Supporting Information for Crystals

Synthesis, Photophysical, and Computational Studies of a Bridged Ir^{III}-Pt^{II} Heterodimetallic Complex

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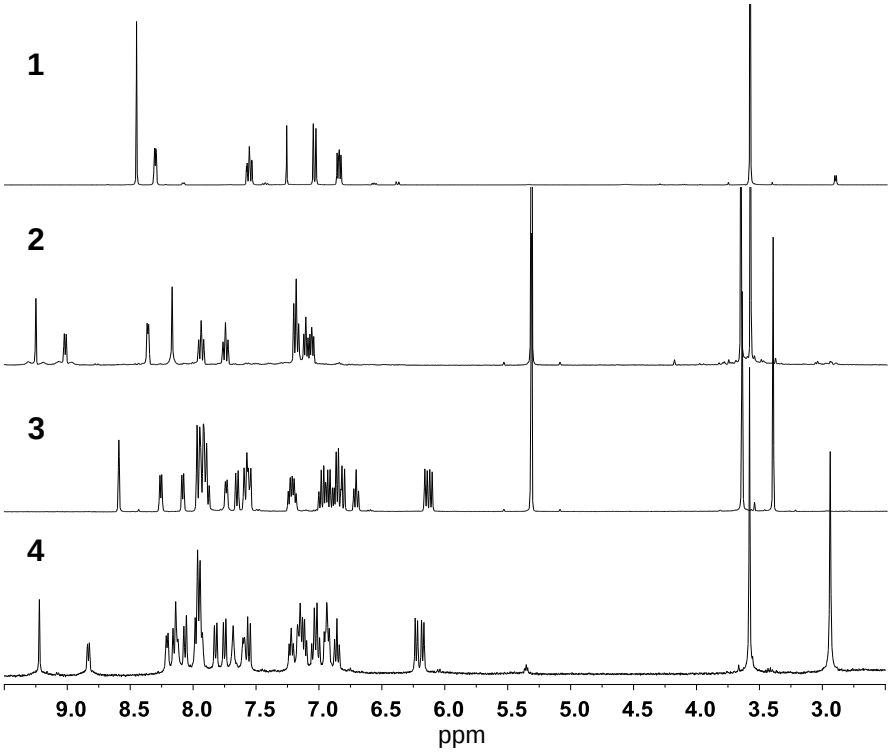

Figure S1. The comparison of ^{1}H NMR spectra of **1**–**4**. The peak at around 5.3 ppm is from the solvent residue.

HPLC grade solvents were obtained from Fisher Scientific. A Shim-pack XR-ODS (Shimadzu, Japan) column (2.2 μm, 75 mm × 4.6 mm, i.d.) was used for analysis. Figure S2 shows the chromatogram of ligand dapz and complex **4**. Compounds were eluted with a CH_3CN gradient in water (10–90% over 0–10 min, followed by isocratic elution of 90% CH_3CN for 5 min). All solvents contain 0.1% TFA. The flow rate was 1.0 mL/min. The detection wavelengths were set at 360 nm and 380 nm for ligand **1** and complex **4**, respectively. Integration results indicated purity of greater than 99% for complex **4**.

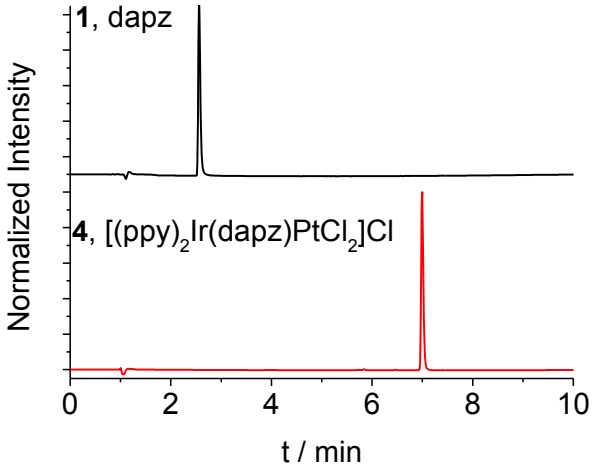

Figure S2. Analytical HPLC of ligand **1** (top) and complex **4** $[(ppy)_2Ir(dapz)PtCl_2]Cl$ (bottom).

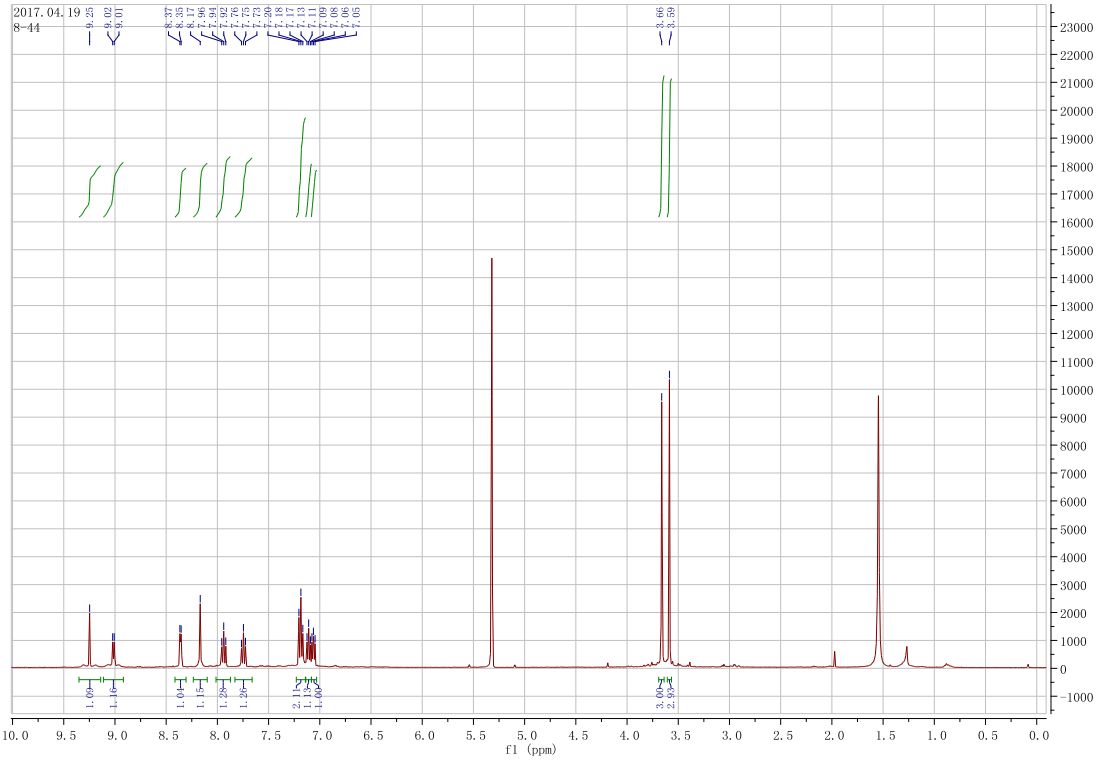

Figure S3. ^{1}H NMR spectrum of complex **2** in CD_2Cl_2.

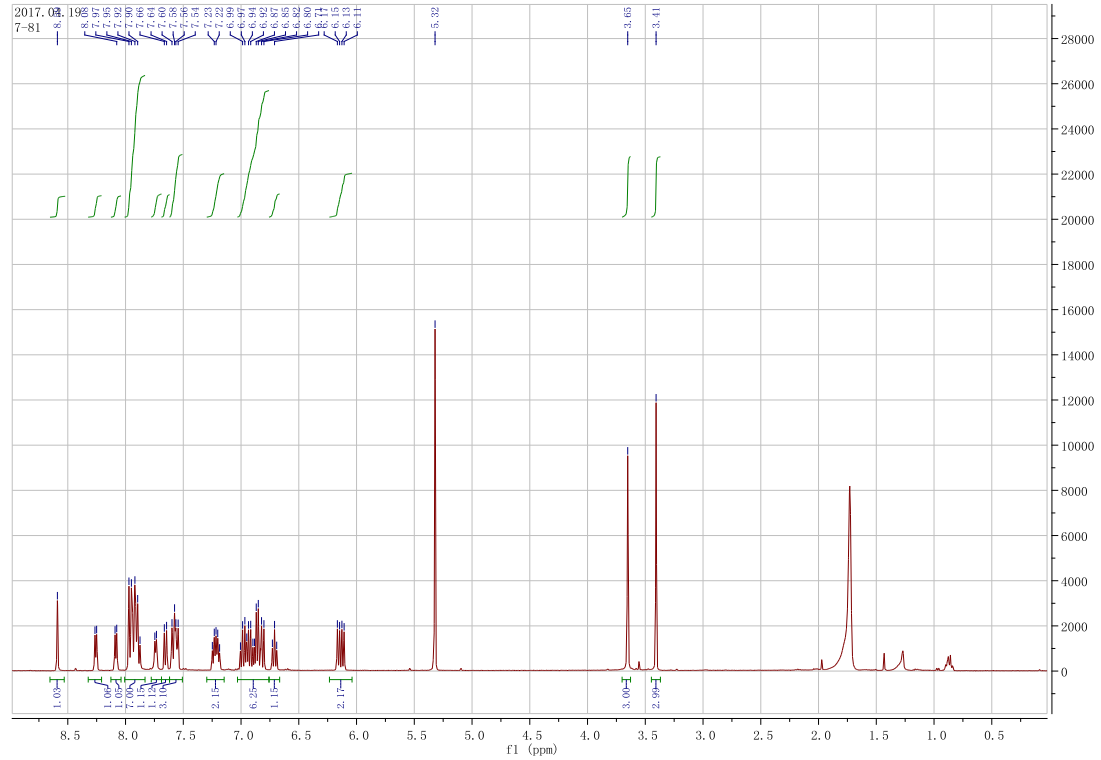

Figure S4. ^{1}H NMR spectrum of complex **3** in CD_2Cl_2.

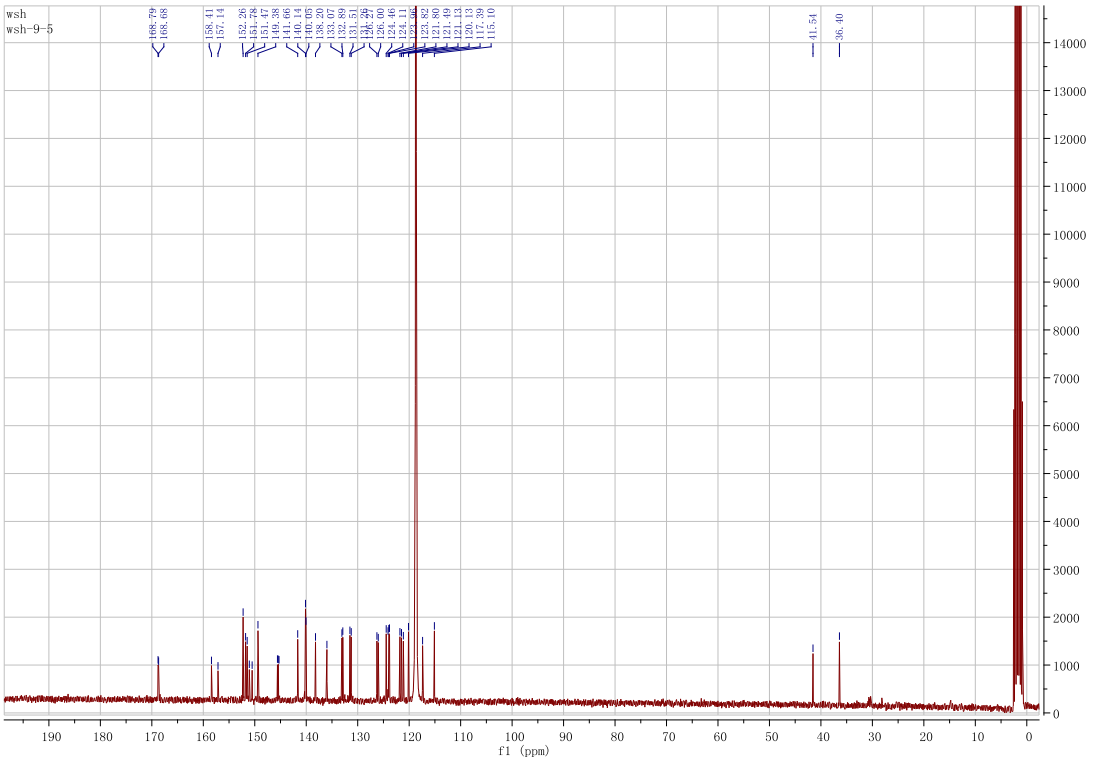

Figure S5. ^{13}C NMR spectrum of complex **3** in $CDCl_3$.

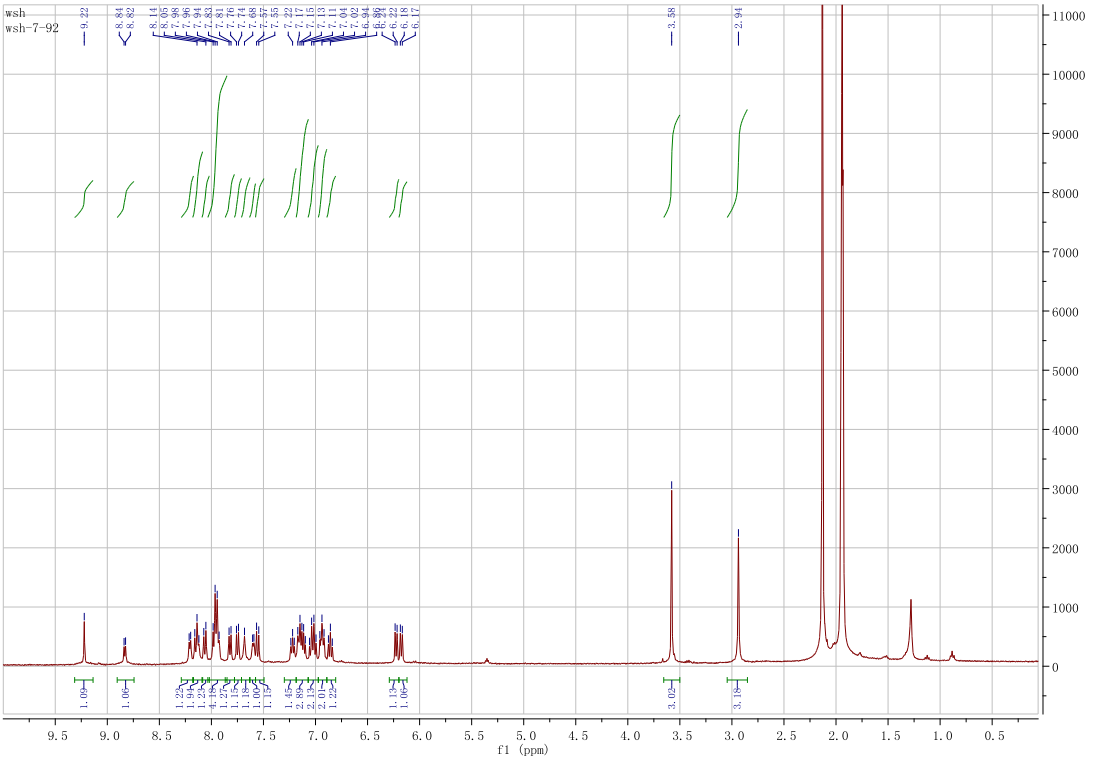

Figure S6. ^{1}H NMR spectrum of complex **4** in CD_3CN.

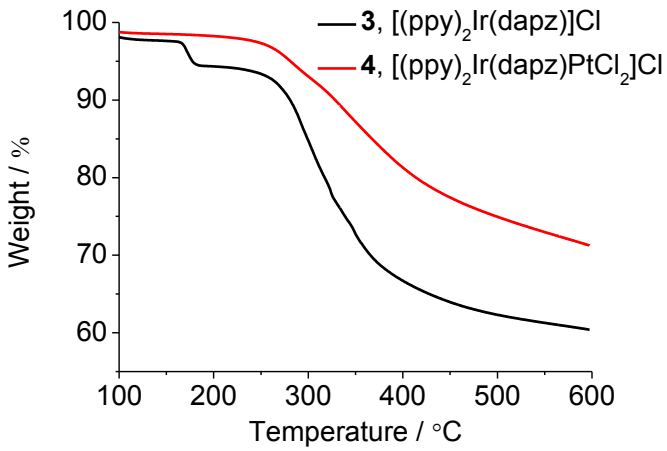

Figure S7. Thermogravimetric traces of complexes **3** (black) and **4** (red)

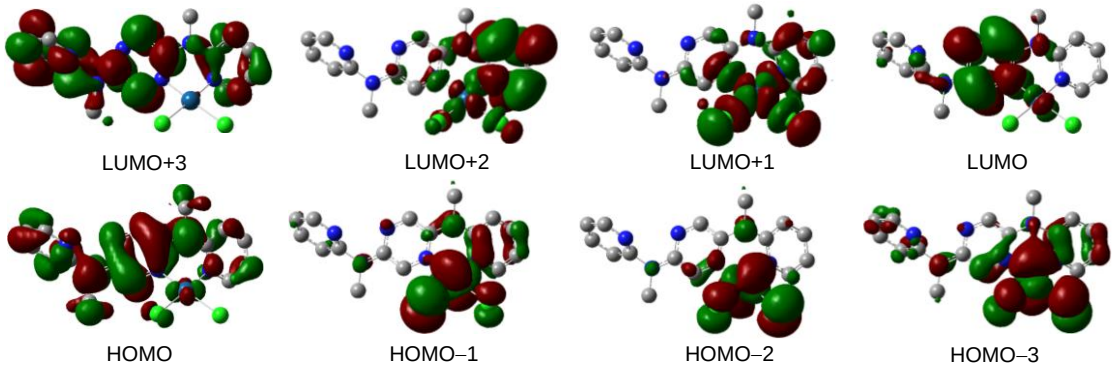

Figure S8. Isodensity plots of selected frontier molecular orbitals of complex **2**. All orbitals were computed at an isovalue of 0.02 e bohr^{-3}.

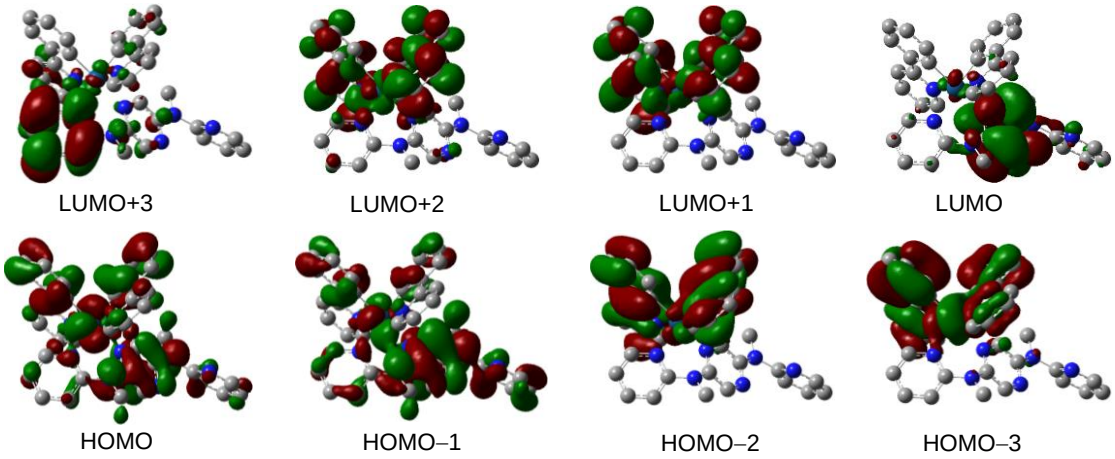

Figure S9. Isodensity plots of selected frontier molecular orbitals of complex **3**$^{+}$. All orbitals were computed at an isovalue of 0.02 e bohr^{-3}.

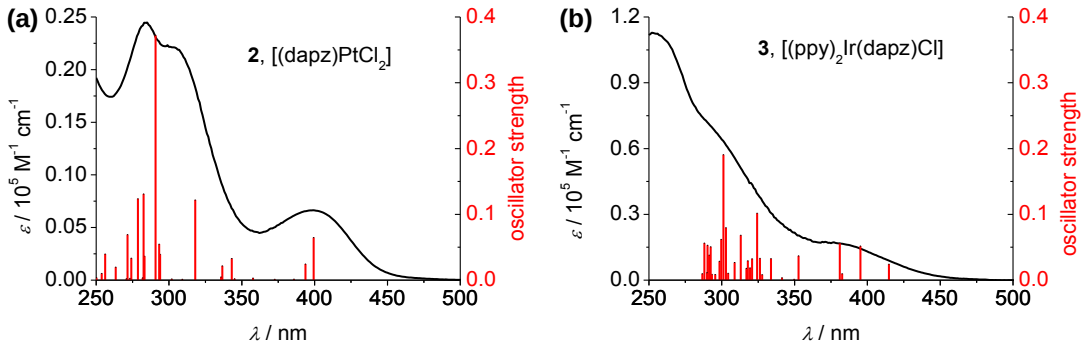

Figure S10. Absorption spectra in CH_3CN and TDDFT results of complex **2** (a) and **3**$^+$ (b).

The structure of **4** was solved using SHELXS-97 and refined with Olex2. The solvent-including crystal packing of **4** was shown in Figure S11. It is difficult to identify the solvent molecules because of its highly crystallographically disordered. The unit cell parameters of **4** keep constant when the disordered solvent molecules were removed. In comparison, after using squeeze, the intermolecular Pt···Pt distance (3.839 Å) keep constant while the intermolecular aromatic plane···plane (3.876 vs 3.886 Å) and Cl···Cl (4.250 vs 4.248 Å) distances display negligible changes due to the weak solute-solvent interactions. As suggested by Figure S11, the complex **4** was surrounded by the disordered solvent molecules. However, no significant effect was observed on crystal packing behavior of **4**.

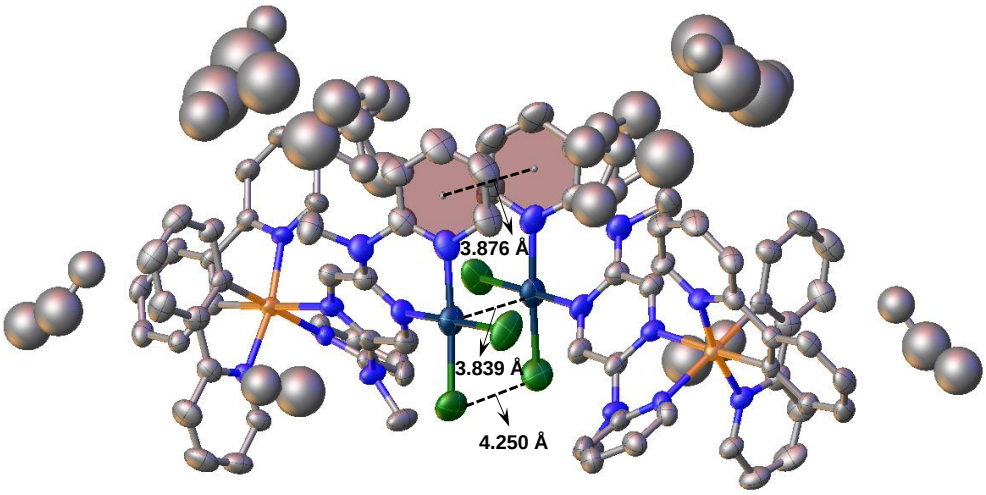

Figure S11. Solvent-including crystal packing of complex **4** with 50% probability of the thermal ellipsoids. For the reason of clarity, H atoms have been omitted. The intermolecular aromatic plane···plane, Pt···Pt and Cl···Cl distances are indicated in panel.

Table S1. Crystallographic data and parameters for complex **4**.

Complex	**4**
CCDC number	1574637
empirical formula	$C_{38}H_{32}Cl_2IrN_8Pt$
formula weight	1058.58
crystal system	monoclinic
a (Å)	13.0437(2)
b (Å)	24.3865(5)
c (Å)	28.8657(5)
V (Å^3)	8982.2(3)
α (°)	90
β (°)	101.971(2)
γ (°)	90
Z value	8
Density (g/cm^3)	1.566
Absorption coefficient (mm^{-1})	6.223
F(000)	4040
R1 (final)	0.0345
wR2 (final)	0.0792
R1 (all)	0.0422
wR2 (all)	0.0826

Table S2. Selected Bond Lengths and Bond Angles.

Complex	bond lengths (Å)		bond angles (°)	
4	Pt(1)-Cl(1)	2.2968(13)	Cl(2)-Pt(1)-Cl(1)	88.83(6)
	Pt(1)-Cl(2)	2.2934(17)	N(1)-Pt(1)-Cl(1)	92.36(12)
	Pt(1)-N(1)	2.032(5)	N(3)-Pt(1)-Cl(2)	90.84(12)
	Pt(1)-N(3)	2.007(4)	N(3)-Pt(1)-N(1)	87.95(16)
	Ir(1)-N(4)	2.167(4)	N(4)-Ir(1)-N(6)	85.94(14)
	Ir(1)-N(6)	2.174(3)	N(4)-Ir(1)-N(7)	89.57(13)
	Ir(1)-N(7)	2.063(3)	N(4)-Ir(1)-N(8)	97.80(14)
	Ir(1)-N(8)	2.055(3)	C(27)-Ir(1)-N(7)	80.63(16)
	Ir(1)-C(27)	2.019(4)	C(38)-Ir(1)-N(8)	80.44(15)
	Ir(1)-C(38)	2.019(4)	N(4)-Ir(1)-N(7)	89.57(13)