CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Ligand oxidation of a deprotonated bis(picolyl)amine Ir^{I}(cod) complex**

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** In honour of Prof. Jan Reedijk, on occasion of his retirement from the University of Leiden.

Crystal data for complex K[3]: $C_{20}H_{23}IrKN_3$, M_r = 536.71, rough platelet translucent dark red crystal (0.21 × 0.10 × 0.03 mm), monoclinic, space group P 21/n, a = 12.039(2), b = 10.4751(10), c = 14.844(2) Å, β = 99.197(10)°, V = 1847.9(4) Å^{-3}, Z = 4, ρ_{calcd} = 1.929 g cm^{-3}, F(000) = 1040, T = 208(2) K, MoK_α radiation. Data collected with a Nonius KappaCCD diffractometer. Of 29099 measured reflections (2θ: 4.1-50°), 3224 were unique (R_{int} = 0.1139); a multi-scan absorption correction[s1] was applied (SADABS program) with min./max. transmission factors of 0.33/0.80 Structure solved by direct methods and difference-Fourier maps; refined using SHELXTL.[s2] Final agreement factors were $R1$ =0.0509 (2349 obs. reflections, $F^2 > 2\sigma(F^2)$) and $wR2$ = 0.1036; data/restrains/parameters 3224/0/226; GOF = 1.057.

DFT calculations

The geometry of **3**$^-$ was optimized with the Turbomole program[S3] coupled to the PQS Baker optimizer.[S4] The geometry was fully optimized as a minimum at the at the b3-lyp level[S5] using the polarized triple-ζ def-TZVP basis[S3c,f] (small-core pseudopotential[S3c,e] on Rh or Ir). Orbitals and spin densities were visualized with the Molden program.[S6]

Selected spectra for the new complexes 2 and K[3].

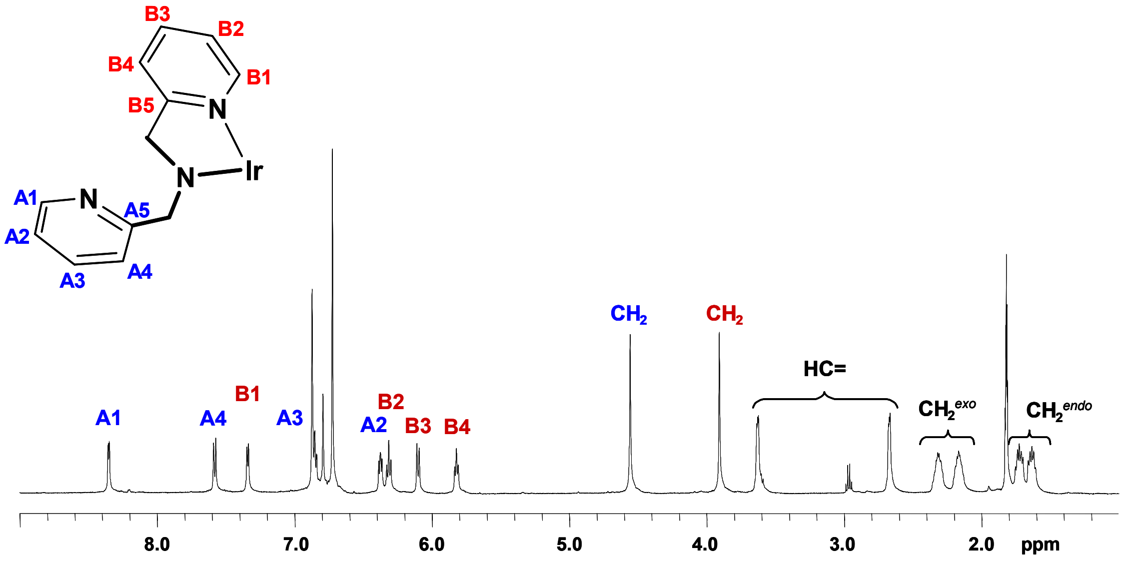

Figure S1. ^{1}H NMR (d^{8}-toluene, -40 ºC) of the amido complex [Ir(bpa-H)(cod)] (**2**).

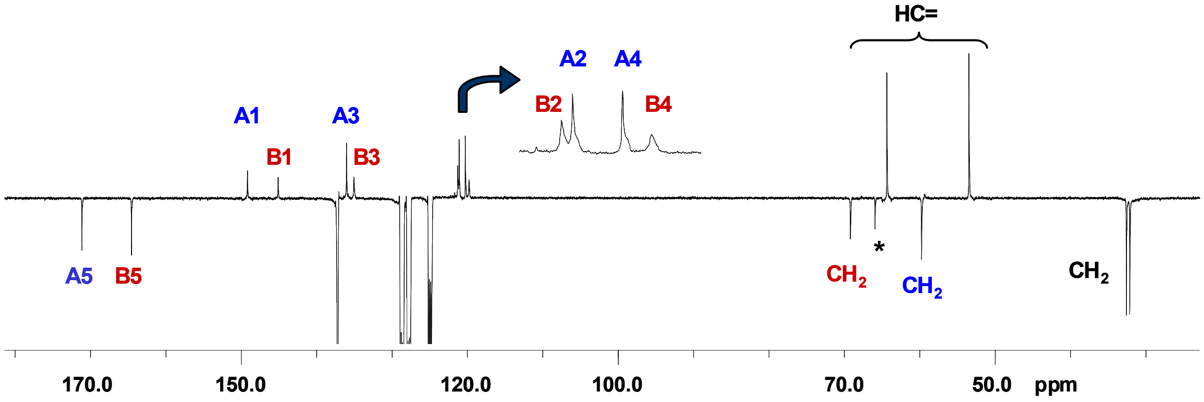

Figure S2. ^{13}C{^{1}H }-apt NMR (d^{8}-toluene, -40 ºC) of the amido complex [Ir(bpa-H)(cod)] (**2**). * denotes the CH$_2$ of the diethyl ether.

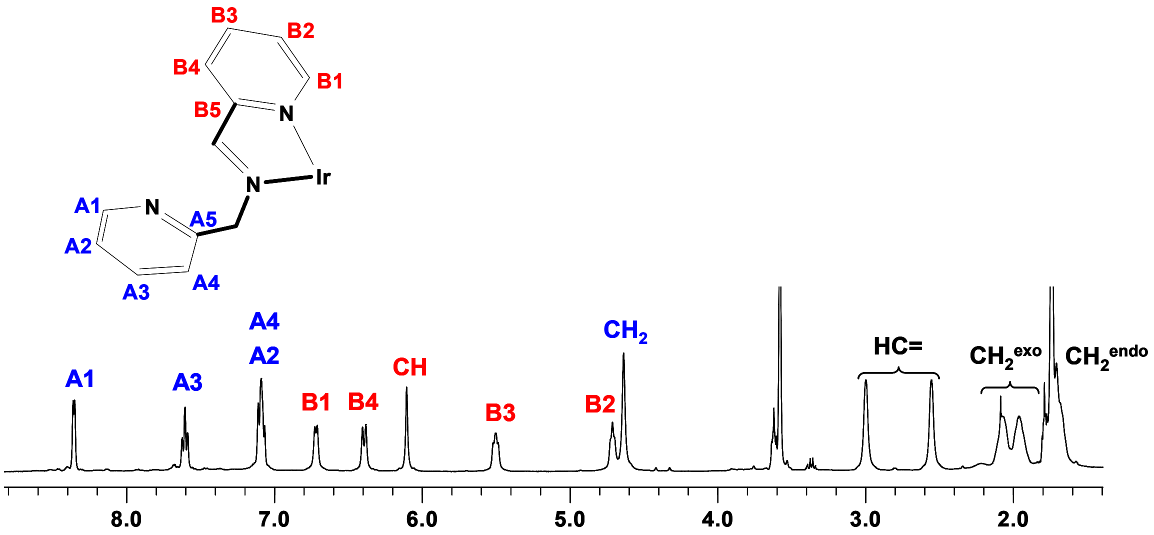

Figure S3. ^{1}H NMR (d^8-thf, – 70 ºC) of the anionic complex K[Ir(bpa-2H)(cod)] (K[**3**]).

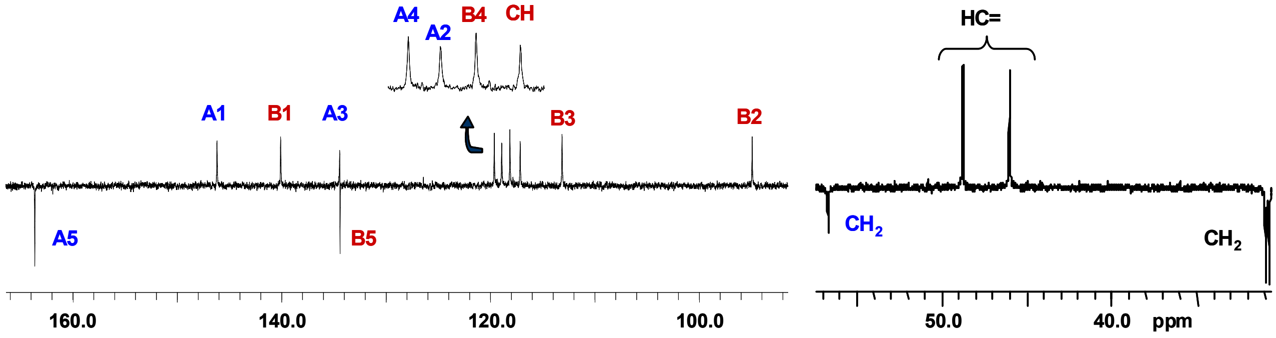

Figure S4. ^{13}C{^{1}H }-apt NMR (d^8-thf, – 70 ºC) of the anionic complex K[Ir(bpa-2H)(cod)] (K[**3**])

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