Direct EXSY NMR observation of reversible Co-Co bond homolysis

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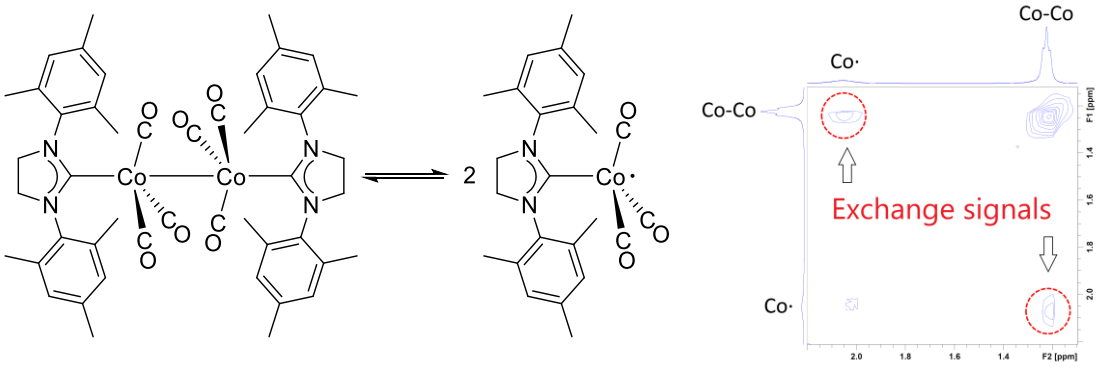
Bond homolysis is one of the two most fundamental bond breaking mechanisms in chemistry. Majority of bond homolysis is reversible reaction that favors recombination of the generated transient radical species. Steric crowding around radical center and delocalization of spin density shift this equilibrium towards generation of persistent radical species,[1] and by virtue of this stabilization, many radical species have been isolated.[2-4] Conventionally, this reversibility is observed as a temperature dependent reversible change of spectra, however real-time observation of reversible bond homolysis is unknown. Two-dimensional exchange NMR (2D EXSY NMR) and 2D IR spectroscopies are powerful methods to observe real-time chemical exchanges. Large number of chemical exchanges with wide range of exchange time scales have been studied using these methods however, it's application to observe reversible homolytic bond cleavage is unknown. *In this talk, we report the first real-time 2D EXSY NMR observation of reversible homolytic bond cleavage using dimeric cobalt complexes.*



(1) Griller, D. & Ingold, K. U. Persistent carbon-centered radicals. *Acc. Chem. Res.* **9**, 13-19 (1976).
(2) Sakamaki, D., Ghosh, S. & Seki, S. Dynamic covalent bonds: approaches from stable radical species. *Mater. Chem. Front.* **3**, 2270-2282 (2019).
(3) Hoff, C. D. Thermodynamic and kinetic studies of stable low valent transition metal radical complexes. *Coord. Chem. Rev.* **206-207**, 451-467 (2000).
(4) Takebayashi, S. & Fayzullin, R. R. [Co(NHC)$(CO)_3$]: Isolation and Reactivity Study of a Model 17-Electron Species in the Oxo Process. *Organometallics* **40**, 500-507 (2021).