Supporting information for

Slow magnetic relaxation in cobalt N-heterocyclic carbene complexes

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Syntheses and Characterizations

Experimental Details. Compounds 1, 2, and 3, were prepared according to previously published procedures as detailed below. All procedures were conducted in a Vacuum Atmospheres glovebox under an atmosphere of purified nitrogen. Solvents were purified by sparging with argon and passage through two columns packed with 4 Å molecular sieves. NMR spectra were recorded in benzene-$d_6$ and referenced to the residual protium resonance of the solvent at 7.16 ppm. Spectra were recorded on a 500 MHz Varian NMR spectrometer. Carbene ligands IMes and IPr and precursor [Co$_2$Cl$_2$(μ-Cl)$_2$(IPr)$_2$] were prepared according to literature procedures. Anhydrous CoCl$_2$ was purchased from Strem chemicals and used as received.

[Co(CH$_2$SiMe$_3$)$_2$(IPr)] (1). A 20 mL scintillation vial was charged with 100 mg (96.6 μmol) of [Co$_2$Cl$_2$(μ-Cl)$_2$(IPr)$_2$] and 2 mL of tetrahydrofuran. The resulting blue solution was chilled to −30 ºC at which point 390 μL of Me$_3$SiCH$_2$MgCl (390 μmol) was added as a solution in diethyl ether (1.0 M). The resulting mixture was allowed to warm to 25 ºC and stirred for 2.5 h. During this time, the mixture became yellow and a precipitate formed. All volatiles were removed in vacuo and the remaining residue was extracted into 10 mL of pentane and filtered through a pad of Celite. The pentane solution was then set aside at −30 ºC for 24 h during which time 50 mg (42%) of single yellow crystals deposited. The crystals were isolated by decanting the mother liquor, washed with pre-cooled pentane, and dried in vacuo. NMR spectra of the crystals were identical to published data: δ +27.9, +27.1, +12.9, −22.1, −26.1, −70.0, −101.9.

[CoCl$_2$(IMes)$_2$] (2). A 20 mL scintillation vial was charged with 489 mg (1.61 mmol) of IMes and 104 mg (0.801 mmol) of CoCl$_2$. Tetrahydrofuran (10 mL) was added to the two solids giving rise to a light blue solution. The mixture was stirred for 5 hours at 25 ºC during which time it took on a darker blue color. All volatiles were removed in vacuo affording 550 mg (93%) of a blue solid. A portion of the crude product (200 mg) was recrystallized by dissolving it in 10 mL of 2-methyltetrahydrofuran and allowing vapor diffusion of pentane. This method afforded 105 mg of single blue crystals, which were isolated by decanting the mother liquor, washing with pentane, and drying in vacuo. NMR spectra of the crystals were identical to published data: δ +33.5, +1.52, +1.00, −0.75.

[CoMe$_2$(IMes)$_2$] (3). A scintillation vial was charged with 130 mg (177 μmol) of 2 and 5 mL of tetrahydrofuran. The resulting blue solution was chilled to −30 ºC at which point 89 μL of MeMgCl (360 μmol) was added as a solution in tetrahydrofuran (4.0 M). The resulting mixture was allowed to warm to 25 ºC and stirred for 3 h during which time it became dark yellow-brown in color. All volatiles were removed in vacuo and the remaining residue was extracted into 5 mL of toluene. The toluene extract was filtered through a pad of Celite and evaporated to dryness. The resulting residue was washed exhaustively with diethyl ether producing 74 mg (60%) of a yellow solid. The solid was recrystallized by vapor diffusion of diethyl ether into a saturated benzene solution affording single yellow crystals. NMR spectra of the crystals were identical to published data: δ +78.3, +41.1, −5.0, −5.9, −6.1.

Magnetic Measurements

DC magnetic measurements were performed on freshly prepared crushed crystalline samples in plastic bags over the temperature range of 2–300 K in an applied magnetic field of 1000 Oe on a Quantum Design SQUID, Model MPMS with 7 Tesla magnet. The diamagnetic contribution of the polypropylene bag was subtracted from the raw data. Pascal’s constants[3] were used to estimate the diamagnetic corrections of the atoms, which were subtracted from the experimental susceptibilities to give the molar paramagnetic susceptibilities (χM). AC magnetic susceptibility measurements were performed on the same sample with an oscillating field of 3 Oe in the range of 1-1500 Hz.
S1. Magnetization (top) and reduced magnetization data (bottom) of 1. Solid lines correspond to best fits using PHI (D = +73.7 cm\(^{-1}\), E = +19.2 cm\(^{-1}\), g = 2.63)
S2. Field dependent AC data (a), Cole-Cole plot (b) and Arhenious plot (c) of 1 under a 1000 Oe DC field.
S3. Frequency dependent AC data (a), Cole-Cole plot (b) and Arhenious plot (c) of 1 under a 750 Oe DC field.
S4. Field dependent AC data (a), Frequency dependent AC data (b) and temperature dependent AC data (c) of a 10% solution of 1 in 2-MeTHF under a 0 Oe DC field.
S5. Temperature dependent AC data (a), frequency dependent AC data (b and c) of a 10% solution of 1 in 2-MeTHF under 1000 Oe DC field.
S6. Cole-Cole plot (a) and Arrhenius plot (b) of a 10% solution of 1 in 2-MeTHF under 1000 Oe DC field.
**S7.** Reduced magnetization data for 2. Solid lines correspond to fits using Anisofit2.0 (D = -9.01 cm⁻¹, E = 1.2 cm⁻¹ , g = 2.32) Inset; field dependent magnetization data at 1.8 K. Solid line corresponds to fit using PHI.

**S8.** Temperature dependence of the AC susceptibility data under a 1000Oe DC field for 1. In-phase (open) out-of-phase (solid).
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**Computational details**

Single point calculations were performed using the crystallographic geometries provided in the cif files. The two-step approach implemented in the ORCA 4.1.0 program with the spin-orbit coupling (SOC) and spin-spin coupling (SSC) relativistic effects included was used to conduct ab initio calculations. \[4\] Several solutions of the non-relativistic Born-Oppenheimer Hamiltonian were calculated using a complete active space self-consistent field (CASSCF) in the first step. The electronic configuration of Co(II) is $d^7$, so the selected active space CAS(7,5) contains 7 electrons in the 5 essentially atomic $d$ orbitals.\[5\] Secondly, the effect of SOC and SSC were taken into account using the quasi-degenerate perturbation theory (QDPT). N-Electron Valence Perturbation Theory (NEVPT2) was employed to evaluate the effects of the dynamic correlations by substituting the diagonal elements of the QDPT matrix with the NEVPT2 corrected state energies. The auxiliary def2-TZV/C basis set for resolution of identity (RI) approximation and the Karlsruhe polarized triple-z basis set (TZVP), were employed.\[6\]

**Table S1.** Energy of the first 5 excited states (cm$^{-1}$) and its main contributions to the D and E values in cm$^{-1}$ at CAS(7,5) NEVPT2 level.

<table>
<thead>
<tr>
<th>State</th>
<th>Multiplicity</th>
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<tr>
<td></td>
<td>Energy</td>
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<td>E</td>
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</table>
Dominant electronic configurations of ground and first, second excited states in 1.
S 15. Dzz axis in 1 (right) and 2 (left)

References