observed, and the starting material was recovered (likewise, when *mer*-**5** is used in these experiments, no isomerization is observed). However, when glycerol (in excess) was added to the refluxing decane solution, isomerization with scrambling was observed. In neat 1-decanol at 200 °C, *mer*-**7**-homo-N-*trans*, was converted to the *fac*-**5**, **6**, **7**, and **8** mixture while decomposition was also observed. In refluxing phenol (184 °C), complete conversion to *fac* isomers, with ligand scrambling, was observed. Subsequently, it was found that, in noncrystalline (50 °C) phenol, *mer*-**7**-homo-N-*trans* was converted to the *fac*-**5**, **6**, **7**, and **8** mixture, however, over a substantially longer time period (compared to the reaction done in refluxing phenol). This is a very important point because it was often believed that a temperature above 150 °C was necessary to facilitate isomerization. In fact, a refluxing solution of 1,2-dichlorobenzene with *mer*-**5** and 10 mol% phenol (compared to *mer*-**5**) showed 40% *mer*-to-*fac* conversion in 24 h. Water, when added to a glycerolic or phenolic solution of *mer*-**7**-homo-N-*trans* and heated to reflux, had *no* effect on the rate of isomerization or on the extent of scrambling.

From the observations made with these solvent tests, we can deduce that, under thermal conditions, the isomerization of *mer* compounds to *fac* compounds is an alcohol-catalyzed reaction.

It was noted that the amounts of individual *fac* isomers in the *fac*-**5**, **6**, **7**, and **8** mixture did not vary considerably in all experiments that were performed. This indicates that conditions did not affect the extent of ligand scrambling and scrambling was a statistical phenomenon.[31]

For real-time analysis of the thermal isomerization process of homoleptic complexes, complex **6** was used because it was the easiest to monitor using ^{1}H NMR.[32] An NMR tube at 70 °C was loaded with *mer*-**6** and d_6-phenol, and spectra were taken at certain time increments. Figure 7 represents the disappearance of the *mer*-**6** complex versus formation of non-*mer*-**6** compounds.[33]

The conversion of *mer*-**6** (all C*H*$_3$'s nonequivalent) did not show a simple disappearance of its three tolyl peaks and a concomitant appearance of one tolyl peak for *fac*-**6** (all C*H*$_3$'s equivalent). In fact, several new and overlapping peaks were observed in the tolyl C*H*$_3$ region of the ^{1}H NMR spectrum during the course of the reaction (see Supporting Information, Figure S5). Two of the new peaks can be assigned as free Htolpy (2.34 ppm) and *fac*-**6** (2.26 ppm). Two other nonequivalent peaks at 2.10 and 2.08 ppm (upfield of all other peaks) are unidentifiable. The peak at 2.10 ppm appears rapidly upon the introduction of *mer*-**6** to the d_6-phenol solution. It then increases in intensity at a similar rate to the consumption of *mer*-**6** aromatic signals. After approximately 40 min, the slope of the plot changes, suggesting a change in the rate-determining process. When the reaction is complete, thus when all *mer*-**6** has been consumed, there are three signals observable in the d_6-phenol solution ^{1}H NMR spectrum. These belong to *fac*-**6** (2.26 ppm) and a small quantity of free Htolpy (2.34 ppm). We have been unable to identify the third peak at 2.08 ppm; however, we believe it may be unreacted intermediate(s). The presence of Htolpy suggests the loss of a ligand in the isomerization process and the formation of an [Ir(C,N)$_2$X] intermediate possibly represented by the peaks at 2.08 or 2.10 ppm. The conversion of *mer*-**6** is rapid until approximately 66% of it has been consumed (∼40 min). After that, there is a slower disappearance of *mer*-**6** until it is completely consumed. This would suggest that there is an equilibrium between *mer*-**6** and an intermediate complex which is not *fac*-**6**. *fac*-**6** is then formed from the intermediate and does not convert back. In fact, no report of a back conversion, of any similar *fac* complexes, has ever been made. We believe the change in slope of the plot is when *mer*-**6** and the intermediate(s) are in equilibrium. Extra heat allows the reaction rate to increase substantially.

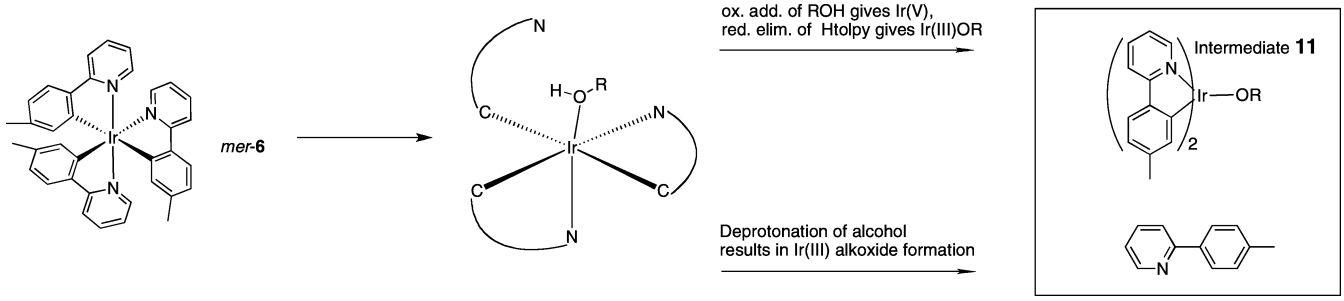
Because ligand scrambling is observed in heteroleptic systems, we assume an iridium−carbon bond breakage. We

(31) Crude tests were done on complexes **5**−**8** to test their response to the MALDI-TOF apparatus. All four complexes had very similar response factors. Figure S1 (Supporting Information) shows a distribution pattern of the thermal reaction of *mer*-**7**-homo-N-*trans* to a *fac*-**5**, **6**, **7**, and **8** mixture (all post-thermal isomerization spectra showed the same distribution pattern). Complex **7** was the most abundant, while only minute amounts of **5** were observed (max. 5%).

(32) We have attempted a wide range of experiments to elucidate the reaction rate and carry out some kinetic tests on the thermodynamic conversion of *mer*-**7** to *fac*-**5**, **6**, **7**, and **8**. ^{1}H or ^{13}C NMR spectroscopy was not possible due to overlapping of the marker signals (tolyl CH_3) of *fac*-**6**, **7**, and **8** and *mer*-**7**. UV−vis is not feasible here because all products have almost exactly the same absorption spectra. When it was attempted, no isosbestic point was observed, but this is due to slight differences in the molar absorptivities of the complexes. The products are not separable by GC or HPLC.

(33) The disappearance of *mer*-**6** was measured by integrating an aromatic peak belonging to *mer*-**6** and comparing it to the integration of all tolyl signals. This relies on the assumption that all *mer*-**6** is eventually converted to *fac*-**6**.

Scheme 6. Intermediate Formation from *mer*-**6** during Thermal Isomerisation in d_6-Phenol



propose that exchange of a N-donor pyridine ligand by alkoxide can occur by either dissociative or associative pathways (Scheme 6). We also propose that all Ir−C bonds remain intact during this exchange. Ligand substitution can now occur in one of two ways: (1) nucleophilic attack on the Ir(III) center, of the hydroxyl, resulting in a loss of Htolpy, and formation of an iridium(III) alkoxide species (**11**) and (2) oxidative addition of the coordinated alcohol, yielding an Ir(V) species. This species could then reductively eliminate Htolpy and result in an iridium(III) alkoxide species (**11**). The formation of an intermediate is substantiated by the fact that an equilibrium between *mer*-**6** and another complex(es) was observed. The observance of a free ligand further supports this theory. The subsequent reaction of the intermediate **11** with released Htolpy can either yield tris-cyclometallated *mer*-type complexes or yield thermodynamically stable *fac*-type complexes. We therefore observe a change in the reaction kinetic profile once the equilibrium has been reached.

If we closely examine how *mer*-**6** loses Htolpy, we can clarify the kinetic measurements further. *mer*-**6**, which has no geometrical isomers, can form different alkoxide intermediates, **11a**−**c**. Either a *trans*-N, *trans*-C, or cis isomer can form (Figure 4, depicted as tbp for clarity, most likely octahedral alkoxide bridged dimers). This observation explains why we see more than one newly formed peak in the tolyl CH_3 region of the ^{1}H NMR kinetic measurements. There are three possible isomers, which would all give contrasting ^{1}H NMR signals. We cannot explain why excess Htolpy and an unidentified compound (peak at 2.08 ppm) are present at the end of the isomerization reaction.

In the following discussion, the monodentate alkoxide

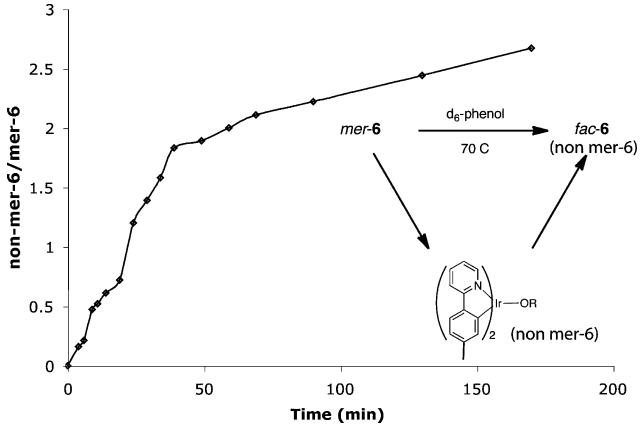


Figure 4. Conversion of *mer*-**6** over time at 70 °C in d_6-phenol.

intermediate complexes **11a**−**c**, when reacting with the formed Htolpy, are believed to behave the same as the monodentate chloride complex **3** in the synthesis of *mer*-**7**-homo-N-*trans*. That is, the remaining cyclometallated Ir-bound ligands of **11a**−**c** do not lose their configuration relative to each other (the *trans*-N, *trans*-C, or cis configuration is held) in the subsequent reaction. It must be noted that a trigonal bipyramidal (tbp) depiction of compounds **11** is for illustrative purposes only and certainly is not the true configuration. However, in terms of how the reaction proceeds, the tbp depiction is the best for illustrative purposes only. When **3** is reacted with Htolpy, the ppy ligands bound to the iridium *never* lose their configuration relative to each other. That is believed to be a result of a high energetic barrier to Berry pseudorotation. Compared to rhodium(III), hexa- and pentacoordinate iridium(III) complexes have an increased effective nuclear charge, and thus metal to ligand σ interactions are strengthened, and thus bond breakage and subsequent rotation is unlikely.[34] In this case, we believe, as a result of experimental evidence (Supporting Information and section 5), that Berry pseudorotation does not occur in these complexes.

In the reaction of **11a**−**c** with released Htolpy, only **11a** can give *fac*-**6**. Intermediates **11b** and **11c** will always revert to *mer*-**6**. The reaction of **11a** with Htolpy would yield either *mer*-**6** or *fac*-**6**. If the incoming Htolpy reacts with N trans to N (of metal-bound ligand), then *mer*-**6** will form. If Htolpy reacts with N trans to C (of metal-bound ligand), then *fac*-**6** will form. The reaction of **11b** with Htolpy will yield either Λ or Δ enantiomers/helimers of *mer*-**6**, nothing else. Likewise the reaction of **11c** with Htolpy will yield either Δ or Λ enantiomers/helimers of *mer*-**6**, nothing else. It must be noted that phenoxide and methoxide are monodentate ligands.[35]

From the observations we have made to this point, the photochemical *mer*-to-*fac* isomerization is completely unrelated to the thermal isomerization. In the photochemical isomerization, no ligand dissociation is believed to occur,

(34) Green, M.; Parker, G. J. *J. Chem. Soc., Dalton Trans.* **1974**, 333–343.

(35) All solvents or activating ligands previously used in the synthesis of *fac*-[Ir(ppy)$_3$] have been bidentate: glycerol, 2-ethoxyethanol, and acac. We believe that a monodentate intermediate state must exist at some stage during the reaction of intermediates of type **11**. We believe the bidentate solvents form intermediate complexes in a similar binding manner to acac. This leads to another variable as to where the attacking arylpyridine will bind in intermediate **11**, trans to a carbon or trans to a nitrogen. This could lead to preferences towards certain *fac*- or *mer*-products over others.

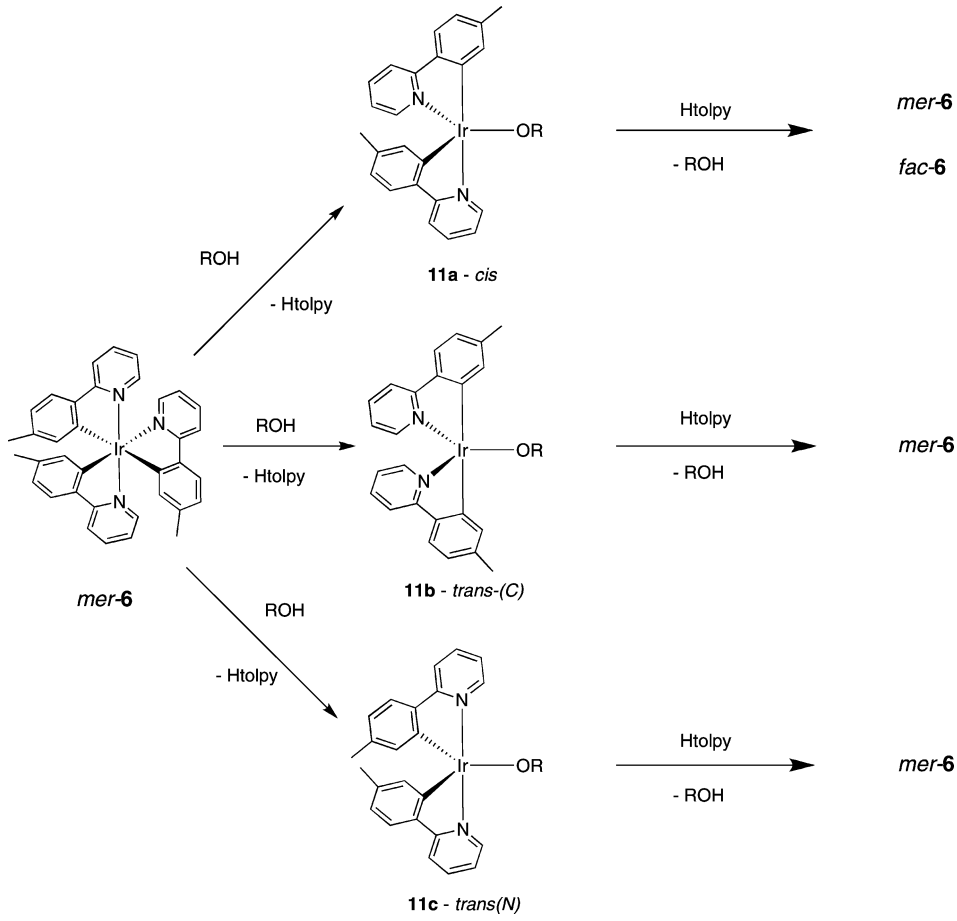


Figure 5. Ligand substitution on *mer*-**6** yielding alkoxide intermediates **11a**−**c** and their subsequent reaction with released Htolpy.

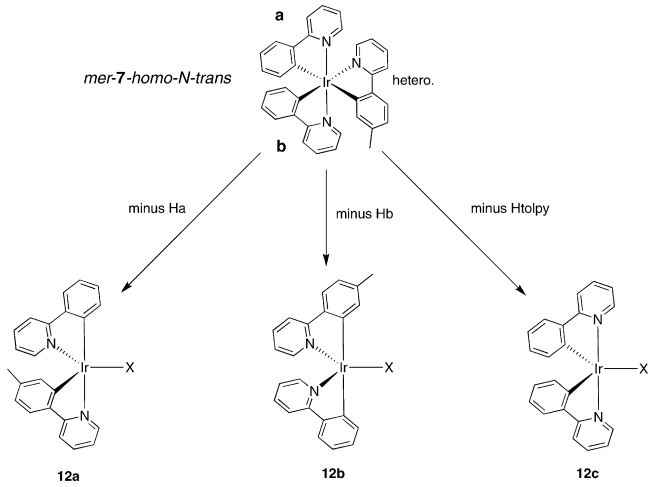


Figure 6. Substitution of ligand of *mer*-**7**-homo-N-*trans* and intermediates.

and the isomerization is mediated through an excited state.[36] *It must, once again, be noted that all experiments in the above section were carried out in the absence of light.*

7. Mechanism of Thermal *mer*-to-*fac* Isomerization of Heteroleptic [Ir(C,N)$_2$(C′,N′)] Complexes. When converting *mer*-**7**-homo-N-*trans* to *fac*-**7** under thermal conditions, it was noted that scrambling of the ligands occurred. When the reaction was carried out photochemically, no scrambling of the ligands was observed, as mentioned in the synthesis of pure *fac*-**7** and -**8**. If we now treat heteroleptic complexes *mer*-**7**- and -**8**-homo-N-*trans* as we have *mer*-**6** in the previous section, and focus on ligand substitution reactions and subsequent reaction of the formed alkoxide intermediates with a released ligand, we get a clear explanation for ligand scrambling. In both homo- and heteroleptic complexes, ligand substitution can be approached in two ways: (1) there is a higher probability for one of the ligands over the other two ligands to be substituted or (2) any of the three ligands can be substituted and further react with the formed intermediates. In the previous section, we saw that only the formation of only one of the intermediates (the cis isomer **11a**) resulted in the formation of the final product *fac*-**6**.

In *mer*-**7**-homo-N-*trans*, each ligand must be treated separately, because they are all bound differently to the iridium center (Figure 5).

Figure 5 depicts the isomers (**12a**−**c**) that can form as a result of substitution of the ligands only in *mer*-**7**-homo-N-*trans*. If ligand **a** is substituted, an intermediate, cis-configured complex, will be formed. If only ligand **a** was substituted, then the only products possible, as a result of reaction of **12a** with only **a** (Hppy), would be *mer*-**7**-homo-N-*trans* and *fac*-**7**. If **b** dissociates, a *trans*-C intermediate is formed. If only ligand **b** was substituted and **12b** had to

(36) (a) See ref 10. (b) Karatsu, T.; Ito, E.; Yagai, S.; Kitamura, A. *Chem. Phys. Lett.* **2006**, *424*, 353–357.

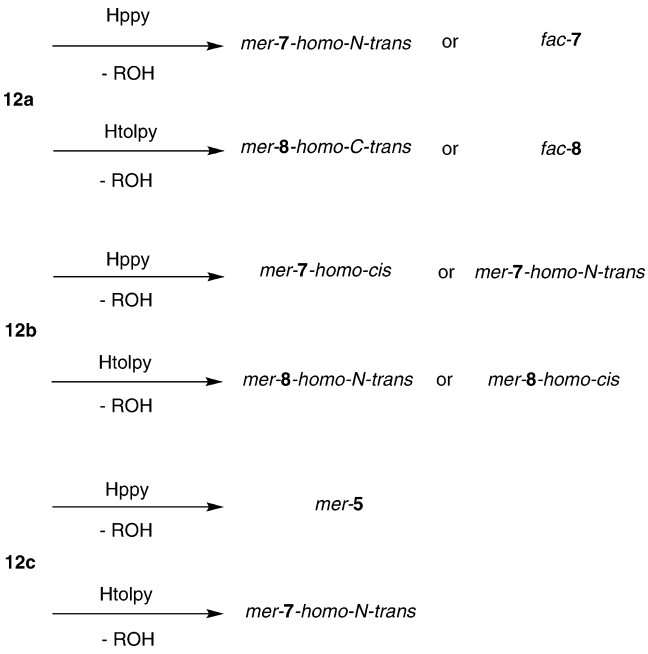


Figure 7. Products from the reaction of Hppy and Htolpy with intermediates **12a**−**c**.

rereact with only **b** (Hppy), *mer*-**7**-homo-N-*cis* or -*trans* would be formed. If the tolpy (heteroligand) were substituted by an alkoxide, a *trans*-N isomer would be formed (**9**). Hypothesizing that only the substituted Htolpy ligand could rereact with **12c** would lead to only different enantiomers/helimers of *mer*-**7**-homo-N-*trans*.

Because ligand scrambling was observed, this suggests that not one single ligand is substituted, and that all ligands can be substituted and react further. It could be that there is a preference for one ligand to be substituted over another; however, we cannot prove this experimentally.

We can now explain why we see *fac* complexes **5**-**8** after the reaction of *mer*-**7**- and *mer*-**8**-homo-N-*trans* under thermal isomerization conditions. Figure 6 only shows half of the possible complexes that can form. The newly formed *mer*-**8**-homo-N-*trans*, *mer*-**7**-homo-*cis*, *mer*-**8**-homo-*cis*, and *mer*-**5** can all react further to give a range of *mer* and *fac* isomers of **5**−**8**. Once a *fac* has formed, it will not rereact.

Conclusions

A number of heteroleptic tris-cyclometallated iridium(III) $[Ir(C,N)_2(C',N')]$ complexes have been synthesized and fully characterized using a range of techniques. The *mer*-homo-N-*trans* isomer of heteroleptic complexes **7** and **8** was synthesized and converted to the *fac* isomer using photochemical techniques. The synthesized *mer*- and *fac*-**7** and -**8** have been fully characterized. The synthesis of *mer* heteroleptic isomers followed by conversion to their *fac* isomer demonstrates a high-yielding, simple protocol for the synthesis of tethered tris-cyclometallated iridum(III) complexes. This is essential for materials science, which requires covalent linkage of lumiphore materials (iridium organometallics) to hole transport and electron transport layers in LEDs.

Under thermal reaction conditions, the conversion of the *mer*-homo-N-*trans* isomers to the *fac* complexes led to ligand scrambling. Phenol was found to be an ideal solvent to facilitate thermal *mer* to *fac* isomerization. It was found that, under conditions where isomerization does not occur, the addition of 10 mol% of phenol facilitated *mer*-to-*fac* isomerization. Bis-cyclometallated iridium(III) alkoxides are proposed intermediates in the *mer*-to-*fac* isomerization of $[Ir(ppy)_3]$-type systems. Analogous *trans*-N configured bis-cyclometallated iridium(III) alkoxide complexes were synthesized and characterized. Furthermore, the reaction of these complexes with Hppy-yielding complex **5** shows that Ir(III) alkoxide species are viable intermediates.

A proposed mechanism of the thermodynamic isomerization reaction was presented, which gives an explanation as to why ligand scrambling is observed. Kinetic examination of the *mer*-to-*fac* isomerization of homoleptic trisphenylpyridine iridium(III) complexes supports the proposed mechanism. The kinetic analysis supported the theory that an iridium(III) alkoxide intermediate is formed. A detailed discussion on possible geometrical isomers of intermediates in both the homo- and heteroleptic systems is presented.

This report is essential to the field of OLED devices for three reasons. First, it demonstrates the synthesis of heteroleptic $[Ir(C,N)_2(C',N')]$ complexes, which are desired for the covalent tethering of these organometallics to polymeric supports. Second, the synthesis of heteroleptic $[Ir(C,N)_2(C',N')]$ complexes opens up the field of electronic fine-tuning of ligands for mixed ligand species. To this point, all complexes developed were tris-cyclometallated homoleptic species, and thus relatively subtle changes in electron densities around the iridium(III) center were not possible. With heteroleptic $[Ir(C,N)_2(C',N')]$ systems, subtle electronic changes can be introduced to provide, for example, emission color changes on demand, while retaining the high quantum yield values these complexes are renowned for. Third, and most importantly, it is the first thorough investigation of *mer* and *fac* heteroleptic octahedral organometallic species. It gives essential insights into how *fac*-tris-cyclometallated iridium(III) species can be synthesized, and the energetic barriers to their synthesis. Furthermore, it gives an explanation of the properties of solvents/materials required for the synthesis of cyclometallated iridium(III) species, and also suggestions for synthesizing these complexes at lower temperatures.

Acknowledgment. Ciba (Basel, CH) is thanked for the provision of $[IrCl_3 \cdot 3H_2O]$ and for financial assistance. Dr. Paul van der Schaaf and Dr. Roger Pretot are acknowledged for their helpful suggestions.

Supporting Information Available: Crystallographic information files (CIF) for *mer*-**7**- and -**8**-homo-N-*trans* and *fac*-**8**, UV−vis absorption and emission data for all synthesized compounds, ^1H NMR spectral data for the kinetic measurements in Figure 7. This material is available free of charge via the Internet at http://pubs.acs.org.

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