Supporting Information for

Rhodium(I) and Iridium(I) Complexes of the Conformationally Rigid IBioxMe$_4$ Ligand: Computational and Experimental Studies of Unusually Tilted NHC Coordination Geometries

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1. Conformer of Rh3-H2'

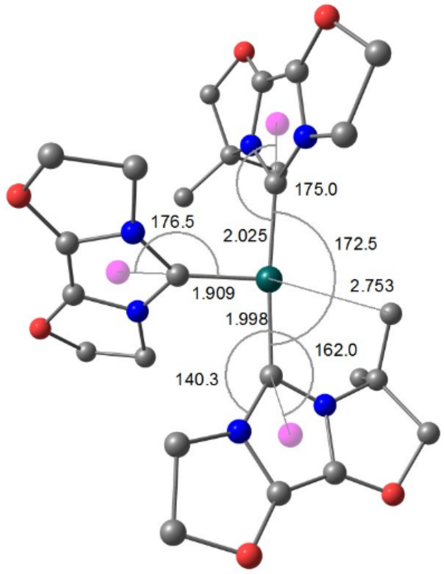

Figure S1: Less stable (+1.7 kJ mol^{-1}) conformer **Rh3-H2'(b)** with strong yawing, pitching and agostic interaction.

Table S1. EDA results for **Rh3-H2'(b)** – fragmentation of the most tilted IBioxMe$_4$ ligand. Energies in kJ mol^{-1} and distances in Å.

	Rh3-H2'(b)	
ΔE_{int}	-328.8	
ΔE_{disp}	-61.6	
ΔE_{Pauli}	820.4	
ΔE_{elstat} [a]	-739.1	(68%)
ΔE_{orb} [a]	-348.6	(32%)
ΔE_{σ} [b]	-168.1	(48%)
	0.664	
ΔE_{π} [b]	-91.2	(23%)
	0.730	
$\Delta E_{agostic}$ [b]	-55.5	(16%)
	0.404	
$\Delta E_{resid.}$ [b]	-35.3	(10%)
ΔE_{prep}	31.9	
ΔE_{bond} (=$-D_e$)	-296.9	
d(M-L)	2.025	

[a] The percentage values give the contribution to the total attractive interactions ΔE_{elstat} + ΔE_{orb}.
[b] The percentage values give the contribution to the total orbital interaction ΔE_{orb}. The character of the interaction is deduced from visual inspection of the NOCV orbitals; eigenvalues (ν) are given below the energy values.

2. Selected NMR spectra

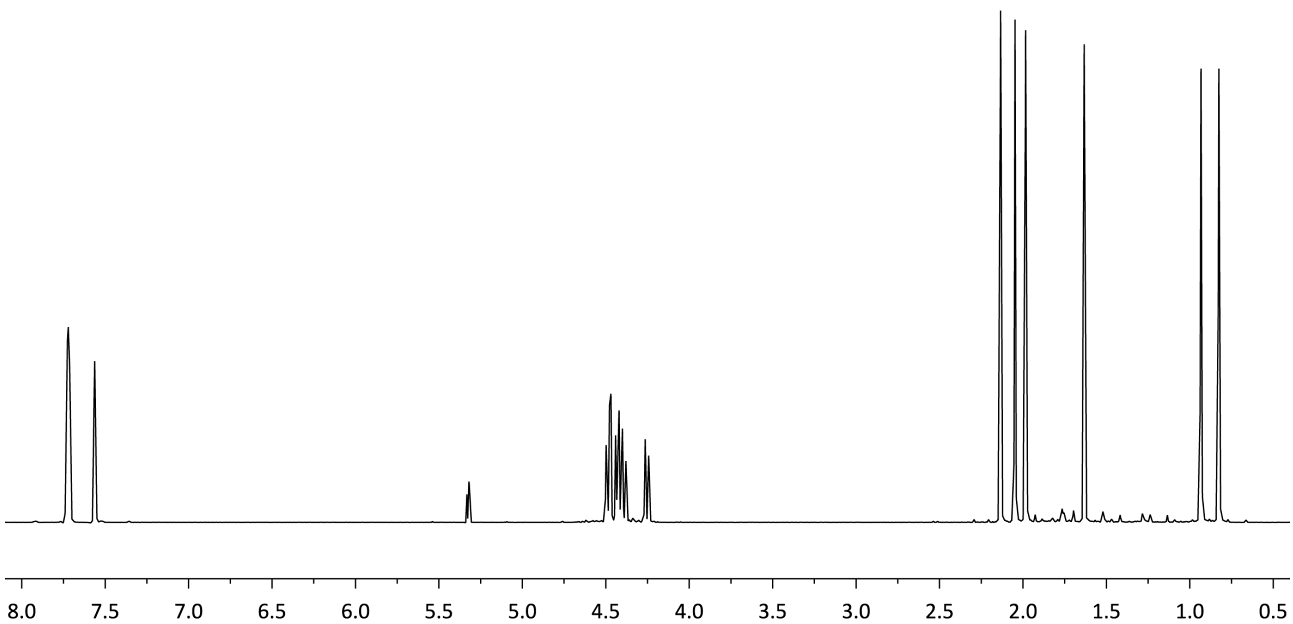

Figure S2: ^{1}H NMR spectrum of **Ir5** (CD_2Cl_2, 400 MHz).

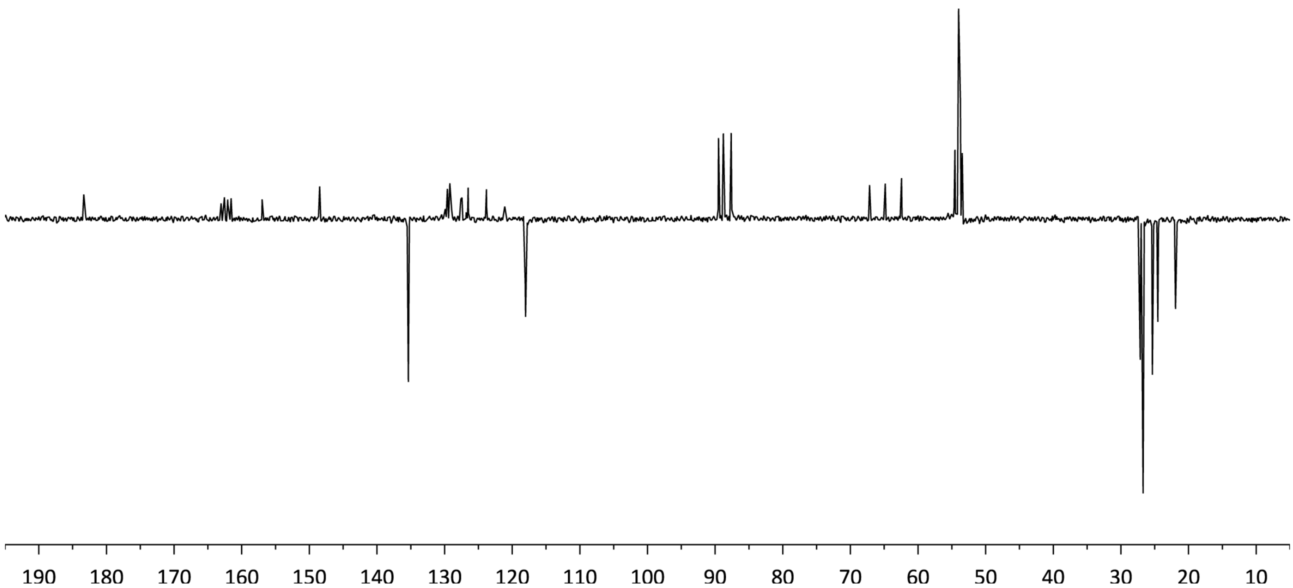

Figure S3: $^{13}C\{^{1}H\}$ APT NMR spectrum of **Ir5** (CD_2Cl_2, 101 MHz).

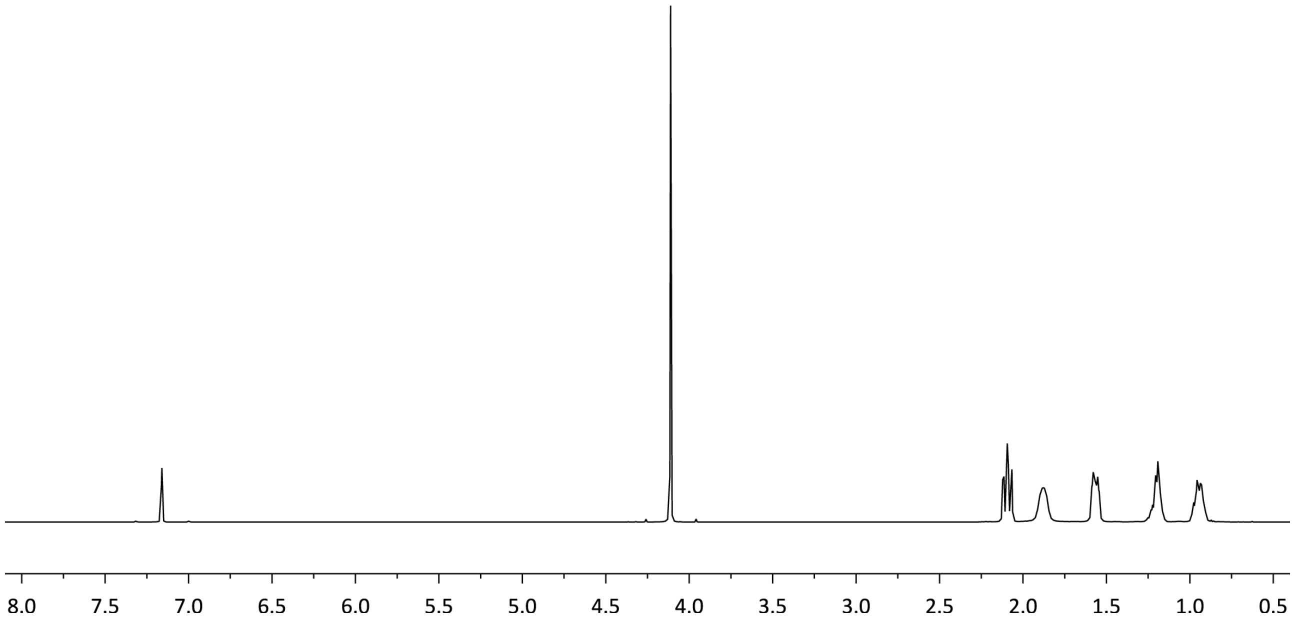

Figure S4: ^{1}H NMR spectrum of **IBiox6** (C_6D_6, 500 MHz).

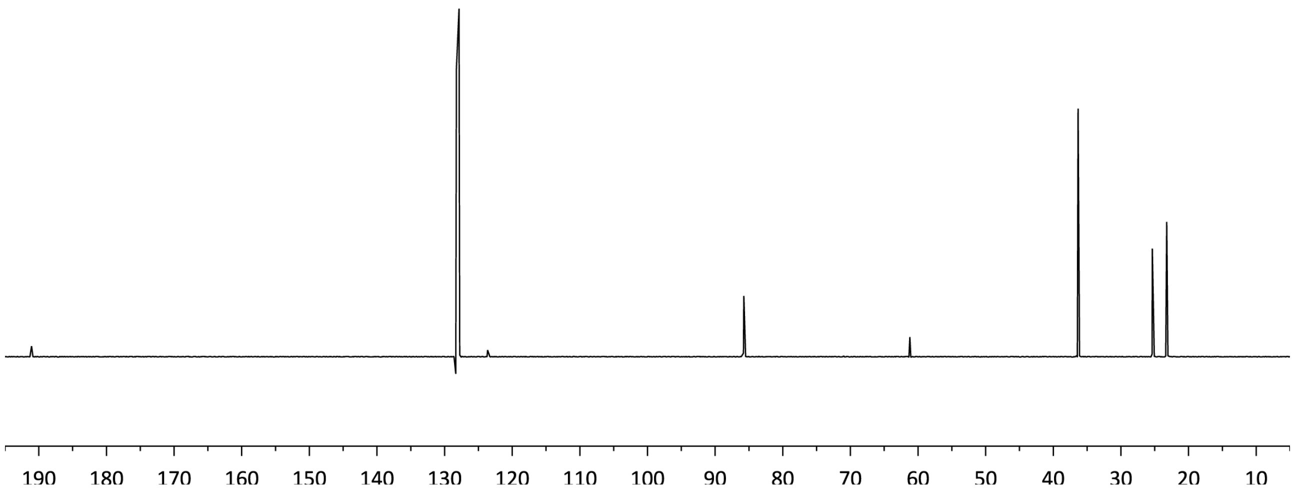

Figure S5: $^{13}C\{^{1}H\}$ APT NMR spectrum of **IBiox6** (C_6D_6, 126 MHz).

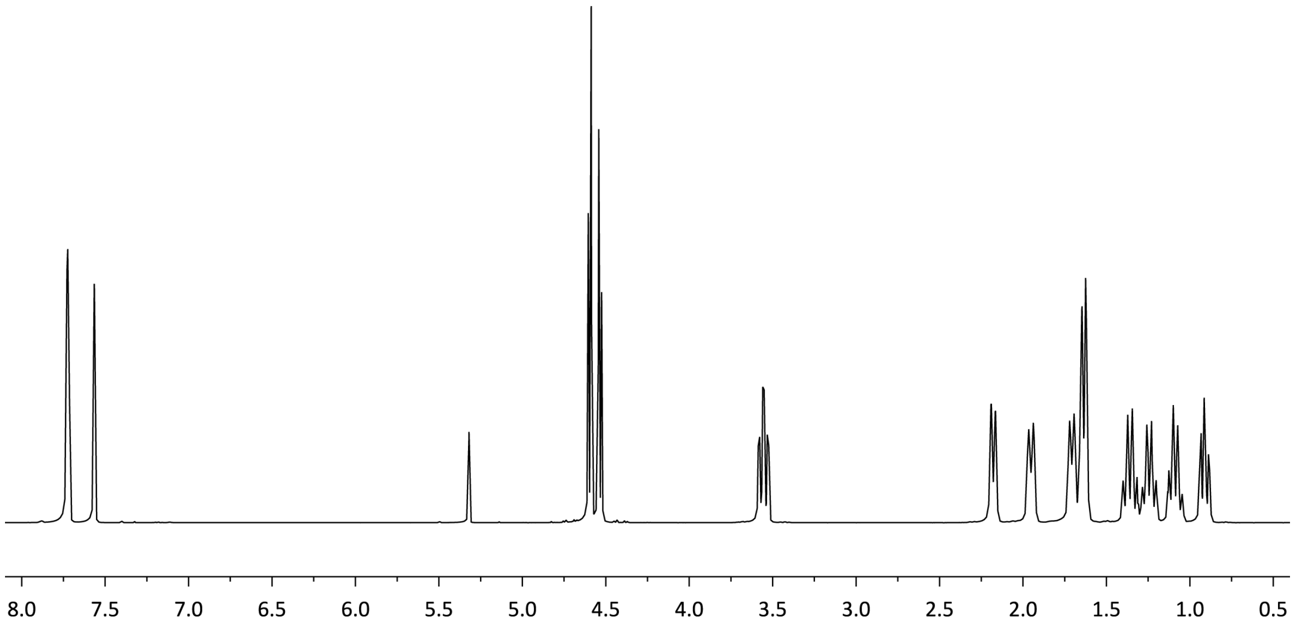

Figure S6: ^{1}H NMR spectrum of **Rh3-Cy** (CD_2Cl_2, 500 MHz).

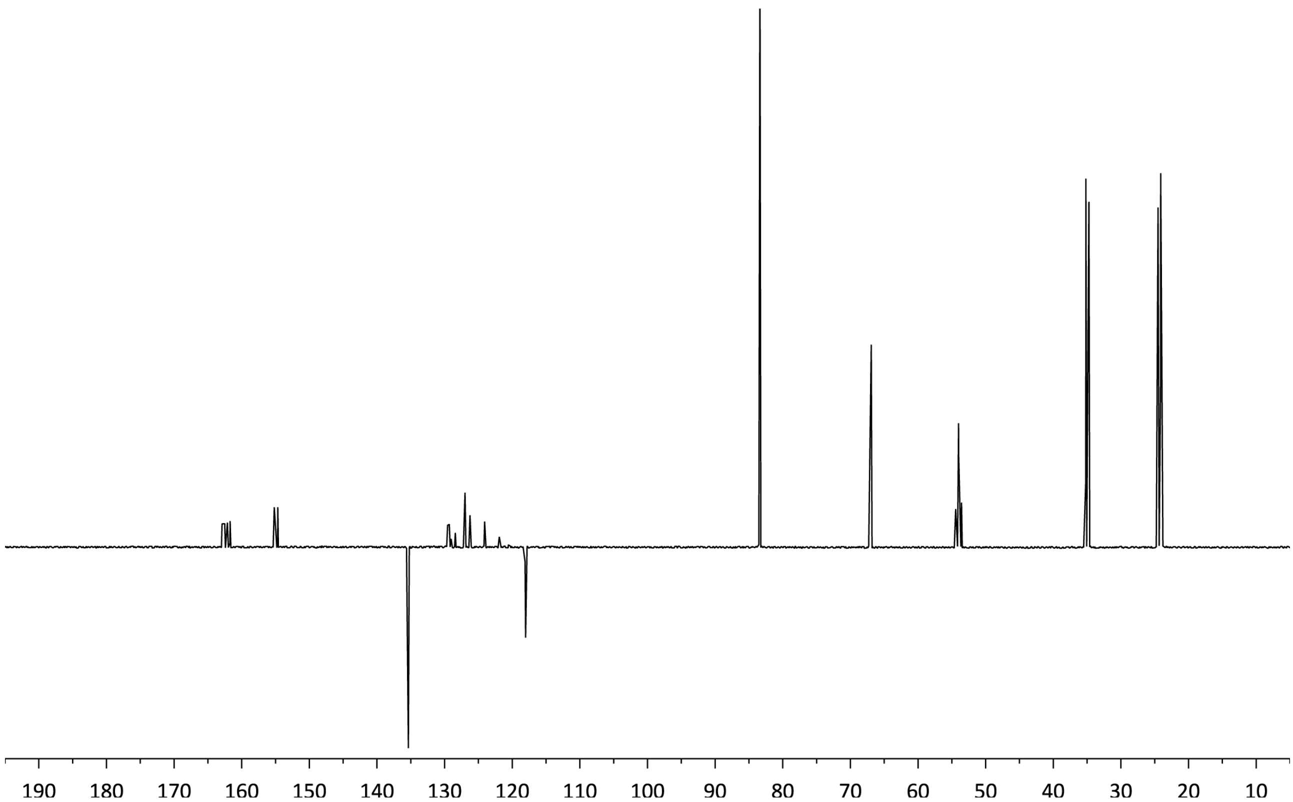

Figure S7: $^{13}C\{^{1}H\}$ APT NMR spectrum of **Rh3-Cy** (CD_2Cl_2, 126 MHz).