Inorg. Chem. 1988, 27, 2955–2958

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Carbon Monoxide Binding by Copper(I) Complexes Supported on Polystyrene

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Received January 13, 1988

This article reports the preparation and characterization of a series of copper(I) complexes consisting of ligands that are covalently attached to cross-linked polystyrene. Reversible binding of CO to these copper(I) complexes is described, and the stability of the systems to oxidation is shown to vary considerably. The complexes [P]-DCEACuX have potential for applications in membrane or pressure-swing recovery of CO from gas streams. The bound complexes are shown to differ from the products of the reaction of copper(I) with the analogous ligands in solution.

Introduction

Earlier research from this laboratory has shown that cobalt(II) complexes covalently attached to polystyrene, [P]-CoSMDPT,[1] will reversibly bind molecular oxygen even though O_2 is not bound by the complex Co(SMDPT) in the solid state.[2] The functionalized polystyrene could be added as a powder to a polystyrene film to facilitate the transfer of molecular oxygen through the membrane.[3] It is of interest to functionalize other transition metal ion complexes and to study their ability to coordinate small gaseous molecules.

The precursor to formation of [P]-SMDPT is [P]DCEA (DCEA = bis(2-cyanoethyl)amine, $HN(CH_2CH_2CN)_2$). The ligand DCEA forms a 2:1 complex with $CuCl_2$.[4,5] The DCEA appears to coordinate through the amine nitrogen. A very weak interaction with the nitriles is evidenced by a single weak ν_{CN} stretch in the IR spectrum at 2258 cm^{-1} (free ligand 2250 cm^{-1}).[13] The shift in frequency to a higher value is indicative of the nitrile being N-bound with little π-back-bonding. The amine–copper bond leads to a value for the ν_{NH} stretch at 3202 cm^{-1}, lower than that of the free ligand (3335 cm^{-1}).[4] These results suggest the possibility of preparing copper complexes with [P]-DCEA.

The reversible binding of carbon monoxide by copper(I) complexes is an area of considerable interest with respect to gas separations. A primary application is the recovery of CO from industrial byproduct gas streams. Liquid absorption processes are commonly used for the separation of carbon monoxide from gas mixtures, and most are based on copper(I) chemistry. The most notable commercial development, the COSORB process, involves a $CuAlCl_4$ complex in an aromatic base.[6,7] Relatively few studies have been conducted on solid-state absorbents, and metal complexes that bind CO in solution often do not bind CO as a crystalline solid because of lattice constraints. Solid copper(I) chloride binds CO only under extreme conditions, and in the presence of moisture it is both light- and air-sensitive.[8,9] However, when CuCl is supported on active carbon, it is a reversible CO carrier that is stable to moisture.[10] Similarly, $CuAlCl_4$, the active component in the CSORB process, was recently supported on active carbon[11,12] and polystyrene[13-15] and was found to be an effective absorbent for CO. Linear- or gel-type cross-linked polystyrene supports were far less active than macroreticular or macroporous supports presumably due to diffusional problems.

In view of the above considerations, it was decided to study the coordination chemistry of [P]-DCEA and DCEA with copper(I). The results of these experiments as well as those of [P]-$N(CH_3)_2$ are reported herein. Reversible binding of CO with the resulting copper(I) complexes is described.

Experimental Section

Infrared spectra were recorded on a Nicolet 5DXB Fourier-transform infrared spectrophotometer using sodium chloride disks for Nujol mulls. X-Band ESR spectra were obtained with a Bruker ER 200D-SRC spectrometer. All syntheses were carried out in a dry inert-atmosphere box unless otherwise specified. Acetonitrile was distilled from P_2O_5 and freeze–pump–thawed prior to use. All other reagents were used as received.

CuCl. Copper(I) chloride was prepared according to the literature procedure and stored in the dark under nitrogen.[9]

CuI. Copper(I) iodide was purchased from Aldrich Chemical Co. and recrystallized from acetonitrile with deionized water. The white solid was dried at 60 °C under vacuum and then stored in the dark under nitrogen.

[P]-CH_2Cl. The chloromethylated linear polystyrene as well as the 4% divinylbenzene (DVB) cross-linked, 90% chloromethylated polystyrene beads were provided by Sybron Corp. This degree of cross-linking imparts macroreticular character to this polymeric support.

[P]-DCEA. Bis(2-cyanoethyl)amine (DCEA) supported on DVB cross-linked polystyrene beads was prepared as previously described.[2]

[P]-DCEA(l). The linear polystyrene-supported DCEA was prepared as follows. Ten grams of [P]-CH_2Cl was dissolved in 150 mL of dioxane. Into the solution was stirred 30 mL of bis(2-cyanoethyl)amine for 30 min at room temperature and then at low heat for 2 days. The solution was filtered and methanol added to the filtrate until a gelatinous precipitate formed. The solid was redissolved in CH_2Cl_2, the solution was filtered, and methanol was added to the filtrate until a white precipitate formed. The isolated [P]-DCEA was dried in vacuo. Anal. Calcd for 40% substitution: C, 74.9; H, 6.5; N, 7.0. Found: C, 73.8; H, 6.8; N, 7.0.

[P]-(DCEA)CuX. Excess copper(I) halide dissolved in dry acetonitrile was slurried with 1 g of [P]-DCEA for 12 h at room temperature in an inert-atmosphere box. The resin was suction-filtered, washed with CH_3CN, and then dried under nitrogen.

[P]-(DCEA)CuCl(l). In a dry inert-atmosphere box 1 g of [P]-DCEA(l) was stirred with 1 g of CuCl in 80 mL of acetonitrile at room temperature for 24 h. The sticky orange resin was suction-filtered and dried in vacuo.

BzlDCEA. Benzylbis(2-cyanoethyl)amine was prepared according to the published procedure.[2]

[P]-$N(CH_3)_2$. Twenty grams of [P]-CH_2Cl was slurried with 50 g of aqueous dimethylamine under argon at room temperature for 20 h. The resin was suction-filtered, washed with dioxane, 50/50 dioxane/water, water, and 50/50 water/tetrahydrofuran, and dried in vacuo at 80 °C.

[P]-$N(CH_3)_2CuCl$. In an inert-atmosphere box 2 g of [P]-$N(CH_3)_3$ was slurried with excess CuCl in 50 mL of acetonitrile for 5 h. The pale yellow resin was suction-filtered, washed with CH_3CN, and dried under N_2.

[P]-$CH_2ClCuCl$. In an inert-atmosphere box 1 g of [P]-CH_2Cl was slurried with excess CuCl in 50 mL of acetonitrile for 24 h at room temperature. The resin was suction-filtered, washed with acetonitrile, and dried under nitrogen.

Results and Discussion

When [P]-DCEA is reacted with $CuCl_2$ in refluxing ethanol, a yellow resin results with the ESR spectrum in Figure 1. The IR spectrum contains a CN stretch at 2248 cm^{-1} (free ligand 2250 cm^{-1}). When soluble non-cross-linked [P]-DCEA(l) and $CuCl_2$

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(1) CoSMDPT = cobalt(II) bis(3-(salicylideneamino)propyl)methylamine; [P] = polystyrene.
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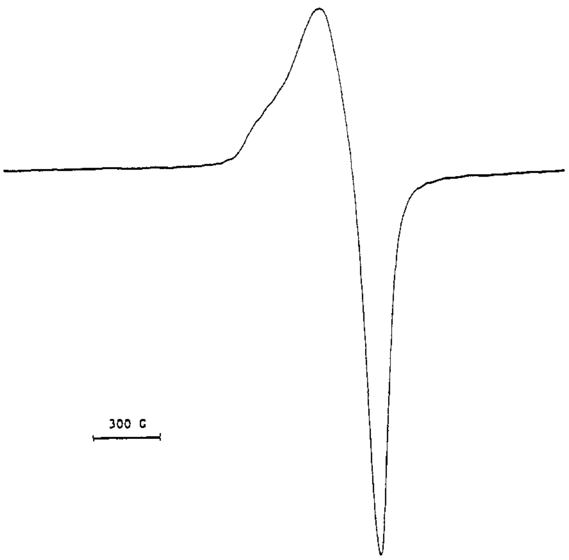
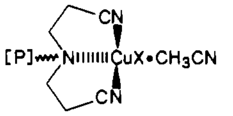


Figure 1. X-Band ESR spectrum of [P]-(DCEA)$CuCl_2$. $g \approx 2.13$ (93 K).

are reacted in boiling acetonitrile, yellow resin results with the same ESR spectrum. In this case, bound nitriles are indicated by a shift in the ν_{CN} value to 2257 cm^{-1}. When CuI or CuCl is reacted with [P]-DCEA, the resulting resin shows no IR shifts in the nitrile region. When this resin is exposed to air and placed in an aqueous ammonia solution, $Cu(NH_3)_4^{2+}$ is leached into the solution, indicating that copper had been incorporated into the resin. This result, coupled with the absence of an ESR signal, indicates that the product of the CuX reaction must contain Cu(I). It should be further noted that dry functionalized polymer remains ESR-silent even upon exposure to air. This Cu(I)-containing resin, which has only been dried under nitrogen, is unreactive toward carbon monoxide. However, if the polymer beads are placed under a vacuum and then exposed to a CO atmosphere, binding of CO is observed. The Cu(I) complex probably is solvated prior to evacuation, rendering the Cu(I) coordinatively saturated and inert toward CO. It is known that copper(I) halides form 1/1 complexes with acetonitrile[16] that are very air-sensitive and easily lose the nitrile. We conclude that the product of the reaction of [P]-DCEA with CuCl or CuI in acetonitrile is [P]-DCEACuX·S:



When X is I$^-$, the complex binds carbon monoxide, leading to a value of ν_{CO} = 2091 cm^{-1}. When X = Cl$^-$, the complex also binds CO reversibly with ν_{CO} = 2100 cm^{-1}. The reversibility was demonstrated by placing the resin in a high-pressure apparatus previously described.[17] After evacuation to less than 1 mmHg, the polymer beads are subjected to 15 psig of CO. The CO is then removed by reducing the pressure to less than 1 mmHg. A typical cycle is shown in Figure 2. Five absorption/desorption cycles were carried out without any loss in activity. Higher CO pressure than 15 psig of CO leads to an increase in the intensity of ν_{CO} for the carbonylated complexes. Figure 2D shows the IR spectrum for a [P]-(DCEA)CuCl sample after exposure to 25 psig of CO (ν_{CO} = 2094 cm^{-1}). Upon exposure of the resin to air after evacuation, the ability of the complex to bind CO was greatly diminished. Placing the air-exposed sample under a vacuum partially restores the ability to bind CO. The Cu(I) complex formed with the linear [P]-DCEA(l) was not observed to bind CO under the same conditions. In this case the Cu(I) may be coordinatively saturated. This is consistent with our having observed a shifted ν_{CN} (2257 cm^{-1}) value for this material, indicating nitrile coordination in the more flexible non-cross-linked resin. The porous nature of the macroreticular resin also provides diffusion pathways for the CO while the CO must permeate through the amorphous regions of the linear polymer. The importance of the nature of the polymeric support is further demonstrated by an attempt to prepare a silica-bound (DCEA)CuX complex. Even with careful preparative techniques, the Cu(I) was oxidized to copper(II).

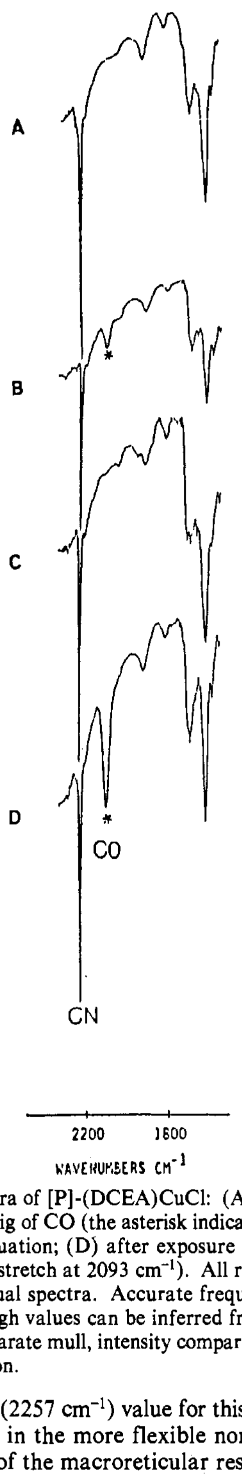


Figure 2. FT-IR spectra of [P]-(DCEA)CuCl: (A) after evacuation; (B) after exposure to 15 psig of CO (the asterisk indicates CO stretch at 2100 cm^{-1}); (C) after evacuation; (D) after exposure to 25 psig of CO (the asterisk indicates CO stretch at 2093 cm^{-1}). All reported IR spectra are composites of individual spectra. Accurate frequencies are reported in the text, and only rough values can be inferred from the figures. Since each spectrum is a separate mull, intensity comparisons can only be made in a qualitative fashion.

In order to discern the nature of the bound species in [P]-(DCEA)CuX, the preparation of a solution analogue was attempted. When copper(I) salts are reacted with DCEA in acetonitrile under Ar, rapid disproportionation occurs, as evidenced by the formation of a copper mirror on the reaction vessel and a green solid. Certain saturated amines are reported[18] to promote the disproportionation of Cu(I). ESR data indicate that the green compound is a Cu(II) complex. The IR spectrum of the copper(II)

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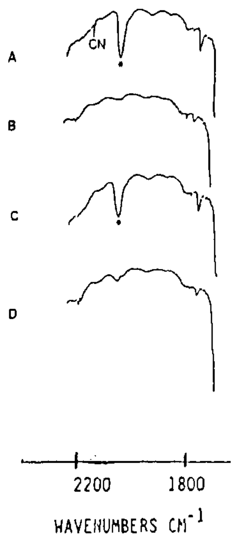

Figure 3. FT-IR spectra of [P]-N$(CH_3)_2$CuCl: (A) after exposure to 25 psig of CO (solvated complex; the asterisk indicates CO stretch at 2065 cm^{-1}); (B) after evacuation; (C) after exposure to 26 psig of CO; (D) after evacuation and exposure to air and then 2k psig of CO.

complex showed no shift in ν_{CN} but ν_{NH} shifted to 3296 cm^{-1}. The reported Cu$(DCEA)_2Cl_2$ is bright purple, so the green solid obtained from the Cu(I) disproportionation probably involves only amine coordination as suggested by the absence of a ν_{CN} shift. Covalent attachment of the DCEA ligand to a solid polymeric support would result in a tertiary amine, so a better solution homologue would be bzlDCEA. Acetonitrile solutions of CuCl and bzlDCEA are unreactive toward carbon monoxide at room temperature. However, at 0 °C two CO stretches are observed in the IR spectrum at 2025 and 1994 cm^{-1}, indicative of a strongly bound terminal CO and possibly a bridging CO. An acetonitrile solution containing only CuCl behaves in the same fashion. It is well-known that copper(I) halides absorb CO in organic solvents at room temperature (CH_3OH, 2070 cm^{-1}; THF, 2085 cm^{-1}).[19] It is sufficient to say that polymer-supported complexes react in a manner unlike that of similar species generated in solution and characterization of the solution species would be irrelevant to the behavior in the polymer.

The unshifted ν_{CN} in the copper(I) complexes of the macroreticular resin suggested our next variation in the synthesis of supported copper(I) complexes. Cross-linked polystyrene beads previously reacted with dimethylamine were reacted with CuCl, yielding a tan complex formulated as [P]-N$(CH_3)_2$CuCl·$n$$CH_3CN$. This complex binds carbon monoxide (ν_{CO} = 2065 cm^{-1}) more strongly than [P]-(DCEA)CuCl, and the binding is also reversible. A typical absorption/desorption cycle is shown n Figure 3. It should be noted that CO is bound when the complex is still partially solvated by acetonitrile and the subsequent loss of the CN stretch with repeated cycles has no noticeable qualitative effect on the CO-binding ability of the complex.

Exposing the tan resin to air instantly changes the color to orange, resulting in the ESR spectrum shown in Figure 4. The orange resin shows a weak peak at 2066 cm^{-1} upon exposure to CO. Placing the orange resin under a 10^{-4} mmHg vacuum for 5 h reduces the intensity of the ESR signal. If the orange resin is allowed to stand in air for several days, it changes to an orange-green color accompanied by an increase in the intensity of the ESR signal, but no changes occur in the general features of the spectrum. The nature and reactivity of [P]-N$(CH_3)_2$CuCl are clearly different from those observed for [P]-(DCEA)CuCl.

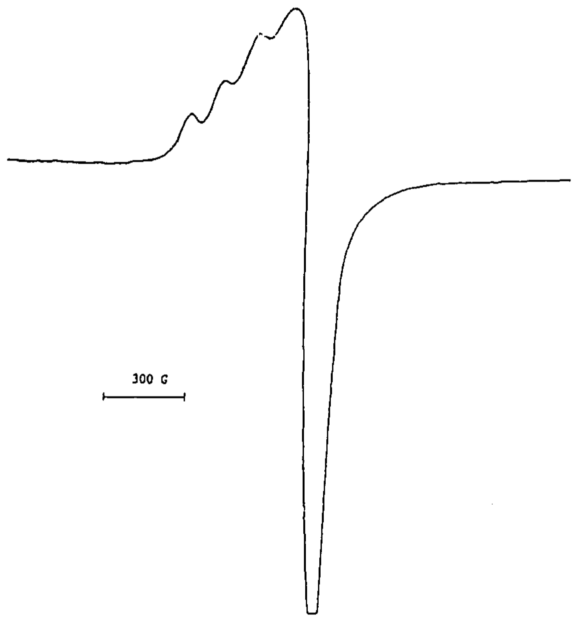

Figure 4. X-Band ESR spectrum of [P]-N$(CH_3)_2$CuCl (orange) after exposure to air. $g_\perp \approx 2.09$, and $g_\parallel \approx 2.28$ (298 K).

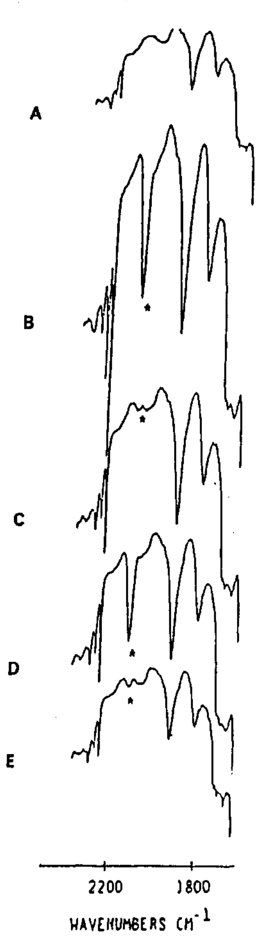

Figure 5. FT-IR spectra of [P]-CH_2Cl·CuCl·$n$$CH_3CN$: (A) after preparation; (B) after exposure to 25 psig of CO (the asterisk indicates CO stretch at 2096 cm^{-1}); (C) after evacuation; (D) after exposure to 25 psig of CO; (E) after evacuation and exposure to air and then to 25 psig of CO.

The next variation involved simply adsorbing CuCl onto the polystyrene beads from an acetonitrile solution. If it is kept in mind that solid copper(I) chloride binds CO only under extreme conditions, it is very interesting that [P]-CH_2Cl·CuCl·$n$$CH_3CN$ reversibly binds CO at room temperature. Apparently, Cu$(CH_3CN)_x$Cl forms a charge-transfer complex with the aromatic rings of polystyrene. Such an interaction has been proposed for the case of $CuAlCl_4$ and polystyrene.[13-15] A typical absorption/desorption cycle is shown in Figure 5. The CO is bound weakly (ν_{CO} = 2096 cm^{-1}) and is not completely removed upon

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exposure to reduced pressure. Also in contrast to the case for the other complexes, the CN stretch (ν_{CN} = 2252 cm^{-1}) does not decrease in intensity even after repated cycling. In the presence of air, the ability of [P]-$CH_2Cl{\cdot}CuCl{\cdot}nCH_3CN$ to bind CO is drastically reduced and an ESR signal is observed. This complex is apparently not present in significant concentrations in [P]-(DCEA)CuX and [P]-N$(CH_3)_2$CuX. In the case of [P]-N-$(CH_0)_2$CuX a large change in ν_{CO} is observed and no CN stretch is observed. Although the ν_{CO} frequencies of [P]-CH_2Cl and [P]-DCEA adducts of CO are similar, the [P]-(DCEA)CuX complex must be pumped on to remove solvating CH_3CN before CO complexation occurs, whereas [P]-$CH_2Cl{\cdot}CuCl{\cdot}nCH_3CN$ binds CO without such pretreatment.

In conclusion, heterogenizing copper(I) halides on functionalized cross-linked polystyrene has afforded both complexes and reactivity not observed in solution. As demonstrated above, the polymer matrix serves to provide a hydrophobic environment that appears to stabilize Cu(I) salts in the solid state. One of the advantages of the polymer-supported complexes is the elimination of lattice energy effects present in many solid-state metal complexes, which prevent small-molecule binding. The permeability and functional groups in the polymer provide variables permitting one to adjust the extent and rates of carbonylation. We expect these supported Cu(I) complexes to find application in pressure-swing recovery or in the facilitated transport of CO in polymer membranes. Efforts in this regard are under way.

Acknowledgment. This research was supported by the National Science Foundation through Grant 86 18761.

Registry No. CuCl, 7758-89-6.

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and Dalian Institute of Chemical Physics, Academia Sinica, Dalian, China

Preparation and Structural-Bonding Characterization of a 50-Electron Triangular Cobalt Cluster, $[Co(C_5H_4CO_2Me)]_3(S)(N^tBu)$, with Triply Bridging Sulfido and Imido Ligands: Singlet-Triplet Equilibrium in Solid and Solution States

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Received January 28, 1988

A 50-electron tricobalt cluster, $[Co(C_5H_4CO_2Me)]_3(S)(N^tBu)$ (**1**), has been prepared by the reaction of $Co(C_5H_4CO_2Me)$(1,5-cyclooctadiene) with bis(*tert*-butylimido)sulfur. A magnetic susceptibility study carried out over a temperature range of 18-294 K revealed that in the solid state **1** has a singlet ground state with a triplet excited state ca. 0.3 kcal/mol above it. The solid-state molecular structure of **1** has been determined at room temperature from a single-crystal X-ray diffraction analysis. This molecule, which possesses a triangular metal framework with capping sulfido and *tert*-butylimido ligands, has no crystallographically imposed symmetry as is expected by the presence of noncylindrical monosubstituted cyclopentadienyl ligands. The metal triangle is significantly deformed from an equilateral configuration by crystal packing forces to give Co-Co bond lengths of 2.537 (1), 2.587 (1), and 2.610 (1) Å. The mean Co-Co bond length in **1** is ca. 0.13 Å longer than that of the known 48-electron $[CoCp]_3(S)(CO)$ cluster: this difference is attributed to the antibonding nature of the trimetal orbitals occupied by the two additional electrons in **1** in that both **1** and $[CoCp]_3(S)(CO)$ have ligands of similar size. Variable-temperature ^1H NMR data for **1** displayed paramagnetic isotropic shifts that were analyzed on the basis of a contact-shift equation in terms of a singlet-triplet equilibrium in solution. For comparison, $[Co(C_5H_4CO_2Me)]_3(S)_2$ (**2**) was prepared and likewise characterized from variable-temperature ^1H NMR measurements. A similar isotropic shift analysis revealed a contrasting singlet-triplet equilibrium for **2** in solution vs that for **1**. At 0 °C in solution, **1** has a triplet ground state with a singlet excited state ca. 0.8 kcal/mol higher in energy whereas **2** has a singlet ground state with a triplet-state energy level at ca. 0.7 kcal/mol higher position. It is suggested that the difference in these magnetic properties in solution originates from the size of the metal triangles, which controls the relative positions of an a_2 orbital and degenerate e orbitals. Complex **1**: triclinic, $P\bar{1}$, a = 10.057 (3) Å, b = 14.716 (4) Å, c = 9.680 (3) Å, α = 92.15 (3)°, β = 111.48 (2)°, γ = 81.34 (3)°, Z = 2, and R = 0.046 for 4339 independent reflections.

Introduction

Several electronically saturated (48 valence electrons) and diamagnetic tricobalt clusters have been reported; they have in common a 42-electron triangular $[CoCp]_3$, $[CoCp']_3$, or $[CoCp^*]_3$ fragment (where Cp = η^5-C_5H_5, Cp′ = η^5-C_5H_4Me, Cp* = η^5-C_5Me_5) containing electron-pair Co-Co bonds and a pair of capping ligands that donate 6 electrons: (CO)(O),[1] (CO)(S),[2,3] (CS)(S),[4] (CO)(NSiMe$_3$),[5] (CO)(N(CO)NH$_2$),[5] and (CO)(NH).[5] As for the 50-electron analogues, only two examples, $[CoCp]_3(\mu_3\text{-}S)_2$ (**3**)[6a] and $[CoCp']_3(\mu_3\text{-}S)_2$ (**3a**),[6b] have been reported. The two additional electrons in $[CoCp]_3(\mu_3\text{-}S)_2$ cause **3** to exist in a solid-state room-temperature phase with two unpaired electrons[2,6a] and in solution to possess a singlet-triplet equilibrium that shifts to the singlet state at lower temperatures.[6a] The corresponding methylcyclopentadienyl analogue was shown to be diamagnetic in the solid state (in accordance with its solid-state structure) but in solution to possess a singlet-triplet equilibrium that likewise shifts to the singlet state at lower temperatures.[6b] Recently, an interesting 46-electron analogue bicapped by two CO ligands, $[CoCp^*]_3(CO)_2$ (**4**), has been prepared and shown by Dahl and co-workers to possess a singlet-triplet equilibrium in solution similar to that of **3**.[7] In order to interpret the magnetic features of this class of compounds and thereby shed light on the spin and

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