The structure of B_8H_{12}[11] has two asymmetric hydrogen bridges, each of which is in a geometrical situation like that of the unique endo hydrogen atom of B_5H_{11}. Although hydrogen atoms H_{10} and H_{12} of B_8H_{12} would not be hindered in a terminal position (Figure 2), each one forms an asymmetric hydrogen bridge (1.493 Å/1.288 Å) not much different from that calculated for B_5H_{11} (1.577 Å/1.228 Å). Thus the C_1 geometry of B_5H_{11} is consistent in a general way with the C_s, rather than C_{2v}, structure of B_8H_{12}.

In summary, the most probable symmetry of B_5H_{11} is C_1, not C_s, and the low barrier for the C_1–C_s–C_1 process suggests a fluxional character for this molecule.

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Registry No. B_5H_{11}, 18433-84-6.

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A New Mixed Tungsten–Nickel Carbonyl Cluster System: The $WNi_6(CO)_{17}^{2-}$ Ion[1]

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The first example of a mixed tungsten–nickel carbonyl cluster anion and the first example of a metal cluster system having a trigonal-bipyramidal arrangement of metal atoms was reported in 1971: the $W_2Ni_3(CO)_{16}^{2-}$ anion.[2]

Although not recognized at the time, a basic structural arrangement of nickel atoms (with respect to carbonylnickelate clusters) was found: the $[Ni(CO)_3(\mu\text{-}CO)_3]$ unit. This was elegantly demonstrated by the synthetic and structural studies of Chini and Dahl and their co-workers,[3-8] who showed that the carbonyl nickelate clusters $Ni_5(CO)_{12}^{2-}$, $Ni_6(CO)_{12}^{2-}$, $Ni_9(CO)_{18}^{2-}$, and $[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$ (n = 2–4) all contain a trigonal arrangement of three nickels atoms, three terminal carbonyl groups, and three bridging carbonyl groups. The nickel–nickel bond distances of the nickels in the trigonal array for the first three above and for the $W_2Ni_3(CO)_{10}^{2-}$ and $Mo_2Ni_3(CO)_{16}^{2-}$ ions are 2.36 ± 0.02 Å, suggesting a similarity in bonding. This appears to be especially true for the $M_2Ni_3(CO)_{16}^{2-}$ and $Ni_5(CO)_{12}^{2-}$ ions.[2,4,8] A qualitative discussion of the bonding in some of these species has suggested some basicity might be retained by the $Ni_6(CO)_{12}^{2-}$ ion. So that this could be checked, the ion was allowed to react with the Lewis acid species $W(CO)_5$.

The work of Chini and Dahl has also helped to clarify some of the earlier reports of clustered carbonylnickelate species such as $Ni_2(CO)_6^{2-}$,[9] $Ni_3(CO)_8^{2-}$,[10] $Ni_4(CO)_9^{2-}$, $Ni_4(CO)_9H^-$, and $Ni_5(CO)_9^{2-}$,[11,12] which were obtained by using various methods of reduction or disproportionation of $Ni(CO)_4$. The basis for assignment of these compositions were elemental analyses and in a few cases infrared spectra. Chini has shown, based on infrared spectra, that the material originally reported as $Ni_4(CO)_9^{2-}$ is most probably $Ni_6(CO)_{12}^{2-}$.[4] Thus some doubt as to the exact nature of the other earlier reported species still exists. The borohydride ion has been found to produce hydridic carbonyl species in the reduction with the group 6 metal carbonyls.[13] It was therefore of interest to determine whether similar results could be obtained with $Ni(CO)_4$.

Exprimental Section

Materials. All reagents were used as obtained from commercial sources. Methylene chloride was dried over molecular sieves, and tetrahydrofuran (THF) was distilled from sodium and benzophenone. All handling of nickel carbonyl was carried out in a vacuum line. All operations were performed in an inert atmosphere by using either Schlenk tube techniques or low-vacuum techniques.[14] *Caution*: $Ni(CO)_4$ is highly toxic and should be handled only in a vacuum line and/or a *good* fume hood.

Preparations of bis(triphenylphosphiniminium) chloride (hereafter referred to as (PPN)Cl)), $(PPN)_2W_2(CO)_{10}$, and $(PPN)_2W_2Ni_3(CO)_{16}$ were by the literature methods.[2,15]

Instrumental Characterization. (A) NMR Spectra. The ^{13}C NMR spectra were recorded with a JEOL PFT-100 spectrometer with Me_4Si as an external reference and acetone-d_6 as an internal lock. ^1H NMR spectra were obtained on a Varian model HA-100 spectrometer. All spectra were obtained at ambient temperature.

(B) Infrared Spectra. All spectra were obtained with a PE Model 621 spectrometer and calibrated with polystyrene or indene.

(C) Conductivity. Conductivities were determined as a function of concentration in nitromethane ($k = 9 \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$) with use of Yellow Springs Instrument Co. Model 31 bridge and a cell with a cell constant of 0.1825 cm^{-1}.

(D) Analyses. Carbon, hydrogen, and nitrogen analyses were performed at the University of Georgia. Metal analyses were provided by Galbraith Laboratories, Inc.

Preparation of $(PPN)BH_4$. A 2.6-g sample of (PPN)Cl was dissolved in 20 mL of boiling water. This solution was added to 1.7 g of $NaBH_4$ dissolved in 50 mL of cold water. The precipitate which formed was immediately filtered. It was then dissolved in 50 mL of CH_2Cl_2, and the solution was dried with $MgSO_4$ and filtered again. The product was crystallized by the addition of 50 mL of diethyl ether, collected by filtration, and dried under vacuum at 100 °C. A yield of 2.25 g (90%) of product was obtained; mp 195–197 °C. Anal. Calcd: C, 69.6; H, 5.64; N, 2.19. Found: C, 69.4; H, 5.59; N, 2.10.

The IR spectrum of $(PPN)BH_4$ shows the expected B–H stretching frequencies in the 2100–2300-cm^{-1} region. $(PPN)BH_4$ is an air-stable, nonhydroscopic solid which is soluble in ethanol, methanol, dichloromethane, and acetonitrile but insoluble in THF, diethyl ether, and ethyl acetate.

Preparation of $(PPN)_2Ni_6(CO)_{12}$. To 50 mL of THF in a 250-mL flask was added 2.0 g of $NaBH_4$. After the flask was attached to the vacuum line and degassed, 5.0 mL (40 mmol) of $Ni(CO)_4$ was condensed into the reactor. The flask was allowed to warm, and a reflux condenser was attached. The mixture was refluxed under nitrogen. The mixture which was initially yellow turned dark red after 1 h. After 2 h at reflux, the solvent was removed under vacuum and the residue was dissolved in 100 mL of CH_2Cl_2 containing 2.0 g (3.5 nmol) of (PPN)Cl. This solution was filtered on Celite®, and 100 mL of ether was added to the filtrate. A 2.2-g sample (68% yield) of $(PPN)_2Ni_6(CO)_{12}$ was obtained; mp 194–196 °C. If extended

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reaction times were employed, only an impure product could be obtained. Anal. Calcd: C, 57.14; H, 3.43; N, 1.59; Ni, 19.95. Found: C, 57.10; H, 3.32; N, 1.48; Ni, 19.65.

$(PPN)_2Ni_6(CO)_{12}$ is soluble in THF, acetone, and CH_2Cl_2 but insoluble in ether, ethyl acetate, and pentane.

Preparation of $(PPN)_2Ni_9(CO)_{18}$. Into a 0.55-g (1.0-mmol) sample of $(PPN)BH_4$ dissolved in 100 mL of CH_2Cl_2 was condensed 4.5 mmol (PVT measurement) of $Ni(CO)_4$. The mixture was warmed to ambient temperature and refluxed. The solution was initially yellow but after 2 h turned red. After 4 h, the deep purple solution obtained was filtered on Celite® and 100 mL of ether was added to the filtrate. Upon standing overnight at −10 °C, a 0.85-g sample (80% yield) of $(PPN)_2Ni_9(CO)_{18}$ crystallized. The product decomposes around 140 °C and is soluble in acetone THF, CH_2Cl_2, and CH_3CN but insoluble in ether, ethylacetate, and pentane. Anal. Calcd: C, 51.24; H, 2.87; N, 1.33; Ni, 25.04. Found: C, 50.9; H, 2.90; N, 1.15; Ni, 24.8.

Preparation of $(PPN)_2WNi_6(CO)_{17}$. A 0.7-g (2.0-mmol) sample of $W(CO)_6$ in 100 mL of THF was photolyzed at 25 °C for 20 min with a G. E., AH-4 spot lamp. The solution was cooled to 0 °C, and 1.77 g (1.0 mmol) of $(PPN)_2Ni_6(CO)_{12}$ in 25 mL of CH_2Cl_2 was added. The mixture was stirred for 1 h and cooled, and the solvents were removed under vacuum. The residue was dissolved in 50 mL of CH_2Cl_2 and then filtered on Celite®; ether (50 mL) was added to the filtrate. Upon standing at −10 °C overnight, a 0.76-g sample (38% yield) of product was obtained as red needlelike crystals; mp 202–204 °C. The product was washed several times with ether and dried under vacuum. Anal. Calcd: C, 51.16; H, 2.80; N, 1.34;, W, 8.80; Ni, 16.86. Found: C, 50.96; H, 3.00; N, 1.27; W, 8.60; Ni, 17.01.

Reaction of $(PPN)_2Ni_6(CO)_{12}$ with $W(CO)_6$. A mixture containing 1.77 g (1 mmol) of $(PPN)_2Ni_6(CO)_{12}$ and 0.70 g of $W(CO)_6$ in 100 mL of THF was refluxed for 4 h. The resulting orange solution was evaporated to dryness and the residue dissolved in 100 mL of CH_2Cl_2 and then filtered on Celite®. Ethyl acetate (100 mL) was added to the filtrate and on standing at −10 °C, a 1.4-g sample (68% yield) of $(PPN)_2W_2Ni_3(CO)_{16}$ was obtained. It was identified by infrared and mixed melting points. In a similar manner, the simultaneous photolysis of $(PPN)_2Ni_6(CO)_{12}$ and $W(CO)_6$ produced $(PPN)_2W_2Ni_3(CO)_{16}$.

Reaction of $(PPN)_2W_2Ni_3(CO)_{16}$ with $Ni(CO)_4$. A mixture containing 1.05 g (0.5 mmol) of $(PPN)_2W_2Ni_3(CO)_{16}$ and 5 mmol (PVT measurement) of $Ni(CO)_4$ in 100 mL of THF was refluxed for 2 h. An infrared spectrum of the solution showed that the primary product was the $Ni_6(CO)_{12}^{2-}$ anion. Continued refluxing for another 2 h produced $Ni_9(CO)_{18}^{2-}$. This was isolated as described above. A 45% yield was obtained.

Reaction of $(PPN)_2W_2(CO)_{10}$ with Excess $Ni(CO)_4$. A flask containing 8.7 g (5.0 mmol) of $(PPN)_2W_2(CO)_{10}$ and 6.0 mL (50 mmol) of $Ni(CO)_4$ in 200 mL of THF was refluxed for 4 h. A 5.3-g sample (50% yield) of $(PPN)_2Ni_9(CO)_{18}$ was obtained.

Results and Discussion

The preparation of the carbonylnickelates and of the $M_2Ni_3(CO)_{16}^{2-}$ ions depends upon the reduction or disproportionation of $Ni(CO)_4$. A number of reagents have been used. These include the alkali metals either as amalgams or with added naphthalene (anthracene), ethylene diamine, or pyridine and alkali-metal hydroxide in alcohol or dimethyl sulfoxide for the nickelates while the anions $M_2(CO)_{10}^{2-}$ (M = Cr, Mo, or W) were used as the reducing agent for the preparation of the $M_2Ni_3(CO)_{16}^{2-}$ ions. As pointed out by Chini, the reduction of $Ni(CO)_4$ is quite complicated and the product isolated depends upon the nature of the reducing agent and more importantly upon the experimental conditions. This is due in part to the existence of a number of facile equilibria[5,6] or reaction with protic solvents.[7]

$$Ni_5(CO)_{12}^{2-} + Ni(CO)_4 \rightleftarrows Ni_6(CO)_{12}^{2-} + 4CO$$

$$Ni_6(CO)_{12}^{2-} + 3Ni(CO)_4 \rightleftarrows Ni_9(CO)_{18}^{2-} + 6CO$$

$$2Ni_6(CO)_{12}^{2-} \xrightarrow{(4-n)H^+} [Ni_{12}(CO)_{21}H_{4-n}]^{n-} + 3CO$$

Since sodium borohydride has successfully been employed as a reducing agent for several carbonyls yielding either reduced species or hydridic[13,16] derivatives, an attempt was made to reduce nickel carbonyl with this reagent. No hydridic species were formed (as shown by ^1H NMR spectroscopy). When sodium borohydride and nickel carbonyl were allowed to react at reflux in THF, the $Ni_6(CO)_{12}^{2-}$ ion was isolated in moderate yield. The preparation of $(PPN)BH_4$ allowed us to repeat the reaction in a homogeneous medium. Similar results were obtained except that $Ni_9(CO)_{18}^{2-}$ could be isolated in good yield. Evidence for the formation of $Ni_6(CO)_{12}^{2-}$ was initially observed, but isolation was difficult in the latter case. This is in contrast to the results previously reported.[6] No apparent explanation is available.

The $[Ni(CO)_3(\mu\text{-}CO)_3]$ unit (D_{3h} symmetry) is a feature common to all the isolated clusters and was first observed in the mixed-metal–nickel carbonyl clusters $M_2Ni_3(CO)_{16}^{2-}$ (M = Cr, Mo, and W).[2] The striking similarity in the Ni–Ni bond distances in the triangular array of nickel atoms in these anionic clusters suggests that it is an essential building block in the formation of the homonuclear as well as the heteronuclear cluster systems. A qualitative description of the bonding in these cluster systems containing the $Ni_3(CO)_6$ triangular fragment was first given for the $M_2Ni_3(CO)_{16}^{2-}$ ions (M = Cr, Mo, and W) and was later extended to the $Ni_5(CO)_{12}^{2-}$ and $Ni_6(CO)_{12}^{2-}$ clusters.[2-4] The salient features of this scheme are as follows: (a) the $Ni_3(CO)_6$ unit is structurally similar although not isoelectronic to the Re_3Cl_6 unit in the $Re_3Cl_{12}^{3-}$ ion and thus it is assumed that the $Ni_3(CO)_6^{2-}$ fragment contains two filled orbitals pointed in opposite directions perpendicular to the plane; (b) the Mo–Ni distance in $Mo_2Ni_3(CO)_{16}^{2-}$ indicates a weak interaction between the Lewis acid unit $Mo(CO)_5$ and the nickel plane; (c) little or no back-bonding from the group 6B metal to the nickel plane occurs. The bonding in the $Ni_5(CO)_{12}^{2-}$ cluster is probably analogous to that of the $M_2Ni_3(CO)_{16}^{2-}$ ions with the Lewis acid $Ni(CO)_3$ unit replacing the $M(CO)_5$ unit. The bond distances between the in-plane and out-of-plane nickels are indicative of a weak interaction. The formation of $Ni_6(CO)_{12}^{2-}$ requires the fusion of two $Ni_3(CO)_6^{2-}$ units with the loss of two electrons from the out-of-plane orbitals respectively and perhaps occurs via oxidation of the unknown $Ni_3(CO)_6^{2-}$ species or more likely $Ni_5(CO)_{12}^{2-}$ with excess $Ni(CO)_4$. This qualitative bonding description suggests that $Ni_6(CO)_{12}^{2-}$ as well as $Ni_9(CO)_{18}^{2-}$ should have two filled out-of-plane orbitals, each one perpendicular to the two triangular faces of the trigonal antiprism (or the two outside trigonal faces of the tristacked $Ni_9(CO)_{18}^{2-}$).

In an effort to determine whether this description was appropriate and whether the cluster $Ni_6(CO)_{12}^{2-}$ contained any residual Lewis basicity, it was allowed to react with $M(CO)_5$·THF (produced photochemically from $M(CO)_6$ (M = Cr, Mo, and W) in THF). The reaction resulted in the formation of the new cluster systems $MNi_6(CO)_{17}^{2-}$. However, only the tungsten derivative could be isolated as the PPN salt. Infrared evidence indicated the formation of the corresponding chromium and molybdenum species in solution, but they could not be obtained pure (see Table I). Analyses and conductivity studies support its formulation as $(PPN)_2WNi_6(CO)_{17}$, since a plot of $\Lambda - \Lambda_c$ vs. $c^{1/2}$ has a slope of 400 in nitromethane indicative of a 1:2 electrolyte type.[17]

No hydridic hydrogen was observed by ^1H NMR spectroscopy. Attempts to obtain a ^{13}C NMR spectrum of this material (at natural abundance levels) were unsuccessful due to reaction with CH_2Cl_2 used as solvent. However, as a check of the experimental system used, the ^{13}C NMR spectra of $W_2Ni_3(CO)_{16}^{2-}$ was obtained at ambient temperature. The spectrum contained peaks at 253.3 (3), 210.1 (1), 209.5 (4),

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Table I. Infrared Frequencies (cm^{-1}) in the Carbonyl Region for Nickel Carbonyl Derivatives

anion[a]	ν_{CO}[b]
$W_2Ni_3(CO)_{16}^{2-}$	2036 (w), 1998 (s), 1930 (mw), 1896 (s), 1835 (m), 1791 (w)
$CrNi_6(CO)_{17}^{2-}$[c]	2060 (w), 2008 (vs), 1971 (w),[d] 1911 (m), 1894 (s), 1940 (m), 1810 (s), 1780 (s), 1867 (s), 1831 (m)
$MoNi_6(CO)_{17}^{2-}$[c]	2059 (w), 2005 (vs), 1969 (m),[d] 1940 (m), 1910 (mw), 1892 (s), 1861 (s), 1831 (m), 1801 (s), 1771 (s)
$WNi_6(CO)_{17}^{2-}$	2056 (w), 2000 (vs), 1954 (sh), 1933 (m), 1903 (m), 1887 (s), 1854 (s), 1822 (m), 1794 (s), 1769 (s)

[a] PPN^+ salts. [b] Nujol mulls. [c] Unable to be isolated. [d] Unreacted $Ni_6(CO)_{12}^{2-}$.

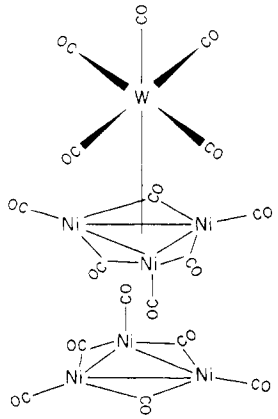

Figure 1. Proposed structure for the $WNi_6(CO)_{17}^{2-}$ ion.

and 197.5 (3) ppm (the numbers in parentheses are the relative peak areas). They are assigned to the bridging carbonyls on nickel, the axial carbonyl on tungsten, the equatorial carbonyl on tungsten, and the terminal carbonyls on nickel, respectively. A suggested structure for the $WNi_6(CO)_{17}^{2-}$ ion is shown in Figure 1.

Although several attempts were made to add two $W(CO)_5$ units to the $Ni_6(CO)_{12}^{2-}$ anion, they were not successful. Using a large excess of $W(CO)_5$·THF led only to the monocapped species while extended reaction times at reflux resulted in the formation of the known $W_2Ni_3(CO)_{16}^{2-}$ cluster. Simultaneous photolysis of $W(CO)_6$ and $Ni_6(CO)_{12}^{2-}$ also produced $W_2Ni_3(CO)_{16}^{2-}$ in moderate yields. It is possible that the $WNi_6(CO)_{17}^{2-}$ ion is an intermediate in the reaction of $W_2CO_{10}^{2-}$ with $Ni(CO)_4$ since upon either refluxing, photolysis, or reaction with excess $W(CO)_6$ it is converted to the $W_2Ni_3(CO)_{16}^{2-}$ cluster. Similar behavior was observed for the other two nickel clusters. Thus, $Ni_5(CO)_{12}^{2-}$ and $Ni_9(CO)_{18}^{2-}$ were converted to $W_2Ni_3(CO)_{16}^{2-}$ upon refluxing with $W(CO)_6$ in THF. That these systems are quite labile and undoubtedly involve a number of equilibria was further demonstrated by allowing the $W_2Ni_3(CO)_{16}^{2-}$ ion to react with excess $Ni(CO)_4$. Either $Ni_6(CO)_{12}^{2-}$ or $Ni_9(CO)_{18}^{2-}$ could be isolated depending on reaction times and the amount of $Ni(CO)_4$ used. In fact, reaction of $Ni(CO)_4$ with the $W_2(CO)_{10}^{2-}$ ion produces the nickel clusters if a very large excess of $Ni(CO)_4$ is employed. These reactions are summarized in Figure 2. Included are some reactions of the clusters $W_2Ni_3(CO)_{16}^{2-}$, $Ni_6(CO)_{12}^{2-}$, $Ni_5(CO)_{12}^{2-}$, and $Ni_9(CO)_{18}^{2-}$ which have previously been reported. The transformations represented in Figure 2 obviously do not represent balanced equations since only the most accessible product(s) were isolated.

The question of characterization of individual clusters in these complex systems is very difficult. Infrared spectroscopy is useful only for identifying known compounds in reaction

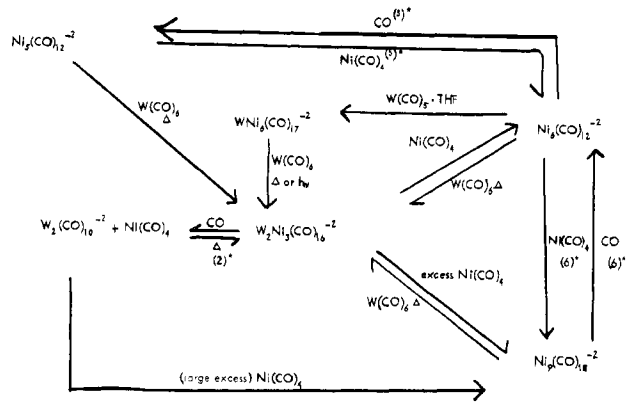

Figure 2. Reaction equilibria in anionic nickel and tungsten carbonylate systems. Asterisks signify known reactions; numbers refer to references.

mixtures (i.e., in this case, $Ni_6(CO)_{12}^{2-}$, $Ni_5(CO)_{12}^{2-}$, $Ni_9(CO)_{18}^{2-}$, and $W_2Ni_3(CO)_{16}^{2-}$). Inferences regarding structure and/or symmetry of new cluster systems are dubious since it is not possible to rely on the group character tables and the lack of accidental degeneracies. The infrared spectra of the new clusters in the CO region are given in Table I. Thus, in the final analysis, X-ray structural determination remains the ultimate tool for characterization.

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Registry No. $(PPN)_2WNi_6(CO)_{17}$, 79466-70-9; $CrNi_6(CO)_{17}^{2-}$, 79391-49-4; $MoNi_6(CO)_{17}^{2-}$, 79391-50-7; $(PPN)_2Ni_6(CO)_{12}$, 60464-20-2; $(PPN)_2Ni_9(CO)_{18}$, 60512-59-6; $(PPN)_2W_2Ni_3(CO)_{16}$, 11059-51-1; $(PPN)BH_4$, 65013-26-5; $(PPN)_2W_2(CO)_{10}$, 52580-40-2; $Ni(CO)_4$, 13463-39-3; $W(CO)_6$, 14040-11-0; (PPN)Cl, 21050-13-5.

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Formation of Bridged Group 4B Metal to Group 8 Metal Polymers

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It is well-known that metal cyanide complexes can act as Lewis bases through the nitrogen atom to form C–N bridges to compounds with Lewis acid centers.[1,2] Indeed, Manzer and Parshall[3] used this property to investigate the order of Lewis acidity of AlR_3 and BR_3 compounds through their reactions with $HPtL_2CN$ (L is PPh_3). They also showed that $HPtL_2CN$ reacts with metal-centered Lewis acids such as $NiCl_2$ to give monomeric cyanide-bridged products. From studies on Prussian blue and its analogues,[4] it is also clear that three-dimensional networks bound by M–C–N–M′ units can form upon crystallization of polyfunctional metal cyanide ions with other transition-metal ions.

These facts suggest that it should be possible to synthesize quasilinear cyanide-bridged metal-containing polymers through the interaction of bifunctional Lewis acid metal atom centers and metal cyanide species which have at least two cyanides and to incorporate in the material a functionally basic metal center. However, Rupp and Shriver[5] found that when Fe-

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