

COMMUNICATION – Supporting Information

Tuning electronic structure through halide modulation of mesoionic carbene cobalt complexes

Received 00th January 20xx,
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

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1 General Methods

All reactions were performed following standard inert atmosphere glove box synthetic techniques unless otherwise noted. All reagents were obtained from commercial suppliers unless otherwise noted. Metal halides and synthesized triazolium salts were dried at 110 °C under vacuum. Solvents were purified on an activated alumina column⁴⁸ and stored over a 1:1 mixture of 3 Å and 4 Å molecular sieves.

Physical Measurements - Single crystal X-ray diffraction data for compounds **1-3** were collected at 100 K on a Bruker κ Diffractometer with a Mo Kα radiation source equipped with an Apex II Area Detector. Structures were solved using Olex⁴⁹ via the SHELXT⁵⁰ routine and refined with SHELXL.⁵¹ Magnetic data was collected on a Quantum Design Magnetic Properties Measurements System 3 (MPMS3) Superconducting Quantum Interference Device (SQUID) Magnetometer in Direct Current scan mode. Magnetic measurements were performed on crushed crystallized samples pressed into plastic sample holders to prevent torqueing. DC susceptibility measurements were collected with $H_{DC} = 1000$ Oe with a sweep rate of 4 K/min. All data were corrected for diamagnetism using Pascal's constants.⁵² Fitting of magnetic data was done using PHI.³² UV-Vis-IR absorption spectroscopy was performed using an Agilent Cary 5000 with dry THF as the solvent. Elemental analysis (CHN) was performed by Midwest Microlab.

Ligand Synthesis [^{Dipp}MIC-H]Cl - Synthesis of the triazolium salt was adapted from literature procedure.⁵³ A neat mixture of 2,6-diisopropylaniline (75 mmol, 13.30 g) was mixed with half an equivalent of isoamyl nitrite (37.5 mmol, 4.39 g) at room temperature. The dark red solution was allowed to sit at room temperature for 4 h and then stored at -20 °C and allowed to crystallize overnight. The resulting slurry was filtered and washed with cold ethanol and the triazene was isolated as large yellow blocks which were used without further purification (yield 42%, 31.5 mmol, 11.5 g). Triazolium chloride salts were synthesized from the resulting triazene in the presence of 1.5 equivalents (47.3 mmol, 5.13 g) of tert-butyl hypochlorite in dry dichloromethane at -78 °C. Upon addition of the oxidant, the solution immediately turned dark purple/brown and was stirred for 30 minutes. A slight excess of phenylacetylene (42.3 mmol, 4.32 g) was then added and the reaction stirred overnight in the dark and allowed to slowly come to room temperature. The solvent was then removed in vacuo, and the resulting purple powder was triturated for 2 hours in diethyl ether. The resulting slurry was filtered and the triazolium salt was isolated as an off-white powder (Yield 65%, 10.3 g). ¹H-NMR (CD₃CN, 300 MHz): 9.17 (s, 1H), 7.77 (td, 2H), 7.61-7.48 (m, 7H), 7.44-7.41 (m, 2H), 2.46 (sept, 2H), 2.38 (sept, 2H), 1.32 (d, 6H), 1.18 (d, 6H), 1.12 (d, 6H), 1.01 (d, 6H).

Metalation - CoX₂^{DippMIC}₂ - Free mesoionic carbene was generated from the deprotonation of [^{Dipp}MIC-H]Cl (1 mmol, 0.502 g) in a slurry of 5 mL THF upon addition K(N(SiMe₃)₂) (1 mmol, 0.199 g) dissolved in 10 mL THF. The resulting mixture instantly turned brown upon addition of base and produced a white precipitate. The reaction was allowed to proceed overnight. KCl was removed via centrifugation and the supernatant containing free ^{Dipp}MIC was added to 0.45 equivalents of CoX₂ (X = Cl, Br, I) and stirred for 6 hours. Solvent was removed in vacuo and the solid was washed with Et₂O to remove excess MIC. The remaining solid was dissolved in THF, transferred into a tared vial, and the solvent was removed in vacuo to produce sapphire blue, aqua, and green

CoCl₂^{DippMIC₂} (**1**), CoBr₂^{DippMIC₂} (**2**), and CoI₂^{DippMIC₂} (**3**) respectively. Yields were 62%, 56%, and 55% for **1**, **2**, and **3** respectively. Sapphire blue, aqua, and green crystals suitable for X-ray analysis respectively were obtained by slow diffusion of pentane into toluene. Solid samples were air stable for at least 6 months stored in room temperature vials but were susceptible to degradation in wet THF—presumably from the protonation of ligand from water. CHN analysis (calc., found) for **1**: C (72.44, 73.23), H (7.41, 7.60), N (7.92, 7.29); for **2**: C (66.84, 67.68), H (6.84, 6.89), N (7.31, 7.36); for **3**: C (61.79, 61.77), H (6.32, 6.38), N (6.76, 6.43).

2 Tables, Equations, and Figures

Table S1: Selected bond lengths, angles, and distortion parameters for complexes 1-3

	d(Co-C) (Å)	d(Co-X) (Å)	α (largest L-Co-L) (°)	β (second largest L-Co-L) (°)	τ_8
CoCl ₂ ^{DippMIC₂} (1)	2.061/2.062	2.256/2.262	117.25(6)	116.87(1)	0.890
CoBr ₂ ^{DippMIC₂} (2)	2.044/2.054	2.408/2.416	116.79(3)	114.28(4)	0.895
CoI ₂ ^{DippMIC₂} (3)	2.089	2.609	117.25(0)	117.25(5)	0.890

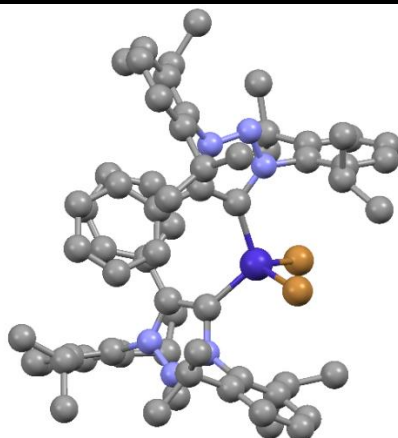


Figure S1: Crystal structure of **2** with spheres representing C (gray), Co (dark blue), N (light blue), and Br (orange). Hydrogen atoms have been omitted for clarity.

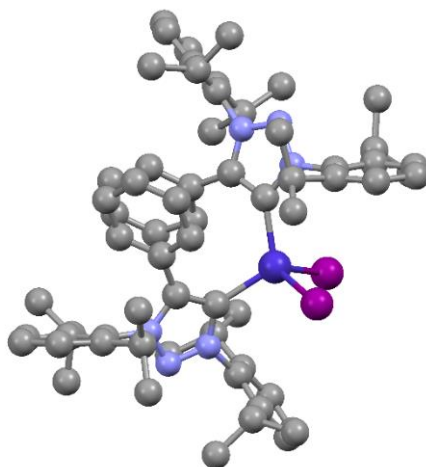


Figure S2: Crystal structure of **3** with spheres representing C (gray), Co (dark blue), N (light blue), and I (purple). Hydrogen atoms have been omitted for clarity.

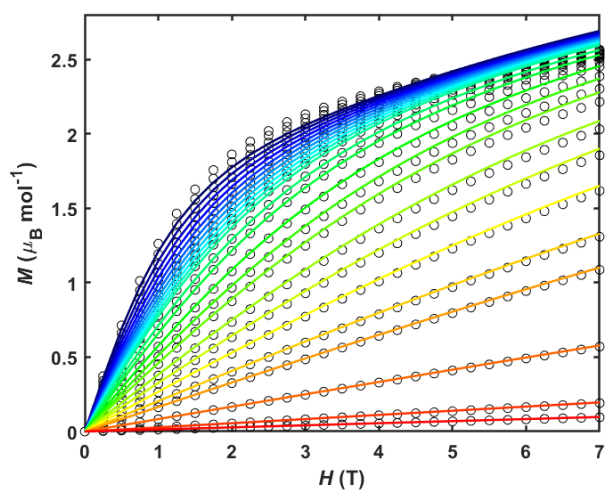


Figure S3: Plot of magnetization vs. magnetic field for **1** (black circles) along with data fits (from 2 K (black line) to 300 K (red line)). Fitting performed simultaneously with χT vs. T fit.

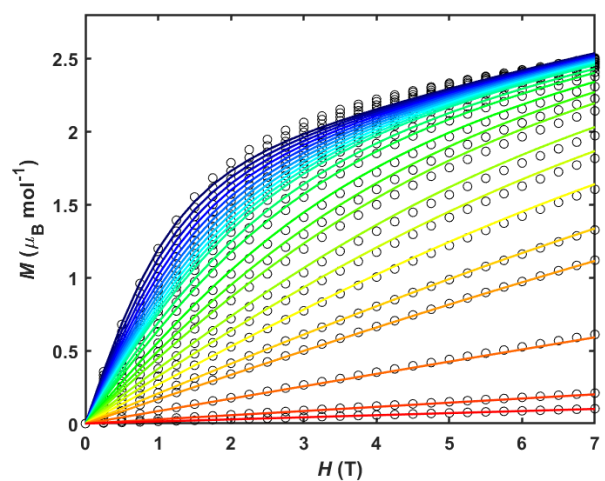


Figure S4: Plot of magnetization vs. magnetic field for **2** (black circles) along with data fits (from 2 K (black line) to 300 K (red line)). Fitting performed simultaneously with χT vs. T fit.

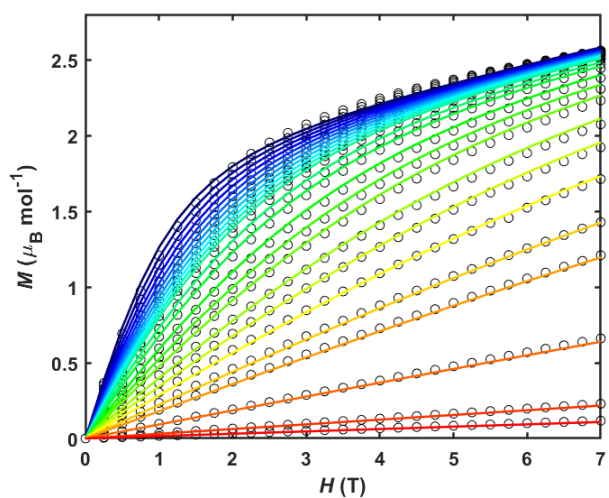


Figure S5: Plot of magnetization vs. magnetic field for **3** (black circles) along with data fits (from 2 K (black line) to 300 K (red line)). Fitting performed simultaneously with χT vs. T fit.

$$Residual = \left[\sum_{i=1}^{points} (M_{exp} - M_{calc})^2 \right] \left[\sum_{i=1}^{points} (\chi_{exp} - \chi_{calc})^2 \right]$$

Equation S1: Equation showing calculation of Residual values in PHI for modelling of magnetometry data

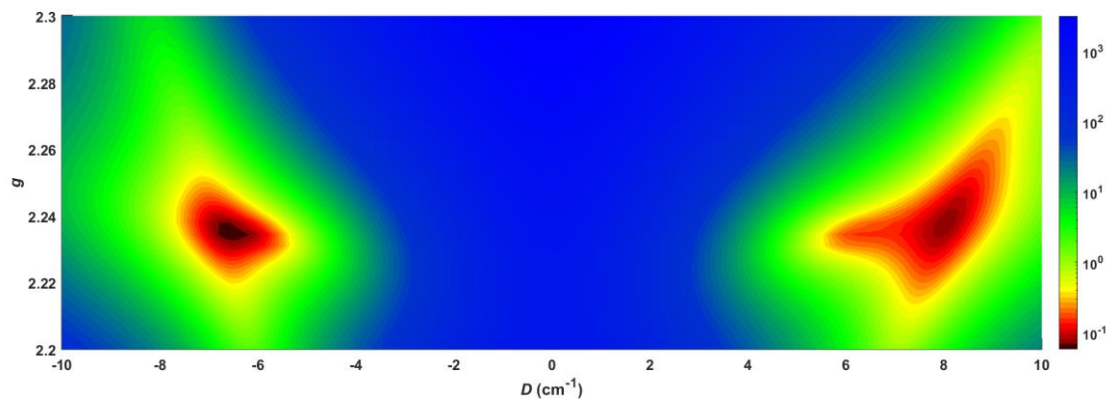


Figure S6: Survey of the effects of D and g on compound **1** showing two minima corresponding to a positive and negative D value. Color represents the magnitude of the residual.

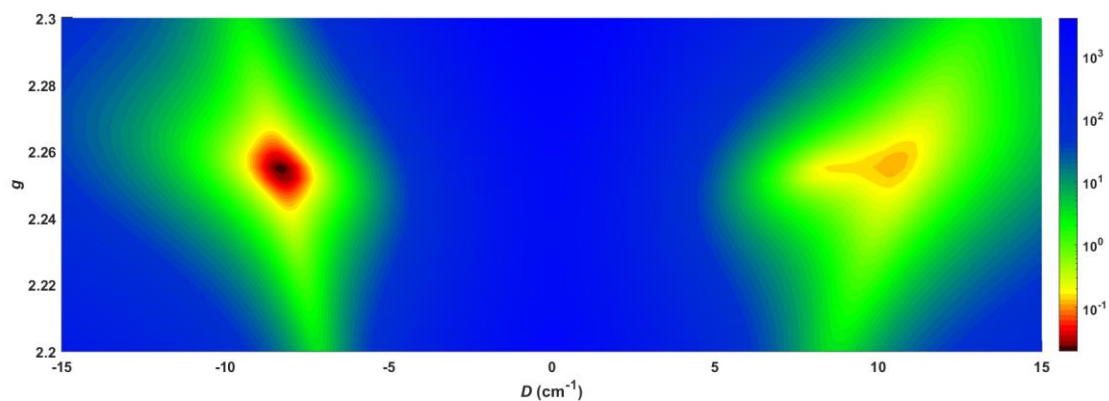


Figure S7: Survey of the effects of D and g on compound **2** showing two minima corresponding to a positive and negative D value. Color represents the magnitude of the residual.

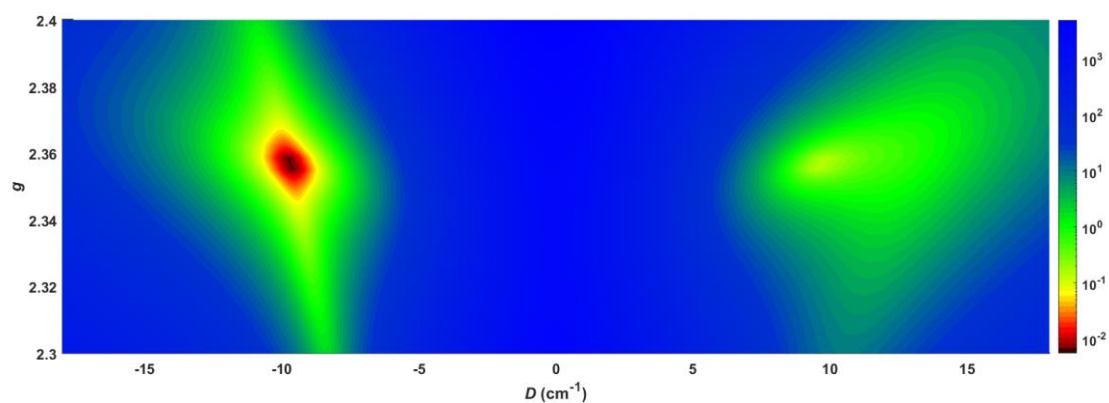


Figure S8: Survey of the effects of D and g on compound **3** showing two minima corresponding to a positive and negative D value. Color represents the magnitude of the residual.

Table S2: Best fits of compounds **1-3** for both positive and negative *D* wells seen in the surveys

	Negative <i>D</i> fit	Negative <i>D</i> residual	Positive <i>D</i> fit	Positive <i>D</i> residual
CoCl ₂ ^{Dipp} MIC ₂ (1)	$D = -6.54 \pm 0.02$ $g = 2.24$	0.05695	$D = 8.04 \pm 0.02$ $g = 2.24$	0.07284
CoBr ₂ ^{Dipp} MIC ₂ (2)	$D = -8.27 \pm 0.01$ $g = 2.25$	0.02008	$D = 10.47 \pm 0.03$ $g = 2.26$	0.12033
CoI ₂ ^{Dipp} MIC ₂ (3)	$D = -9.67 \pm 0.01$ $g = 2.36$	0.00518	$D = 9.68 \pm 0.02$ $g = 2.36$	0.12586

3. References

Note: References in SI are presented as an extension to those in the main text to allow for appropriate inclusion in citation metrics

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