

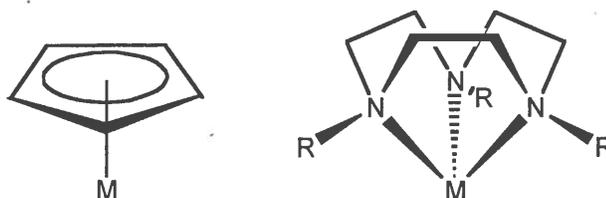
An Organometallic Approach to Iron Triazacyclononane Coordination Complexes

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Traditionally, coordination chemistry has been dominated by oxygen and nitrogen containing ligands. Recently, a renaissance in coordination chemistry has occurred by the application of the synthetic technique of organometallic chemistry to coordination compounds. Some of the advantages gained are air and water stability along with the absence of organic solvents. For example, a new breed of olefin polymerization catalysts based on iron imines has recently been discovered with activities that rival the metallocenes.¹ In this work, iron complexes of 1,4,7-triazacyclononane (TACN) and 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3TACN) are prepared. Their structures and properties are compared to the analogous organometallic (CpFe) complexes. TACN and Cp^- are similar in that they both bind facially and provide six electrons to the metal, yet they differ in charge and donating ability, leading to differences in the reactivity of the resulting complexes.²



A series of $(\text{Me}_3\text{TACN})\text{Fe}^{\text{II}}$ complexes with π -acceptor coligands has been prepared. Treatment of FeCl_2 with Me_3TACN gave a compound with the empirical formula $(\text{Me}_3\text{TACN})\text{FeCl}_2$. X-ray crystallography shows this complex to have the structure $[(\text{Me}_3\text{TACN})_2\text{Fe}_2\text{Cl}_3]^+[(\text{Me}_3\text{TACN})\text{FeCl}_3]^-$ (Figure 1). Treatment of $(\text{Me}_3\text{TACN})\text{FeCl}_2$ with NaBPh_4 gives $[(\text{Me}_3\text{TACN})_2\text{Fe}_2\text{Cl}_3](\text{BPh}_4)^3$ and treatment of $(\text{PPh}_4)_2[\text{FeCl}_4]$ with Me_3TACN gives $(\text{PPh}_4)[(\text{Me}_3\text{TACN})\text{FeCl}_3]$.

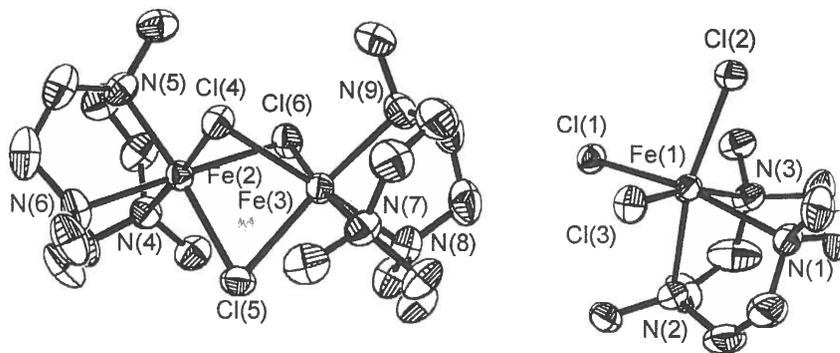
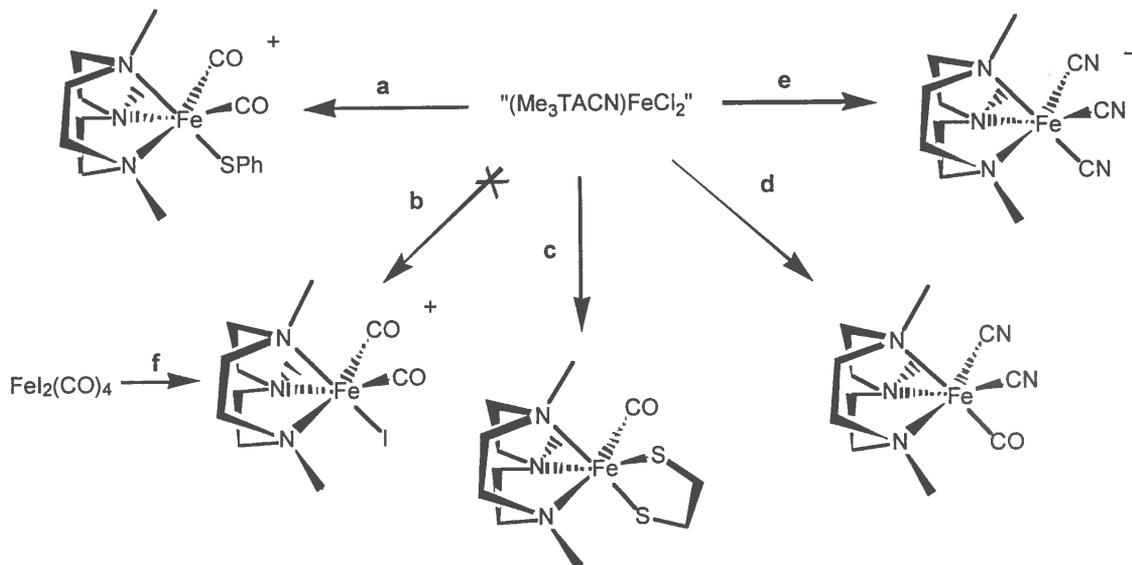


Figure 1

Solutions of $(\text{Me}_3\text{TACN})\text{FeCl}_2$ and thiolates absorb CO to give $[(\text{Me}_3\text{TACN})\text{Fe}(\text{CO})_2(\text{SPh})](\text{BPh}_4)$ ($\nu_{\text{CO}} = 2039, 1988 \text{ cm}^{-1}$) and $(\text{Me}_3\text{TACN})\text{Fe}(\text{CO})(\text{S}_2\text{C}_2\text{H}_4)$ ($\nu_{\text{CO}} = 1896 \text{ cm}^{-1}$). The reaction of $\text{Fe}(\text{CO})_4\text{I}_2$ and Me_3TACN affords $[(\text{Me}_2\text{TACN})\text{Fe}(\text{CO})_2\text{I}]$, a halide supported dicarbonyl with labile CO ligands ($\nu_{\text{CO}} = 2051, 2003 \text{ cm}^{-1}$). These reactions are summarized in as follows:



Conditions (25 °C): a, NaSPh, CO; b, CO (no reaction); c, $\text{Na}_2\text{S}_2\text{C}_2\text{H}_4$, CO; d, 2 CN^- , CO; e, excess CN^- ; f, Me_3TACN .

The reaction of $(\text{Me}_3\text{TACN})\text{FeCl}_2$ with excess cyanide affords $[(\text{Me}_3\text{TACN})\text{Fe}(\text{CN})_3]^-$, isolated as the PPh_4^+ salt. The tricyanide reacts with MeO_3SCF_3 to give the isocyanide complex, $(\text{Me}_3\text{TACN})\text{Fe}(\text{CN})_2(\text{CNMe})$. When two equiv. of cyanide is added to $(\text{Me}_3\text{TACN})\text{FeCl}_2$ under a CO atmosphere, $(\text{Me}_3\text{TACN})\text{Fe}(\text{CN})_2(\text{CO})$ is produced. This complex has a similar infrared signature to the NiFe hydrogenase enzymes.^{4,5} The oxidation potentials of these cyanide complexes were determined to vary widely based on the nature of the ligands and the polarity of the solvent.

The active site of NiFe hydrogenase features a bis(thiolate) bridged nickel-iron site, where the iron is bound to two carbonyls and a cyanide.⁷ The reaction of the square planar $\text{Ni}(\text{N}_2\text{S}_2)$,⁸ where $(\text{N}_2\text{S}_2)^{2-} = ^-\text{SCH}_2\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{S}^-$ and $(\text{Me}_3\text{TACN})\text{FeCl}_2$ gives $[\text{Ni}(\text{N}_2\text{S}_2)\text{FeCl}(\text{Me}_3\text{TACN})](\text{BPh}_4)$, a complex with a bis(thiolate) bridge between nickel and iron. The reactivity of this complex with CN^- and CO was explored.

References:

- (a) Britovsek, G. J. P.; Gibson, V. C.; Kimberly, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. "Novel Olefin Polymerization Catalysts based on Iron and Cobalt," *Chem. Comm.* **1998**, 849. (b) Small, B. L.; Brookhart, M.; Bennett, A. M. A. "Highly Active Iron and Cobalt Catalysts for Olefin Polymerization," *J. Am. Chem. Soc.* **1998**, *120*, 4049.

2. Chaudhuri, P.; Wieghardt, K. "The Chemistry of 1,4,7-Triazacyclononane and Related Tridentate Macrocyclic Compounds," *Prog. Inorg. Chem.* **1987**, *35*, 329.
3. Bossek, U.; Nuhlen, D.; Bill, E.; Glaser, T.; Krebs, C.; Weyhermüller, T.; Wieghardt, K.; Lengen, M.; Trautwein, A. X. "Exchange Coupling in an Isostructural Series of Face-Sharing Bioctahedral Complexes $[LM^{II}(-X)_3M^{II}L]BPh_4$ (M = Mn, Fe, Co, Ni, Zn; X = Cl, Br; L = 1,4,7-Trimethyl-1,4,7-Triazacyclononane)," *Inorg. Chem.* **1997**, *36*, 2834.
4. Volbeda, A.; Garcin, E.; Piras, C.; de Lacey, A. L.; Fernandez, V. M.; Hatchikian, E. C.; Frey, M.; Fontecilla-Camps, J. C. "Structure of the [NiFe] Hydrogenase Active Site: Evidence for Biologically Uncommon Fe Ligands," *J. Am. Chem. Soc.* **1996**, *118*, 12989.
5. (a) Darensbourg, D. J.; Riebenspies, J. H.; Lai, C-H.; Lee, W-Z.; Darensbourg, M. Y. "Analysis of an Organometallic Iron Site Model for the Heterobimetallic Unit of [NiFe] Hydrogenase," *J. Am. Chem. Soc.* **1997**, *119*, 7903. (b) Lai, C-H.; Lee, W-Z.; Miller, M. L.; Riebenspies, J. H.; Darensbourg, D. J.; Darensbourg, M. Y. "Responses of the Fe(CN)₂(CO) Unit to Electronic Changes as Related to Its Role in [NiFe] Hydrogenase," *J. Am. Chem. Soc.* **1998**, *120*, 10103.
6. Mascharak, P. K. "Convenient Synthesis of Tris(tetraethylammonium) Hexacyanoferrate(III) and Its Use as an Oxidant with Tunable Redox Potential," *Inorg. Chem.* **1986**, *25*, 245.
7. Volbeda, A.; Charon, M-H.; Piras, C.; Hatchikian, E. C.; Frey, M.; Fontecilla-Camps, J. C. "Crystal Structure of the Nickel-Iron Hydrogenase from *Desulfovibrio gigas*," *Nature* **1995**, *373*, 580.
8. Karlin, K. D.; Lippard, S. J. "Sulfur Bridged Binuclear Iron(II) Complexes. Effect of Ligand Constraints on their Physical Properties; Reaction with Carbon Monoxide and Alkyl Isocyanides," *J. Am. Chem. Soc.* **1976**, *98*, 6951.

