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Toward the Design of Double Metal Cyanides for the Copolymerization of CO_2 and Epoxides

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The coupling of CO_2 and epoxides to afford polycarbonates has received increased interest over the past decade,[1] following the initial discovery of this process by Inoue in 1969.[2] Indeed, research activity in this area is spurred on by the potential of synthesizing these extremely important thermoplastics via an environmentally benign route.[3] Further progress in this endeavor is hindered by the observation that upon replacing *alicyclic* epoxides, such as cyclohexene oxide, with *aliphatic* epoxides, cyclic carbonate production is dominant over polycarbonate formation at desirable reaction conditions.[4] In the patent literature there exists a heterogeneous catalyst system which appears to overcome some of the shortcomings of the recently developed homogeneous catalysts which are so active for alicyclic epoxides.[5] This catalyst system is referred to as a Double Metal Cyanide (DMC) and is comprised of a metal ion (M^1) which form a strong bond to oxygen and a metal (M^2) cyanide salt, e.g., $[M^1]_n[M^2(CN)_6]_m$. One of the most preferable catalyst precursors is zinc hexacyanoferrate(III). To achieve high activity with these catalysts, an organic coordinating reagent is also required, such as an alcohol. Similar catalysts are also shown to be useful for epoxide polymerization to polyethers.[6] Nevertheless, these rather complex catalysts are poorly defined with respect to a detailed understanding of their structures and reaction pathways. Because of our interest in the CO_2/epoxide copolymerization process and in the design of new metallacyclic polygons,[7] we report herein the syntheses and structures of heterometallic derivatives of zinc(II) and iron(II) containing bridging cyanide ligands.

In an effort to prepare a soluble complex which might possess structural and reactivity properties similar to those of the Dow DMC polycarbonate catalyst, we reacted $[K][CpFe(CN)_2CO]$ with an aqueous solution of zinc chloride. The selection of $[K][CpFe(CN)_2CO]$ as a cyanometalate source was made since the cyclopentadienyl and carbonyl groups should hinder the three-dimensional aggregation that usually occurs when using metal hexacyanide reagents. Indeed, reaction of this salt with copper(I) in the presence of phosphines led to a variety of soluble diamond-shaped metallocyanide complexes possessing Fe(II) and Cu(I) centers bridged by cyanide ligands.[7,8] However, the product resulting from the reaction of $ZnCl_2$ with the $CpFe(CN)_2(CO)^-$ anion was found to be insoluble in water and all common organic solvents. Elemental analysis indicated a complex with an Fe/Zn of two and no detectable chloride, i.e., a simple metathesis product $[Zn][CpFe(CN)_2(CO)]_2$, **1**.[9] The solid-state (KBr) infrared spectrum of complex **1** revealed two cyanide and two carbonyl stretching vibrations at 2139 and 2119 cm^{-1}, and 1986 and 1973 cm^{-1}, respectively. These are all shifted to higher wavenumbers as compared to the $[K][CpFe(CN)_2CO]$ starting reagent, which is suggestive of bridging cyanide ligands. This is substantiated by the solid-state ^{13}C and ^{15}N NMR spectra, where the CN ligands are all shown to be magnetically equivalent with a carbon resonance at 158.3 ppm, which is shifted downfield by 15.9 ppm from that of the free complex, and the nitrogen resonance at 251.7 ppm, which is shifted by 64.3 ppm upfield from that of the free complex. Hence, the structure of $[Zn][CpFe(CN)_2CO]_2$ appears to possess a motif with bridging cyanide groups tetrahedrally coordinated to the zinc centers (Figure 1).

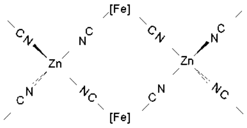

Figure 1. Skeletal representation of $Zn[CpFe(CN)_2CO]_2$, complex **1**.

To synthesize a more tractable derivative, zinc iodide was reacted with $[K][CpFe(CN)_2PPh_3]$ which afforded a product found to be soluble in acetonitrile, $[CpFe(PPh_3)(\mu\text{-}CN)_2ZnI(CH_3CN)]_2$, **2**. Complex **2** exhibits ν(CN) vibrational modes at 2092 and 2082 cm^{-1} in CH_3CN which are, as in complex **1**, shifted to higher wavenumbers over those of the parent salt, where the vibrational modes occur at 2059 and 2053 cm^{-1}. Although single crystals of **2a** were obtained from a THF/hexane solution, thus far the structure refinement is not sufficient for publication. Nevertheless, the atom connectivity is clear where the iron and zinc metal centers are linked by cyanide ligands, with PPh_3 and Cp ligands on opposite sides of the $[FeCNZn]_2$ plane (see Supporting Information).

The solid-state structure of a closely corresponding derivative of complex **2a** has been determined. That is, X-ray quality crystals of the complex prepared from the reaction of zinc iodide with $[KCpFe(CN)_2PPh_2(CH_2)_{1.5}]_2$ (**3**) in acetonitrile were obtained from THF/hexane at −20 °C.[10,11] Complex **3** was synthesized photo-

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[9] Elemental analysis calculated for $Zn[CpFe(CN)_2CO]_2\cdot H_2O$: C, 39.59; H, 2.49; N, 11.54; O, 9.89. Found: C, 39.30; H, 2.15; N, 12.16; O, 10.30; Cl, <0.3.

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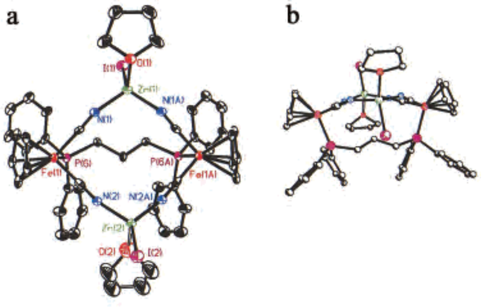
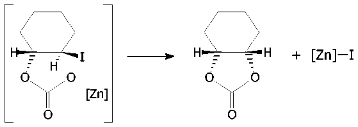


Figure 2. (a) Molecular structure of **4**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Fe−C(1) 1.838(10), Fe−C(2) 1.851(11), Zn(1)−N(1) 1.943(8), Zn(2)−N(2) 1.946(8), Zn(1)−O(1) 2.058(10), Zn(2)−O(2) 2.046(5), Fe(1)−C(1)−N(1) 178.6(9), Fe(1)−C(2)−N(2) 178.5(9), Zn(1)−N(1)−C(1) 156.0(8), Zn(2)−N(2)−C(2) 167.9(7), N(1)−Zn(1)−N(1)$^{\#}$1 110.8(5), N(2)−Zn(2)−N(2)$^{\#}$1 106.5(4), I(1)−Zn(1)−O(1) 106.7(3), I(2)−Zn(2)−O(2) 119.7(2). Corresponding interatomic parameters in $Na_2Zn_3[Fe(CN)_6]_2{\cdot}9H_2O$:[14] Fe−C 1.881(3), Zn−N 1.9685(7) Å, Fe−C−N 178.8(7), Zn−N−C 159.7(6), and N−Zn−N 110(4)°. b) View of molecular structure of **4** with the $[FeCNZn]_2$ unit perpendicular to page.

chemically from $[K][CpFe(CN)_2CO]$[12] and 0.5 equiv of dppp(diphenylphosphinopropane).[13] Figure 2 depicts a thermal ellipsoid representation of complex **4**, $[CpFe(\mu\text{-}CN)_2ZnI(THF)]_2\text{-}\mu\text{-}dppp$. As is readily seen in Figure 2, the structure of **4** consists of a nonplanar diamond-shaped arrangement of $[FeCNZn]_2$ with a bridging dppp ligand and two cyclopentadienyl ligands on opposite sides of the metal grouping. Unlike complex **2a**, the phosphine ligands bound to the two iron(II) centers are restricted to the same face of the $[FeCNZn]_2$ core. The puckering in the metallocyanide plane is caused by the short carbon chain bridging the phosphine ligand which links the $CpFe(CN)_2$ units (Figure 2b). The zinc centers coordination spheres are completed by an iodide and a THF ligand. As noted in Figure 2, the interatomic parameters seen in complex **4** are similar to those found in the anionic framework of the porous ion-exchange solid $Na_2Zn_3[Fe(CN)_6]_2{\cdot}9H_2O$.[14] These latter type zinc hexacyanoferrate(II) species are of great interest and have been examined in considerable detail because of their role in the isolation of ^{137}Cs from other radionuclides.[14,15] These derivatives exist as octahedral $[Fe(CN)_6]^{-4}$ units linked to tetrahedral Zn^{2+} ions, leading to hexagonal bipyramidal cages which are capable of encapsulating alkali metal ions,[16] and to our knowledge, these derivatives represent the only other single crystals containing the $[FeCNZn]_2$ unit crystallographically characterized.

The structure of complex **4** reveals each zinc center to possess a site for epoxide binding in addition to an anion for intramolecularly ring-opening the activated epoxide monomer. Our initial attempt at employing complex **4** as a catalyst for the copolymerization of carbon dioxide and cyclohexene oxide resulted mostly in the production of cyclic carbonate (*cis*-7-9-dioxabicyclo[4.3.0]nonan-8-one), about 80% of the total $\nu(CO_2)$ intensity, and low-molecular weight polycarbonate, which contained 16% polyether linkages. Interestingly, the cyclic carbonate produced was exclusively of cis stereochemistry.[17] In related studies involving bis(phenoxide)zinc catalysts, which are quite active for polycarbonate production, the small quantity of cyclic cyclohexene carbonate produced is exclusively trans, as expected from the degradation of the polymer or growing polymer chain.[4] Evidently, the cis cyclic carbonate afforded in this instance is the consequence of a double inversion process at the epoxide carbon center, as illustrated in eq 1.[18]



This might be anticipated here because there is little polymer formation and a good leaving group(iodide) present, both features which should facilitate cis cyclic carbonate production. Initial observations indicate that replacing the iodide ligand with phenoxide, a better initiator, affords polycarbonates with >85% carbonate linkages in significantly greater quantities than trans cyclic carbonate. In the underdefined DMC catalysts in the literature, the initiator is presumably a hydroxide or alkoxide ligand.[1b,5,6]

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Supporting Information Available: A ball-and-stick representation of complex **2a**; complete details of the X-ray diffraction study of complex **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) A slurry of 0.23 g of ZnI_2 in CH_3CN was added to 0.30 g of **3** via cannula under an argon atmosphere. The orange reaction mixture rapidly turned yellow and turbid. The solution was allowed to stir for approximately 30 min followed by solvent evaporation to dryness. Dry THF was then added to the crude product, and the KI byproduct was removed by filtration through Celite. The solvent was removed under vacuum to yield 0.31 g of yellow $[CpFe(\mu\text{-}CN)_2ZnI(THF)]_2\text{-}\mu\text{-}dppp$ (**4**). ^{31}P NMR(THF): 71.8 ppm. IR(THF): ν_{CN} 2088 and 2082 cm^{-1}.

(11) Crystallographic data for **4**: $C_{30}H_{30}Fe_2I_2N_4O_2P_2Zn_2$, M = 1036.76, orthorhombic, space group *Pnma*, $a = 29.029(11)$, $b = 18.924(7)$, $c = 9.052(4)$ Å, V = 4973(3) Å^3, $Z = 6$, $\rho_{calcd} = 2.077$ mg/m^3, μ(Mo Kα) = 4.282 mm^{-1}, T = 110(2) K, $R(F^2)(R_w(F^2)) = 0.0541(0.1276)$ for 6279 data with $I > 2\sigma(I)$.

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(13) A mixture of 0.75 g of $[K][CpFe(CN)_2CO]$[12] and 1.29 g of dppp in $MeOH/CH_3CN$, 1:1 by volume, was added to a cylindrical Pyrex photolysis vessel and irradiated using a mercury lamp for 40 min under a nitrogen purge. The solvent mixture was removed under vacuum, and the resulting solid was redissolved in methanol. The solution was filtered through Celite, and again, the solvent was removed by vacuum to yield 1.38 g of a dark orange $[KCpFe(CN)_2]_2\text{-}\mu\text{-}dppp$ (**3**). ^{31}P NMR(MeOH): 76.9 ppm. IR(MeOH): ν_{CN} 2050, 2032 cm^{-1}.

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