Electronic Supporting Information

Atropisomerism in a Thermally Switchable, Cyclometallated Iridium Complex

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Experimental Section

All experiments were performed under an inert nitrogen atmosphere, using standard Schlenk-line techniques. Toluene was dried over activated alumina with a copper catalyst. All other solvents and reagents were obtained from commercial sources and used as received. Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. Chloro(1-phenylpyrazole)iridium(III) dimer $[IrCl(ppz)_2]_2$,[1] 1-nitropyrene,[2] and 1-aminopyrene[3] were prepared according to literature procedures. ^{1}H NMR and ^{13}C NMR spectra were obtained using a Bruker AV-300 or AV-400 spectrometer and referenced to the residual protonated solvent peak. Electrospray ionization mass spectrometry data were obtained on a Bruker Esquire LC ion trap mass spectrometer. Microwave reactions were performed on a Biotage Initiator 2.5 microwave synthesizer. X-ray crystallographic analyses were performed by Dr. Brian Patrick using a Bruker X8 Apex CCD diffractometer.

Synthesis of $[Ir(NN_{Me}Pyr)(ppz)_2][PF_6]$ (1a/b)

$[IrCl(ppz)_2]_2$ (0.070 g, 0.068 mmol), 2-acetylpyridine (0.017 mL, 0.15 mmol), 1-aminopyrene (0.0326 g, 0.150 mmol) and potassium hexafluorophosphate (0.025 g, 0.14 mmol) were placed in a microwave vial with 3.5 mL of ethanol. The suspension was degassed with nitrogen for 4 minutes. The vial was placed in the microwave reactor and heated under

microwave irradiation for 30 minutes at 100 °C (18 bar, 155 W). The solvent was then removed *in vacuo* and the solid residue dissolved in 10 mL CH_2Cl_2. The resulting deep red solution was passed through a Celite pad and the filtrate reduced in volume. Layering with hexanes yielded the desired product as a mixture of diasteromers. The mixture was purified by column chromatography using MeCN to elute any unreacted 1-aminopyrene and then MeCN:H_2O:$KNO_{3(aq)}$ (96:3:1) to elute the diastereomers (0.041 g, yield 76%). Diastereomer **1a** was separated by precipitation from methanol. **1a** and **1b** were each dissolved in DCM and layered with hexanes to yield red crystals suitable for X-ray crystallographic analysis. **1a:** ^{1}H NMR (CD_3CN, 400MHz, proton numbering is the same as in the X-ray structure): δ 8.45 (1H, d, J = 8.0, H_4), 8.41 (1H, d, J = 3.0, H_{35}), 8.27 (1H, d, J = 7.0, H_3), 8.24-8.23 (1H, m, H_9), 8.17 (1H, d, J = 8.0, H_{21}), 8.13 (1H, d, J = 2.5, H_{33}), 8.06-8.05 (1H, m, H_1), 7.76 (1H, d, J = 3.0, H_{26}), 7.70-7.68 (1H, m, H_2), 7.65 (1H, d, J = 9.5, H_{15}), 8.18-7.64 (5H, m, $H_{10,19,20,22,23}$),7.45 (1H, d, J = 7.5, H_{37}), 7.40 (1H, d, J = 2.5, H_{24}), 7.03-7.01 (1H, m, H_{38}), 6.82-6.80 (1H, m, H_{39}), 6.78 (1H, s, H_{34}), 6.72 (1H, t, J = 2.5, H_{25}), 6.65 (1H, d, J = 9.5, H_{14}), 6.24-6.22 (1H, m, H_{30}), 6.19-6.17 (1H, m, H_{28}), 6.15-6.13 (1H, m, H_{40}), 6.12-6.10 (1H, m, H_{29}),5.92-5.90 (1H, m, H_{31}), 2.54 (3H, s, H_{7abc}). ^{13}C NMR (CD_3CN, 100 MHz): 153.0 (C_3), 141.6 (C_{33}), 140.9 (C_9), 140.5 (C_{24}), 134.5 (C_{31}), 133.9 (C_{40}), 131.4 (C_2), 130.7 (C_4), 129.9 (C_{35}), 129.3-127.9 (overlap 4 × C_{Pyr}), 128.9 (C_{15}), 128.7 (C_{Pyr}), 127.8 (C_{39}), 126.6 (C_{21}), 126.2 (C_{30}), 126.0 (C_{Pyr}), 124.5 (C_{38}), 122.8 (C_{29}), 121.4 (C_{26}), 121.0 (C_{14}), 113.5 (C_{37}), 111.0 (C_{28}), 109.8 (C_{34}), 109.3 (C_{25}), 19.2 (C_7). HR ESI MS: Calcd for $C_{41}H_{30}N_6Ir$: 797.2138; Found: 797.2152 $[M]^+$.

1b: ^{1}H NMR (CD_3CN, 400MHz): δ 8.46 (1H, d, J = 8.0, H_4), 8.40 (1H, d, J = 2.5, H_{26}), 8.34 (1H, dd, J = 9.5, 3.0, H_{35}), 8.30-8.28 (1H, m, H_3), 8.26-8.23 (1H, m, H_1), 8.15-8.13 (1H, m, H_{14}), 8.09-8.08 (1H, m, H_{33}), 7.93 (1H, d, J = 9.0, H_{15}), 7.72-7.69 (1H, m, H_{10}), 7.66-7.64 (1H, m, H_2),

8.30-7.59 (5H, m, $H_{19,20,21,22,23}$),7.41 (1H, d, J = 8.0, H_{37}), 7.35-7.34 (1H, m, H_{24}), 7.02-6.99 (1H, m, H_{38}), 6.94-6.91 (1H, m, H_{28}), 6.82 (1H, m, H_{25}), 6.79-6.77 (1H, m, H_{39}), 6.69 (1H, d, J = 1.0, H_{34}), 6.23 (1H, td, J = 7.5, 1.5, H_{29}), 6.11 (1H, d, J = 7.5, H_{40}), 6.04 (1H, d, J = 7.0, H_9), 5.73 (1H, t, J = 8.0, H_{30}),5.52 (1H, d, J = 7.5, H_{31}), 2.60 (3H, s, H_{7abc}). ^{13}C NMR (CD_3CN, 100 MHz): 153.4 (C_{14}), 143.2 (overlap 4 × C_{Pyr}), 140.9 (C_{24}), 140.7 (C_3), 134.3 (C_9), 133.7 (C_{40}), 133.2 (C_{31}), 132.6 (C_{Pyr}), 131.2 (C_2), 131.0 (C_4), 130.3 (C_{26}), 130.1 (C_{33}), 129.7 (C_{10}), 128.9 (C_{35}), 128.0 (C_{15}), 127.8 (C_{25}), 127.2 (C_1), 126.8 (C_{39}), 126.0 (C_{30}), 124.7 (C_{38}), 124.5 (C_{28}), 123.3 (C_{29}), 113.5 (C_{37}), 109.1 (C_{34}), 19.7 (C_7). HR ESI-MS: Calcd for $C_{41}H_{30}N_6Ir$: 797.2138; Found: 797.2134 $[M]^+$.

Synthesis of [Ir(NN$_H$Pyr)(ppz)$_2$][PF$_6$] (2)

$[IrCl(ppz)_2]_2$ (0.070 g, 0.068 mmol), 2-pyridinecarboxaldehyde (0.014 mL, 0.15 mmol), 1-aminopyrene (0.0326 g, 0.150 mmol) and potassium hexafluorophosphate (0.025 g, 0.14 mmol) were placed in a microwave vial with 3.5 mL of ethanol. The suspension was degassed with nitrogen for 4 minutes. The vial was placed in the microwave reactor and heated under microwave irradiation for 30 minutes at 100 °C (18 bar, 155W). The solvent was then removed *in vacuo* and the solid residue dissolved in 10 mL CH_2Cl_2. The resulting deep red solution was passed through a Celite pad and the filtrate reduced to approximately 2 mL in volume. Layering with hexanes yielded the desired product as a dark orange precipitate. The product was purified by column chromatography using MeCN to elute any unreacted 1-aminopyrene and then MeCN:H_2O:$KNO_{3(aq)}$ (96:3:1) to elute complex **2** (0.021 g, yield 40%). ^{1}H NMR (CD_3CN, 400 MHz): δ 9.42 (1H, s, H_6), 8.43 (1H, d, J = 3.0, H_{35}), 8.39 (1H, d, J = 8.0, H_4), 8.26 (1H, t, J = 7.5, H_3), 8.21 (1H, d, J = 8.0, H_1), 8.28-8.01 (8H, m, $H_{9,10,19,20,21,22,23,33}$), 7.90 (1H, s br., H_{26}), 7.77 (1H, s br., H_{15}), 7.70-7.66 (1H, m, H_2), 7.47 (1H, d, J = 8.0, H_{24}), 7.45 (1H, s br., H_{37}), 7.08-7.03

(1H, m, H_{38}), 6.92 (1H, s br., H_{14}), 6.86 (1H, t, J = 7.5, 7.5, H_{39}), 6.77 (1H, s, H_{34}), 6.74 (1H, s, H_{25}), 6.54 (1H, s br., H_{28}), 6.32 (2H, s br., $H_{29,30}$), 6.22 (1H, d, J = 7.5, H_{40}), 6.01 (1H, s br., H_{31}). ^{13}C NMR (CD_3CN, 100 MHz): 152.1 (C_{Pyr}), 140.6 (C_{Pyr}), 140.2 (C_1), 139.8 (C_{37}), 133.3 (C_{31}), 132.7 (C_{40}), 131.3 (C_4), 130.5 (C_2), 130.3 (C_{15}), 128.5 (C_{35}), 128.4 (C_{33}), 127.4-136.9 (overlap 4 × C_{Pyr}), 126.6 (C_{39}), 125.7 (C_{30}), 125.5 (C_{Pyr}), 124.4 (C_{26}), 123.9 (C_{38}), 123.3 (C_6), 122.3 (C_{29}), 111.9 (C_{24}), 110.7 (C_{28}), 109.0 (C_{25}), 108.5 (C_{34}), 108.1 (C_{14}). HR ESI-MS: Calcd for $C_{40}H_{28}N_6Ir$: 783.1981; Found: 783.1975 $[M]^+$.

Synthesis of $NN_{Me}Pyr$ (3)

2-Acetylpyridine (0.026 mL, 0.23 mmol) and 2 drops of formic acid catalyst were added to a solution of 1-aminopyrene (0.100 g, 0.460 mmol) in 5 mL of degassed benzene. The yellow-brown solution was heated to reflux under nitrogen for 18 hours and then allowed to cool to room temperature. Benzene was removed *in vacuo* to give a red-yellow oil. The product was recrystallized from hot hexanes to yield yellow crystals (0.042 g, yield 57%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.67 (1H, d, J = 4.8, H_4), 8.19 (1H, d, J = 7.5, H_9), 8.13 (1H, d, J = 7.5, H_1), 8.07-7.82 (7H, m, $H_{10,15,19,20,21,22,23}$), 7.78 (1H, td, H_3), 7.44-7.41 (2H, m, $H_{2,14}$), 2.75 (3H, s, H_7).^{13}C NMR (CD_3CN, 100 MHz): 169.2 (C_4), 157.0 (C_3), 147.7-140.1 ($C_{10,15,19,20,21,22,23}$), 147.3 (C_2), 147.1 (C_1), 144.7 (C_9), 133.5 (C_{14}), 45.1 (C_7). HR ESI-MS: Calcd for $C_{23}H_{17}N_2$: 321.1392; Found: 321.1392 $[M+H]^+$.

Synthesis of NN_HPyr (4)

2-Pyridinecarboxaldehyde (0.088 mL, 0.92 mmol) was added to a solution of 1-aminopyrene (0.200 g, 0.921 mmol) in 20 mL of toluene. The yellow solution was heated to reflux under nitrogen for 18 hours and then allowed to cool to room temperature. The solution was dried over $MgSO_4$. Toluene was removed *in vacuo* to give an orange-yellow oil. The product was

recrystallized from hot hexanes to yield orange needle crystals (0.244 g, yield 86%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.91 (1H, s, H_6), 8.81-8.78 (1H, m, H_4), 8.74 (1H, d, J = 9.5, H_9), 8.54 (1H, d, J = 8.0, H_1), 8.24-8.00 (7H, $H_{10,15,19,20,21,22,23}$), 7.94 (1H, td, J = 7.5, 7.5, 1.5, H_3), 7.86 (1H, d, J = 8.0, H_{14}), 7.45 (1H, ddd, J = 7.5, 5.0, 1.5, H_2).^{13}C NMR (CD_3CN, 100 MHz): 150.4 (C_4), 137.0 (C_3), 127.6-125.2 ($C_{10,15,19,20,21,22,23}$), 125.5 (C_2), 123.3 (C_9), 122.1 (C_1), 115.3 (C_{14}), 110.8 (C_6). HR ESI-MS: Calcd for $C_{22}H_{15}N_2$: 307.1235; Found: 307.1230 $[M+H]^+$.

NMR Assignments

In all cases, the TOCSY spectra show correlations between protons in a given ring system. This aids in assigning the signals for the phenyl, pyrazole and pyridine protons. Correlations between all nine protons in the pyrene ring system are weak and therefore not readily observed in these spectra. In addition to the TOCSY data, there are a few diagnostic signals in the NOESY spectra which help to confirm these assignments (see main text). Other notable differences in the spectra include the upfield shift of phenyl H_{26} in **1a** compared to **1b** (7.76 - 7.77 ppm vs. 8.40 – 8.41 ppm). In **1a**, H_{26} lies over the pyrene ring system and is therefore affected by ring current, whereas in **1b** H_{26} is on the opposite side of the complex to the pyrene.

Rotational Energy Barrier

The experimental energy barrier to rotation was calculated by constructing an Eyring plot (Figure S1). First-order reaction kinetics were observed and rate constants were obtained from the slope of a plot of $\ln[1b_t-1b_e]$ vs. time at different temperatures, where $1b_t$ = concentration of **1b** at time t and $1b_e$ = concentration of **1b** at equilibrium (Figure S2).

Slope from Eyring plot = $-\Delta H/R$

$-\Delta H = -12099 \pm 1166.5 \times 8.314 = 100.6 \pm 9.8 kJ/mol$

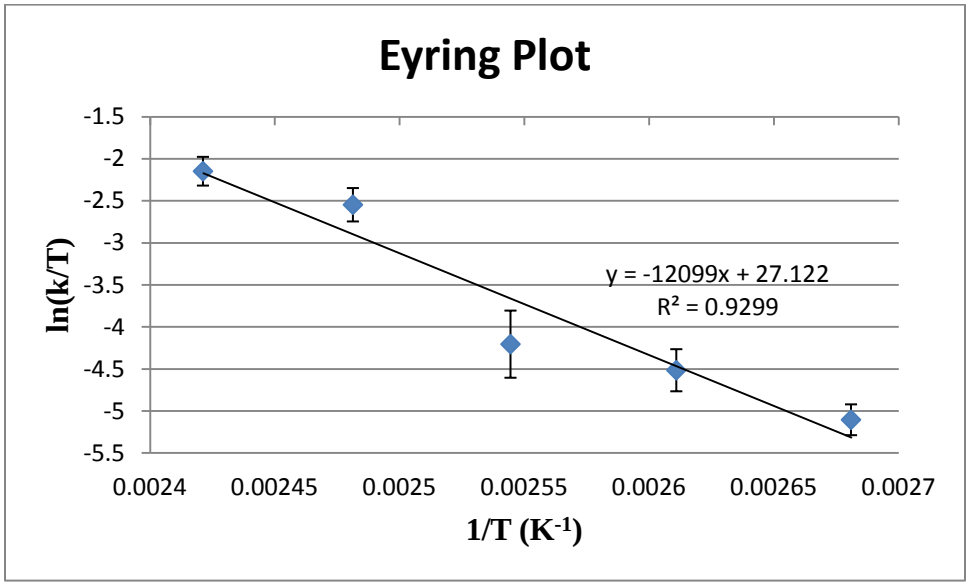

Figure S1. Eyring plot for reaction kinetics of **1b→1a** from 100°C - 140°C.

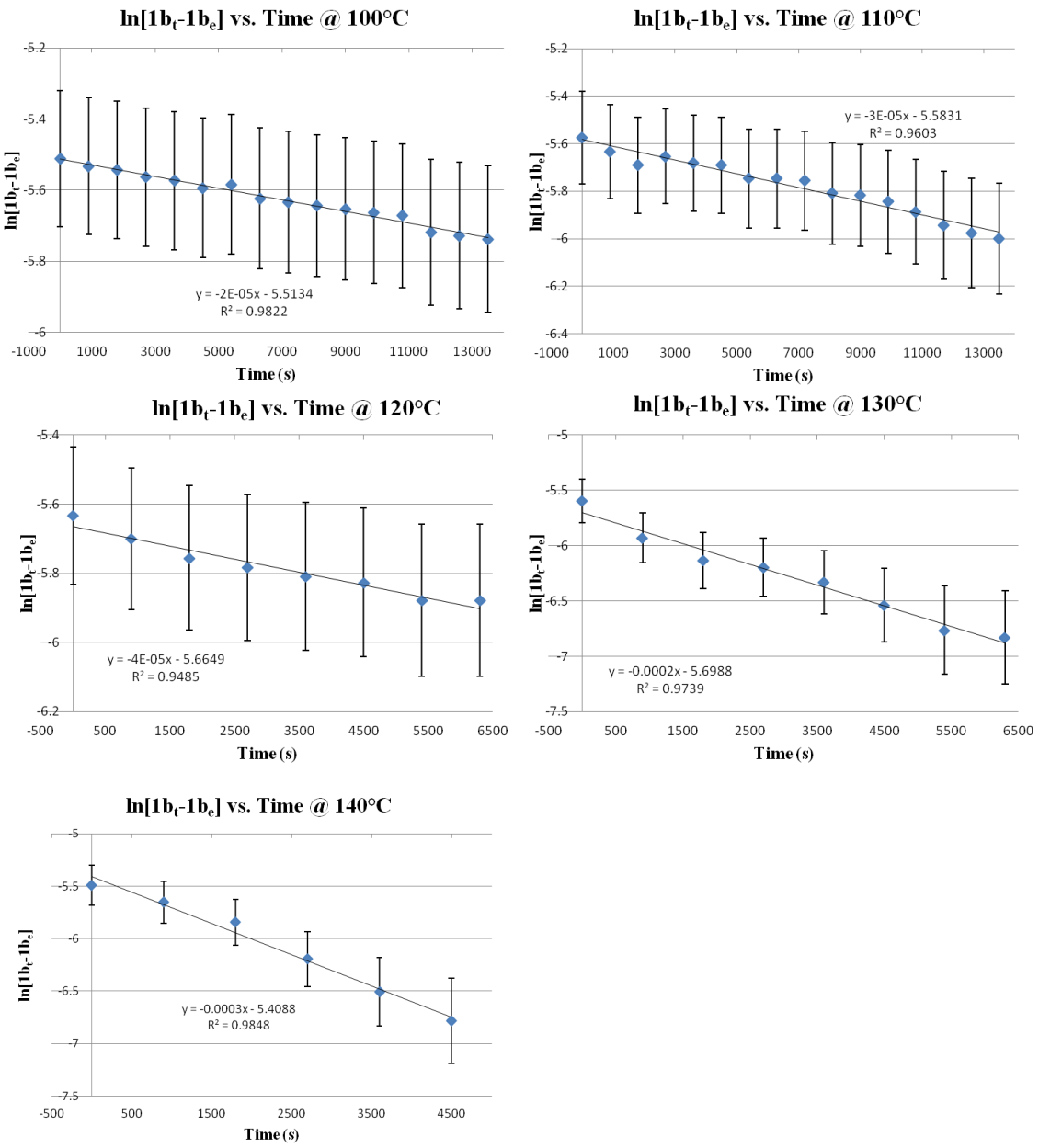

Figure S2. ln[$1b_t$-$1b_e$] vs. time plots for **1b→1a** from 100°C to 140°C.

DFT Calculations

DFT computations were applied by using the recent meta-hybrid xc functional known as M06[4] as implemented in the Gaussian09 suite of programs.[5] Geometry optimizations were performed using the Dunning/Huzinaga double-ζ (D95) basis sets,[6] adding a set of polarization functions to

the same basis set in case of C**,** and N atoms. The most recent Stuttgart/Dresden ECP basis set including f polarization function and pseudopotential for small core taking into account relativistic effects were used for Ir.[7] Default gradient and displacement thresholds were used for the geometry optimization convergence criteria. The dichloromethane (DCM) solvent environment were modeled according to the IEPCM[8] model. To confirm that the obtained geometries are relative minima or transition states (TS) of the molecular energy, analytical computation of the Hessian matrix with respect to the nuclear coordinates at the same level of theory was performed. The program GaussView 5.0.8 [9] were used to draw chemical structures and generate movies of the normal mode of vibration corresponding to the transition vector (TV), i.e., the normal mode associated with the imaginary frequency.

Table S1. Computed bond lengths (Å), torsion angles (°) and energies for **1a/b**.

	^C_9-C_6	d(N_2-Ir)	^C_9-Ir	E(a.u)	ΔE(a.u.)	ΔE(kJ/mol)
TS2	167.61	2.4518	42.79	-2012.148542	0.05334	140.0
1a	114.22	2.1640	-71.84	-2012.201826	5.61E-05	0.1
TS(**1a'**,**1a**)	111.22	2.1623	-74.02	-2012.20177	0.000112	0.3
1a'	98.59	2.1614	-83.57	-2012.201882	0	0.0
TS1	17.69	2.6567	159.41	-2012.159204	0.042678	112.1
1b'	-68.60	2.1753	94.16	-2012.200481	0.001401	3.7
TS(**1b**,**1b'**)	-98.97	2.1805	72.94	-2012.197835	0.004047	10.6
1b	-110.32	2.1871	66.40	-2012.198276	0.003606	9.5

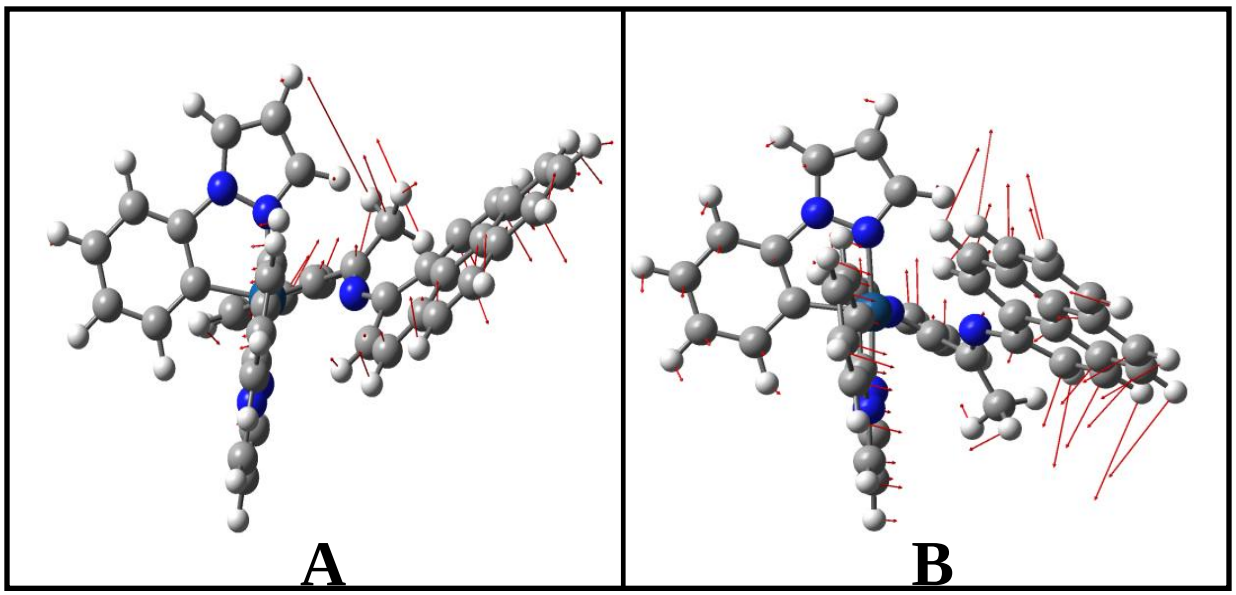

Figure S3. Transition vectors A) process **1a→1b** imaginary frequency 43.38 cm^{-1}: 140 kJ mol^{-1}; B) process **1a'→1b'**. imaginary frequency 24.77 cm^{-1}; 112 kJ mol^{-1}

Table S2. Computed bond lengths (Å), torsion angles (°) and energies for **2**.

	^C_9-C_6	d(N_2-Ir)	^C_9->Ir	E (a.u)	ΔE(a.u.)	ΔE(kJ/mol)
TS2(**2b**,**2a**)	176.98	2.3562	345.41	-1972.887112	0.022535	59.2
2a	115.57	2.1668	287.86	-1972.909647	0	0.0
TS(**2a**,**2a'**)	97.50	2.1649	275.53	-1972.907419	0.002228	5.9
2a'	66.02	2.1927	258.45	-1972.908173	0.001474	3.8
TS1(**2a'**,**2b'**)	11.25	2.5584	180.81	-1972.883619	0.026029	68.3
2b'	-58.42	2.1871	99.11	-1972.907826	0.001821	4.8
TS(**2b'**,**2b**)	-93.59	2.1793	76.111	-1972.903392	0.006255	16.4
2b	-123.14	2.1993	58.91	-1972.905362	0.004286	11.3

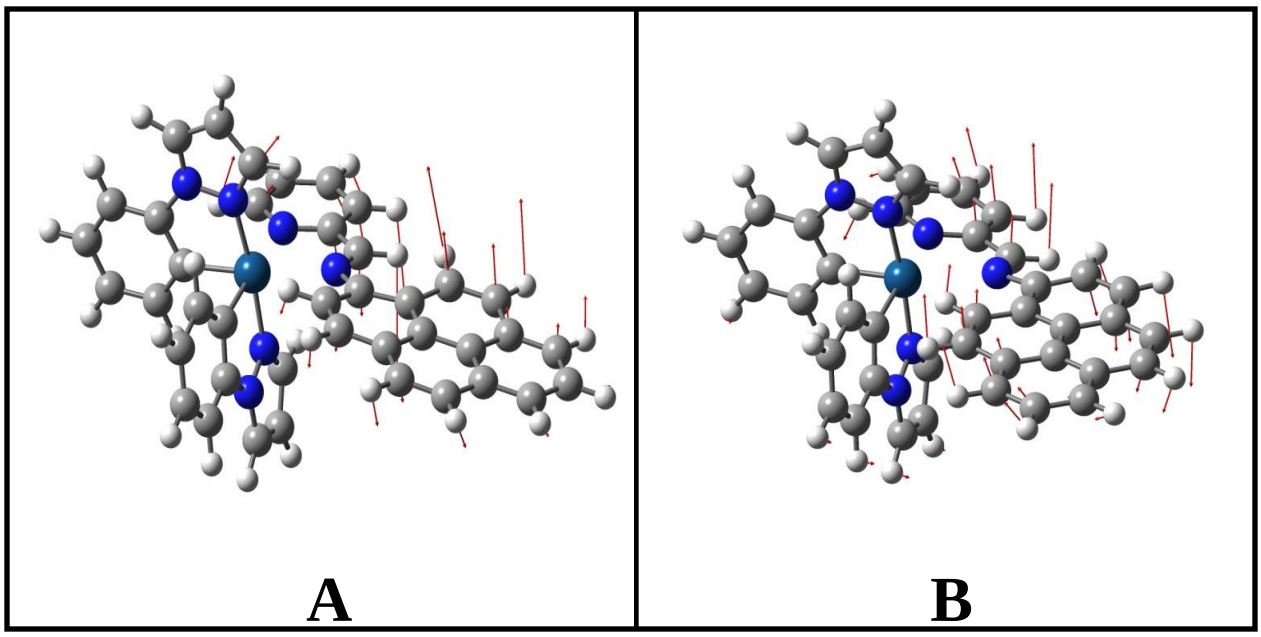

Figure S4. Transition vectors A) process **2a→2b** imaginary frequency 43.38 cm^{-1}: 140 kJ mol^{-1}; B) process **2a'→2b'**. imaginary frequency 24.77 cm^{-1}; 112 kJ mol^{-1}

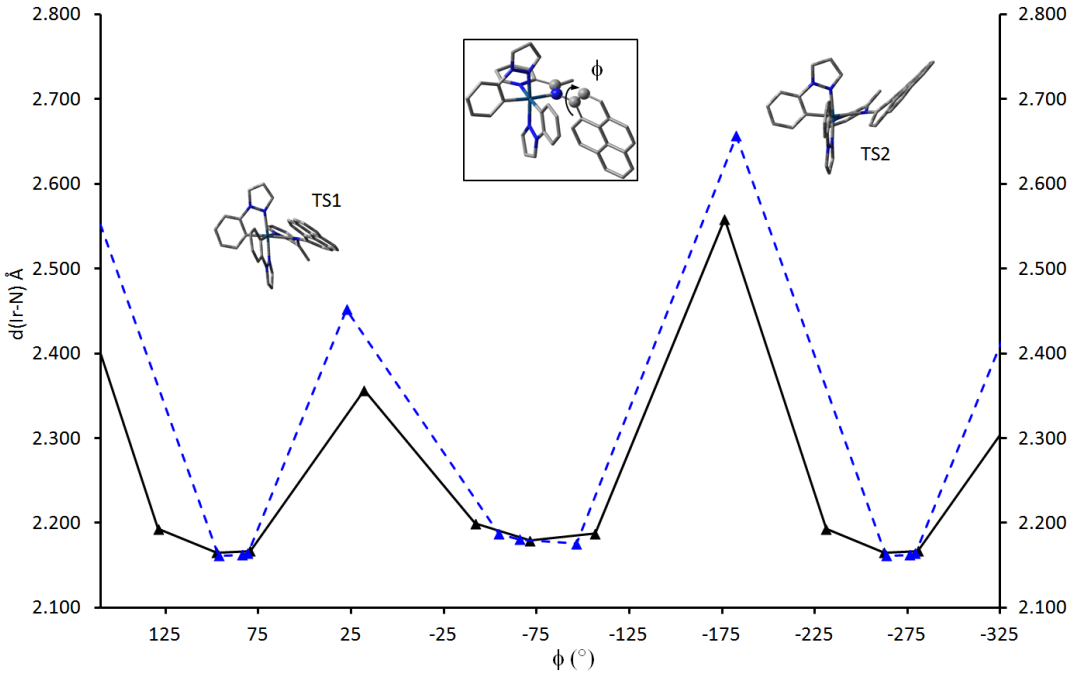

Figure S5. Reaction coordinate showing the Ir-N_2 bond length vs. torsion angle (^C_9-C_6) for complexes **1 (---)** and **2 (—)**.

Cartesian coordinates for Calculated Structures

Complex 1a

C	3.20800000	2.48619100	0.69307500
C	3.63449600	3.81360100	0.64492900
C	2.84361900	4.74767000	-0.01950200
C	1.65405200	4.32389100	-0.61272000
C	1.29198600	2.98002000	-0.52532400
C	0.03242100	2.45271400	-1.09598500
C	-0.91102200	3.38343000	-1.78183000
C	-1.39575900	0.55533200	-1.29653600
C	-1.39581300	-0.36753600	-2.34492700
C	-2.55317100	-1.06171200	-2.67683400
C	-3.73456700	-0.87335400	-1.94296700
C	-3.73566100	0.04427500	-0.85518600
C	-2.55543700	0.77287800	-0.52331300
C	-2.59596500	1.67647200	0.59408200
C	-3.73727500	1.85396400	1.31700900
C	-4.94318100	1.14573700	0.99562400
C	-4.92726700	0.23524500	-0.09733900
C	-6.10955800	-0.48409800	-0.43146700
C	-7.27422300	-0.28000800	0.32526800
C	-7.28044400	0.61592800	1.39506800
C	-6.12550800	1.32417100	1.72984600
C	-6.07851800	-1.40117500	-1.53658900
C	-4.93885300	-1.58747600	-2.26056600
C	0.01170600	0.88464900	2.78168600
C	-0.88749100	0.29422200	3.68513800
C	-1.20893900	-0.93525000	3.12688800
C	-0.41213400	-2.07645100	0.99405900
C	-1.14722700	-3.25660300	1.08591300
C	-0.95747200	-4.23091700	0.10428100
C	-0.04178100	-4.00591600	-0.92992600
C	0.67760700	-2.80770700	-0.99482000
C	0.50397700	-1.79848600	-0.03877300
C	2.59296400	0.02496900	-2.85843200
C	3.77802700	-0.44814300	-3.44617500
C	4.49896300	-1.01239000	-2.40468400
C	3.98667100	-1.23054700	0.07871000
C	5.16127100	-1.85918900	0.48690000
C	5.30742500	-2.17342500	1.83902800
C	4.28544900	-1.85558400	2.74024900
C	3.11604500	-1.22677700	2.29744000
C	2.93177100	-0.89074200	0.94871900
Ir	1.36375600	0.02603800	0.06135400
N	2.06751600	2.07895600	0.12803700
N	-0.16625200	1.18096000	-0.94263600
N	0.21793900	0.06462600	1.74765100
N	-0.52970900	-1.04586500	1.96403000
N	2.59558600	-0.24142700	-1.54959500
N	3.76671000	-0.87089200	-1.27727500
H	4.39844400	-2.10368800	3.79487500
H	6.21461500	-2.66526400	2.18410400
H	5.95090100	-2.10383300	-0.22305100
H	2.33212400	-0.99741900	3.02290300

H	5.46881500	-1.49392000	-2.39363600
H	4.06995500	-0.38673100	-4.48579400
H	1.75387000	0.54140200	-3.31182700
H	-1.25595700	0.70558500	4.61515900
H	0.51567500	1.84467800	2.82323800
H	-1.86422500	-1.72348300	3.47610800
H	1.38219800	-2.65735800	-1.81651100
H	0.11290300	-4.77040200	-1.69045500
H	-1.51878700	-5.16191100	0.15200300
H	-1.85132300	-3.42463800	1.90056500
H	-0.47442600	-0.53549400	-2.90130600
H	-2.54462000	-1.76862200	-3.50585100
H	-4.91842700	-2.28570600	-3.09718000
H	-6.98982200	-1.94639000	-1.78240400
H	-8.17766800	-0.83208400	0.06592900
H	-8.19174600	0.76298500	1.97186600
H	-6.13153400	2.02356800	2.56589800
H	-3.74925900	2.53919400	2.16493000
H	-1.69441200	2.22081200	0.87472900
H	-0.39085100	3.93029400	-2.57735200
H	-1.75148300	2.84193300	-2.22222900
H	-1.30578800	4.12517500	-1.07567500
H	1.01708600	5.03299800	-1.13491300
H	3.14417100	5.79109800	-0.07622200
H	4.56869900	4.09522900	1.12276700
H	3.79406100	1.72131400	1.20344800

Complex 1b

C	3.30706400	-2.37497200	-0.75135800
C	3.72380800	-3.55694400	-1.36352600
C	2.83549800	-4.22805900	-2.20009900
C	1.56211200	-3.69350700	-2.39675000
C	1.21454000	-2.50768700	-1.75039000
C	-0.11926300	-1.88369900	-1.89685900
C	-1.11193500	-2.49588000	-2.82903500
C	-1.57750700	-0.12980300	-1.20836200
C	-1.62351000	1.12459900	-1.82296000
H	-0.74422100	1.48236800	-2.35915400
C	-2.77702600	1.89745400	-1.77313000
H	-2.80056300	2.87078700	-2.26240900
C	-3.91181200	1.44326700	-1.08393200
C	-3.87989400	0.16100900	-0.46797900
C	-2.70579000	-0.64641900	-0.53919200
C	-2.73238200	-1.94987700	0.06843400
C	-3.84109800	-2.40687600	0.71604600
C	-5.02700000	-1.60568100	0.82148700
C	-5.03441400	-0.31848600	0.21604200
C	-6.20474300	0.48846800	0.29436600
C	-7.33032300	0.00048900	0.97673800
C	-7.31203300	-1.26193600	1.57053900
C	-6.17123300	-2.06202100	1.49293700
C	-6.20391300	1.78174400	-0.33040800
C	-5.10466500	2.23740300	-0.99457600

C	2.44376500	1.06405300	-2.80531800
C	2.51831000	2.32343200	-3.42389900
C	1.91044100	3.20134900	-2.53782800
C	0.79907100	2.81483100	-0.27694700
C	0.33355800	4.10622400	-0.03964700
C	-0.39703800	4.34058200	1.12665700
C	-0.64419400	3.28746700	2.01433600
C	-0.15833500	2.00218800	1.74799500
C	0.57855600	1.72584300	0.58869600
C	0.03345000	-1.69057100	2.30527400
C	0.37849300	-1.99590100	3.63203200
C	1.62920000	-1.42878000	3.82048700
C	3.11596900	-0.07032400	2.27076400
C	4.20782700	0.10604500	3.11820500
C	5.28651600	0.86337300	2.65888900
C	5.24839900	1.41791500	1.37517700
C	4.13704600	1.22108100	0.54726900
C	3.03362000	0.46717800	0.97171800
N	2.08631400	-1.86211200	-0.93682700
N	-0.32710700	-0.81570900	-1.19233800
N	1.83099600	1.17624200	-1.62365100
N	1.50841700	2.48515800	-1.46342200
N	1.01140000	-0.98979400	1.72700800
N	1.98488200	-0.83134600	2.66126000
Ir	1.36020100	-0.02482400	-0.04597600
H	6.15123300	1.01667500	3.30131000
H	6.09008800	2.00875300	1.01608700
H	4.13880800	1.66730200	-0.44974000
H	4.22942900	-0.33413400	4.11459500
H	2.27495600	-1.40953300	4.68960700
H	-0.20471600	-2.54977200	4.35510400
H	-0.87154600	-1.92058300	1.75386000
H	-0.36604600	1.20078200	2.46063100
H	-1.21820900	3.46946800	2.92203600
H	-0.77271600	5.33986900	1.33722200
H	0.52605800	4.91763900	-0.74094900
H	2.80626500	0.09936400	-3.14407600
H	2.95632800	2.56301500	-4.38339100
H	1.74330300	4.26937800	-2.60264600
H	-1.85904200	-2.59729000	-0.01381200
H	-3.84505400	-3.40030800	1.16455200
H	-6.15933200	-3.04975500	1.95364200
H	-8.19345100	-1.62551000	2.09549400
H	-8.22375200	0.62201900	1.03664700
H	-7.10609400	2.38971600	-0.26328800
H	-5.10833600	3.21750100	-1.47122700
H	-0.66482700	-2.63104800	-3.82092900
H	-1.42190500	-3.48590700	-2.46964600
H	-2.00187200	-1.87008400	-2.92820600
H	0.84713900	-4.19729400	-3.04180400
H	3.12534600	-5.15256000	-2.69363900
H	4.72643600	-3.93239200	-1.17891500
H	3.97171600	-1.81550400	-0.09236000

TS1

Ir	1.31622100	-0.01052800	0.02432600
N	-0.39532200	1.95705300	-0.47799300
N	2.39908800	1.73288000	-0.63028100
C	3.66826500	1.68170200	-1.06039100
C	4.38597500	2.81596700	-1.42444700
C	3.76289100	4.05833300	-1.31904000
C	2.45034500	4.11423500	-0.85681000
C	1.78353700	2.92809100	-0.53418200
C	0.35385900	2.96353400	-0.12441100
C	-0.00553100	4.16542800	0.71277400
C	-1.80551700	1.99164300	-0.39960000
C	-2.52997100	3.20101800	-0.28882000
C	-2.56384000	0.79555100	-0.58299000
C	-1.98159700	-0.44200100	-1.00151900
C	-2.72409000	-1.57233100	-1.17246000
C	-3.90719300	3.23433000	-0.15802500
C	-4.65898000	2.05130900	-0.16106100
C	-3.98492300	0.82770300	-0.42251100
C	-4.13048900	-1.58730300	-0.91468400
C	-4.75699400	-0.36455800	-0.55404900
C	-6.16597700	-0.33751100	-0.34731300
C	-6.80349100	0.91025700	-0.03907800
C	-6.07869400	2.06269600	0.03372700
C	-4.89849900	-2.75698800	-1.03214400
C	-6.27327500	-2.72622700	-0.79975100
C	-6.90310500	-1.52640500	-0.46510800
H	-2.24589300	-2.49320100	-1.50794400
H	-4.40547600	-3.68915400	-1.30896800
H	-6.85954200	-3.63896300	-0.88826600
H	-7.97983600	-1.49937200	-0.29751300
H	-7.88222100	0.91794400	0.11713200
H	-6.56347600	3.01623000	0.24226300
H	-4.41533000	4.19270000	-0.05620200
H	-2.01938300	4.15251100	-0.34709800
H	-0.91542900	-0.47068300	-1.19926600
C	1.37504600	1.62561000	2.73335600
C	0.78061500	1.49332200	3.99794800
C	0.03164400	0.32717700	3.92562100
C	-0.22354800	-1.39660900	2.07234900
C	-1.01035600	-2.32756400	2.74801500
C	-1.29268400	-3.53781300	2.11244500
C	-0.76841800	-3.79279000	0.83997300
C	0.00207100	-2.82794300	0.18453400
C	0.26950800	-1.58272300	0.76843800
C	1.10628400	-0.73993500	-3.05436400
C	1.79539000	-1.60348600	-3.92366200
C	2.77366800	-2.20237600	-3.14524000
C	3.36903400	-1.90584300	-0.68731500
C	4.46898400	-2.75607100	-0.60386600
C	5.12696700	-2.87305100	0.62119200
C	4.67547900	-2.14540200	1.72721300
C	3.56548900	-1.30003400	1.62168500
C	2.88968000	-1.15620400	0.40514500
N	1.00241700	0.61221800	1.94524500

N	0.18394700	-0.18051100	2.68340200
N	1.63000200	-0.81734700	-1.82823300
N	2.65212300	-1.70924700	-1.89147700
H	5.18788000	-2.23990800	2.68337300
H	5.98807100	-3.53188000	0.70964500
H	4.81246000	-3.31818900	-1.47123400
H	3.22655500	-0.75106500	2.50122100
H	3.53588300	-2.92918900	-3.39809500
H	1.60772500	-1.76604500	-4.97631500
H	0.27423700	-0.07215600	-3.25126000
H	0.88569300	2.15149900	4.84967500
H	2.06291400	2.38022500	2.36619000
H	-0.58244800	-0.16689300	4.66839200
H	0.37511100	-3.04619300	-0.81989300
H	-0.96994600	-4.74659100	0.35352100
H	-1.90454700	-4.28265800	2.61720500
H	-1.38974700	-2.12999000	3.74997200
H	-0.29167100	5.04508500	0.12213800
H	-0.82630600	3.93166500	1.39771700
H	0.86787800	4.45742400	1.30693900
H	1.93918400	5.06973600	-0.77232900
H	4.28876000	4.97090300	-1.58997100
H	5.41034700	2.71664800	-1.77203300
H	4.12843300	0.69445100	-1.09617400

TS2

C	3.30706400	-2.37497200	-0.75135800
C	3.72380800	-3.55694400	-1.36352600
C	2.83549800	-4.22805900	-2.20009900
C	1.56211200	-3.69350700	-2.39675000
C	1.21454000	-2.50768700	-1.75039000
C	-0.11926300	-1.88369900	-1.89685900
C	-1.11193500	-2.49588000	-2.82903500
C	-1.57750700	-0.12980300	-1.20836200
C	-1.62351000	1.12459900	-1.82296000
H	-0.74422100	1.48236800	-2.35915400
C	-2.77702600	1.89745400	-1.77313000
H	-2.80056300	2.87078700	-2.26240900
C	-3.91181200	1.44326700	-1.08393200
C	-3.87989400	0.16100900	-0.46797900
C	-2.70579000	-0.64641900	-0.53919200
C	-2.73238200	-1.94987700	0.06843400
C	-3.84109800	-2.40687600	0.71604600
C	-5.02700000	-1.60568100	0.82148700
C	-5.03441400	-0.31848600	0.21604200
C	-6.20474300	0.48846800	0.29436600
C	-7.33032300	0.00048900	0.97673800
C	-7.31203300	-1.26193600	1.57053900
C	-6.17123300	-2.06202100	1.49293700
C	-6.20391300	1.78174400	-0.33040800
C	-5.10466500	2.23740300	-0.99457600
C	2.44376500	1.06405300	-2.80531800
C	2.51831000	2.32343200	-3.42389900

C	1.91044100	3.20134900	-2.53782800
C	0.79907100	2.81483100	-0.27694700
C	0.33355800	4.10622400	-0.03964700
C	-0.39703800	4.34058200	1.12665700
C	-0.64419400	3.28746700	2.01433600
C	-0.15833500	2.00218800	1.74799500
C	0.57855600	1.72584300	0.58869600
C	0.03345000	-1.69057100	2.30527400
C	0.37849300	-1.99590100	3.63203200
C	1.62920000	-1.42878000	3.82048700
C	3.11596900	-0.07032400	2.27076400
C	4.20782700	0.10604500	3.11820500
C	5.28651600	0.86337300	2.65888900
C	5.24839900	1.41791500	1.37517700
C	4.13704600	1.22108100	0.54726900
C	3.03362000	0.46717800	0.97171800
N	2.08631400	-1.86211200	-0.93682700
N	-0.32710700	-0.81570900	-1.19233800
N	1.83099600	1.17624200	-1.62365100
N	1.50841700	2.48515800	-1.46342200
N	1.01140000	-0.98979400	1.72700800
N	1.98488200	-0.83134600	2.66126000
Ir	1.36020100	-0.02482400	-0.04597600
H	6.15123300	1.01667500	3.30131000
H	6.09008800	2.00875300	1.01608700
H	4.13880800	1.66730200	-0.44974000
H	4.22942900	-0.33413400	4.11459500
H	2.27495600	-1.40953300	4.68960700
H	-0.20471600	-2.54977200	4.35510400
H	-0.87154600	-1.92058300	1.75386000
H	-0.36604600	1.20078200	2.46063100
H	-1.21820900	3.46946800	2.92203600
H	-0.77271600	5.33986900	1.33722200
H	0.52605800	4.91763900	-0.74094900
H	2.80626500	0.09936400	-3.14407600
H	2.95632800	2.56301500	-4.38339100
H	1.74330300	4.26937800	-2.60264600
H	-1.85904200	-2.59729000	-0.01381200
H	-3.84505400	-3.40030800	1.16455200
H	-6.15933200	-3.04975500	1.95364200
H	-8.19345100	-1.62551000	2.09549400
H	-8.22375200	0.62201900	1.03664700
H	-7.10609400	2.38971600	-0.26328800
H	-5.10833600	3.21750100	-1.47122700
H	-0.66482700	-2.63104800	-3.82092900
H	-1.42190500	-3.48590700	-2.46964600
H	-2.00187200	-1.87008400	-2.92820600
H	0.84713900	-4.19729400	-3.04180400
H	3.12534600	-5.15256000	-2.69363900
H	4.72643600	-3.93239200	-1.17891500
H	3.97171600	-1.81550400	-0.09236000

X-ray Crystallography

Table S3. Selected crystal structure data for complexes **1a** and **1b**.

	1a	**1b**
Formula	$C_{42}H_{32}N_6F_6Cl_2IrP$	$C_{41}H_{30}N_6IrPF_6.C_6H_{14}$
Habit	orange, tablet	orange, tablet
dimensions/ mm	0.16 x 0.25 x 0.60	0.14 x 0.24 x 0.30
temperature/ K	173(1)	173(1)
crystsyst	Monoclinic	Monoclinic
space group	*P* $2_1/n$	*C* 2/*m*
a/ Å	12.333(1)	17.731(2)
b/ Å	12.691(1)	23.624(2)
c/ Å	25.377(2)	21.585(2)
α/ °	90	90
β/ °	102.052(5)	107.697(4)
γ/ °	90	90
V/ $Å^3$	3884.6(6)	8613(2)
Z	4	8
ρ_{calc}/ g cm^{-3}	1.759	1.589
μ (Mo Kα)/ cm^{-1}	36.86	32.05
R^a (I>2.0σ(I))	0.0504	0.0312
$R_w{}^a$ (I>2.0σ(I))	0.1662	0.0786
Goodness of fit	1.30	1.07

[a]Function minimized. $\Sigma w(F_o^2-F_c^2)^2$,R1 = Σ ||F_o| - |F_c||/Σ |F_o|,*w*R2 = [Σ (w (F_o^2- F_c^2)^2)/Σw(F_o^2)^2]$^{1/2}$.

Table S4. Selected bond lengths (Å) and angles (°) for **1a**.

Bond Lengths (Å)	
Ir(1) – N(1)	2.122(7)
Ir(1) – N(2)	2.125(6)
Ir(1) – N(3)	2.021(7)
Ir(1) – N(5)	2.026(7)
Ir(1) – C(32)	2.021(8)
Ir(1) – C(41)	2.031(8)
C(1) – N(1)	1.339(10)
C(1) – C(2)	1.382(12)
C(5) – N(1)	1.370(9)
C(5) – C(6)	1.474(11)
C(6) – N(2)	1.308(10)
C(8) – N(2)	1.436(10)

Angles (°)	
N(3) – Ir(1) – C(32)	80.3(3)
N(1) – Ir(1) – N(2)	76.6(2)
C(1) – N(1) – C(5)	118.4(7)
C(1) – N(1) – Ir(1)	126.9(5)
C(5) – N(1) – Ir(1)	114.5(5)
C(6) – N(2) – C(8)	121.4(6)
C(6) – N(2) – Ir(1)	116.9(5)
C(8) – N(2) – Ir(1)	121.6(5)

Torsion Angles(°)	
C(9) – C(8) – N(2) – C(6)	110.1(8)

Table S5. Selected bond lengths (Å) and angles (°) for **1b**.

Bond Lengths (Å)	
Ir(1) – N(1)	2.131(3)
Ir(1) – N(2)	2.173(2)
Ir(1) – N(3)	2.013(3)
Ir(1) – N(5)	2.035(3)
Ir(1) – C(32)	2.023(3)
Ir(1) – C(41)	2.009(3)
C(1) – N(1)	1.343(4)
C(1) – C(2)	1.384(5)
C(5) – N(1)	1.359(4)
C(5) – C(6)	1.486(4)
C(6) – N(2)	1.300(4)
C(8) – N(2)	1.446(4)

Angles (°)

N(3) – Ir(1) – C(32)	80.01(12)
N(1) – Ir(1) – N(2)	75.86(10)
C(1) – N(1) – C(5)	118.7(3)
C(1) – N(1) – Ir(1)	125.3(2)
C(5) – N(1) – Ir(1)	116.0(2)
C(6) – N(2) – C(8)	118.8(3)
C(6) – N(2) – Ir(1)	116.3(2)
C(8) – N(2) – Ir(1)	124.6(2)

Torsion Angles(°)	
C(9) – C(8) – N(2) – C(6)	-110.0(3)

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