Substitution of CO by PH_3 in $Co(CO)_4^-$ is seen from Table II to enhance the strength (ΔE_{A_1}) of the donor–acceptor interaction 9. The protonation energy ΔE_P is as a result calculated to by 29 kJ mol^{-1} larger for $Co(CO)_3(PH_3)^-$ than for $Co(CO)_4^-$, and this is in line with experimental findings,[16] since $HCo(CO)_4$ with $K_a \approx 1.0$ is observed to be a stronger acid than $Co(CO)_3(PPh_3)$ with $K_a = 10^{-7}$. We note with reference to eq 3 that $\langle 1s|a_1\rangle$ is influenced very little by the substitution, $\langle 1s|a_1\rangle = 0.4648$ for $Co(CO)_4^-$ and $\langle 1s|a_1\rangle = 0.4624$ for $Co(CO)_3(PH_3)$, whereas $\epsilon(a_1)$ is raised by 0.8 eV on substitution. The higher energy of a_1 in $Co(CO)_3(PH_3)^-$ compared to $Co(CO)_4^-$ reflects an increase in the antibonding interaction between the axial σ orbital and $3d_{z^2}$ as CO is substituted by PH_3. The stronger antibonding interaction is brought about by a better overlap, $\langle\sigma_{PH3}|3d_{z^2}\rangle = 0.2134$ and $\langle\sigma_{CO}|3d_{z^2}\rangle = 0.1834$, as well as a considerable higher energy of σ_{PH_3} compared to σ_{CO}.

We hope, by means of our decomposition scheme, further to delineate the role played by the coligands in determining the nucleophilicity of a metal complex in a forthcoming communication.

Concluding Remarks

Orders of nucleophilicity have been established experimentally and rationalized theoretically, for numerous series of organic molecules. We have in the present study discussed the possible order of nucleophilicity for a homologous and isoelectronic series of metal complexes ML_n with respect to the position of the transition-metal M in the periodic table, based on an analysis of the calculated protonation energies for some d^8 and d^{10} metal carbonyls. Our calculations are approximate due to the limitations of the HFS method as well as the use of standard structural parameters rather than optimized geometries. We believed however that more involved calculations too would find that ΔE_{elec} from the interaction between ML_n and an electrophile increases with respect to M vertically down a triad and decreases along a transition series with increasing nuclear charge on M.

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$Cp_6Ni_2Zn_4$—An Unusually Electron-Rich Octahedral Cluster

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The title compound was prepared by heating Cp_2Zn and $Ni(COD)_2$ in benzene. It is surprisingly stable and can be heated to 250 °C without decomposition. Its structure was determined by a single-crystal X-ray diffraction study. The compound forms tetragonal crystals, space group $P4_2/mnm$, with two molecules in a cell of dimensions a = 9.352 (5) Å and c = 16.32 (1) Å. The molecule consists of an octahedron with apical nickel atoms and equatorial zinc atoms, each carrying an η^5-bound Cp group. The octahedron is compressed along the Ni–Ni axis, giving eight Ni–Zn bonds of 2.398 (2) Å, one long Ni–Ni bond of 2.571 (1) Å, and four nonbonded Zn–Zn distances of 2.86 Å (average). The formation of the compound is discussed in terms of the insertion of coordinatively unsaturated Ni into Cp–Zn bonds. $Cp_6Ni_2Zn_4$ is unusually electron-rich for an octahedral cluster. The electronic structure is discussed in a qualitative way.

Introduction

Although many zinc–transition-metal compounds are known, the compounds described in the literature are largely confined to derivatives of group 6 and 7 metals[17] and those of the iron and cobalt groups. In particular, no nickel–zinc compounds have been reported, although nickel–cadmium and nickel–mercury compounds are known.[1] In this paper, we describe the preparation and characterization of a nickel–zinc cluster compound and discuss its electronic structure. [For a preliminary account, see ref 2.]

Experimental Section

General Remarks. All manipulations were carried out in an atmosphere of dry, oxygen-free nitrogen. All solvents were dried and distilled under nitrogen prior to use. NMR spectra were recorded on Varian EM-390 and Bruker WP-200 spectrometers. $Ni(COD)_2$[3] and Cp_2Zn[4] were prepared according to literature methods.

Preparation of $Cp_6Ni_2Zn_4$. A mixture of 5 g of Cp_2Zn and 4 g of $Ni(COD)_2$ in 100 mL of benzene was heated in the course of 1 h from 20 to 75 °C. Initially, the solution was light yellow with white, suspended Cp_2Zn. Upon warming, the solution turned light green while the solid became orange. From about 50 °C on, the solution became deep green and dark green crystals of $Cp_6Ni_2Zn_4$ began to separate; the orange color of the solid disappeared. The reaction mixture was stirred for another hour at 75 °C, and the benzene was removed in vacuo. The residue was washed three times with 30 mL of pentane (from these washings, ca. 0.5 g of Cp_2Ni can be recovered by concentrating the solution and cooling to -40 °C). The green product was washed twice with 20 mL of a 3:1 diethyl ether-THF mixture to remove the excess of Cp_2Zn and dried in vacuo to yield 3.7 g (67%) of dark green $Cp_6Ni_2Zn_4$. NMR data (C_6D_6, δ in ppm relative to internal Me_4Si):

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Table I. Crystal Data and Details of the Structure Determination

Crystal Data	
formula	$C_{30}H_{30}Ni_2Zn_4$
mol wt	769.47
cryst system	tetragonal
space group	No. 136, $P4_2/mnm$
a, Å	9.352 (5)
c, Å	16.32 (1)
V, Å^3	1428 (3)
Z	2
D_{calcd}, g/cm^3	1.790
F_{000}	772
μ(Mo Kα), cm^{-1}	46.99
cryst size, mm	0.2 × 0.2 × 0.2
Data Collection	
θ_{min}, θ_{max}, deg	0.1, 25.0
radiation	Mo Kα (Zr-filtered), 0.710 69 Å
$\omega/2\theta$ scan, deg	$0.60 + 0.35 \tan \theta$
max time/refl, min	1.5
horizontal and vertical aperture, mm	3.0 and 3.0
ref reflctn	$0\bar{4}0$ (σ = 1%)
h,k,l range	0-11; 0-11; -19-0
total data	1478
total unique	604
obsd data ($I > 2.5\sigma(I)$)	321
R(merge)	0.068
Refinement	
no. of refined parameters	86
weighing scheme	$w^{-1} = (\sigma^2(F) + 0.001F^2)/2.29$
final $R_F = \Sigma \lvert F_o - \lvert F_c \rvert \rvert / \Sigma F_o$	0.042
final $R_{wF} = \{\Sigma w(F_o - \lvert F_c \rvert)^2 / \Sigma w F_o^2\}^{1/2}$	0.041
rms deviation of reflct of unit wt	1.72
max and min residual density, e/Å^3	1.0 and −0.5

^{1}H NMR 6.23 (s, Cp(Zn)), 4.64 (s, Cp(Ni)); ^{13}C{^{1}H} NMR 106.9 (Cp(Zn)), 88.5 (Cp(Ni)).

Data Collection and Structure Determination. The crystal that was used for the data collection was obtained by crystallization from hot benzene. An octahedral specimen was sealed in a Lindemann glass capillary and transferred to an Enraf-Nonius CAD4F diffractometer. Unit cell dimensions and standard deviations were determined in the usual way[5] from the settings of seven carefully centered reflections (20° < 2θ < 30°). The space group was determined as $P4_2/mnm$ or $P4_2nm$ from the observed systematic absences, and the data belonging to one octant (+h,+k,−l) of the reflection sphere were collected in the $\omega/2\theta$ scan mode using Zr-filtered Mo Kα radiation. No decay was observed during the 25 h of X-ray exposure time as monitored by one reference reflection. The data were corrected for Lorentz and polarization effects and averaged into a unique set of reflections in the previously described way.[5] The resolution of the data turned out to be rather poor in view of the observed disorder (vide infra) in the Cp rings, resulting in a limited data set. A psi scan for a close to axial reflection ($23\bar{6}$) showed that correction for absorption could be neglected. Details of the data collection and structure determination are summarized in Table I.

The metal atoms were located from a Patterson map, assuming the centrosymmetric space group $P4_2/mnm$ (which also has been found for the closely related Cp_6Ni_6 cluster[6]). A difference Fourier map showed the positions of the disordered Cp rings. Subsequent to some unsuccessful attempts to refine ordered Cp rings (including a model in the polar space group $P4_2nm$) and in view of the limited amount of data available, it was decided to introduce them as rigid pentagons and to refine their position and orientation only. The resulting Cp(Zn) and Cp(Ni) rings are then two- and fourfold disordered, respectively, corresponding to local C_s and C_{2v} site symmetry and were taken care of in the refinement with occupancy factors of 0.5 and 0.25. All non-hydrogen atoms were assigned anisotropic thermal parameters. The hydrogen atoms were placed at calculated positions; the groups of Cp(Zn) and Cp(Ni) hydrogen atoms were each assigned a variable overall thermal parameter. Weights were introduced in the final refinement stages.

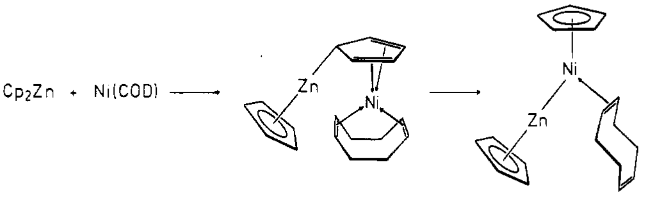
Neutral-atom scattering factors were taken from ref 7 and corrected for anomalous dispersion.[8] All calculations were carried out on the Cyber 175 of the University of Utrecht Computer Center. Programs used include SHELX-76 (structure refinement[9]), PLATO (geometry analysis[10]), and PLUTO (plotting program[10]).

Results and Discussion

Formation of $Cp_6Ni_2Zn_4$. $Ni(COD)_2$ is not very stable, and on heating it easily decomposes into metallic nickel and cyclooctadiene. The first step is presumably the (reversible) dissociation of one COD ligand (eq 1). In

$$Ni(COD)_2 \rightleftarrows Ni(COD) + COD \qquad (1)$$

analogy with the mechanism we recently suggested for the formation of $(CpZn)_2Co(Cp)PPh_3$ from Cp_2Zn and $HCo(N_2)(PPh_3)_3$[11] the coordination of Cp_2Zn to Ni(COD), followed by insertion of Ni into the Cp–Zn bond, seems likely (eq 2). The η^2-bound COD ligand will only be weakly bound, and dissociation again produces a reactive, coordinatively unsaturated nickel compound. This can coordinate with Cp_2Zn and insert into the Cp–Zn bond, although no η^5 Cp–Ni bond can be formed this time (eq 3). Instead, homolytic cleavage of the σ Cp–Ni bond is postulated. This produces $(CpZn)_2NiCp$ radicals, which then dimerize to $(CpZn)_4(NiCp)_2$ (eq 4). Some but not all of the Cp radicals produced can be recovered as Cp_2Ni.



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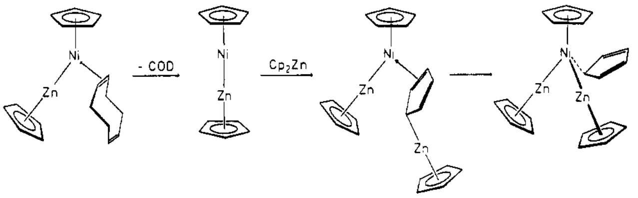

(3)

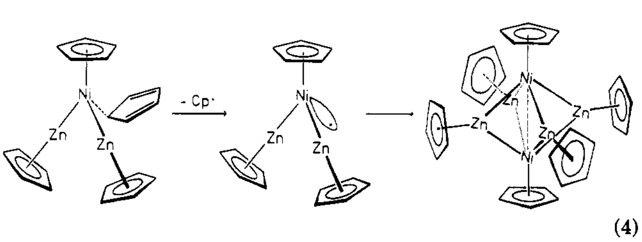

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Table II. Fractional Atomic Coordinates and Thermal Parameters

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zn(1)	0.1079 (1)	0.1079 (1)	0.0880 (1)	0.0777 (8)	0.0777 (8)	0.063 (1)	−0.0205 (6)	−0.0205 (6)	−0.009 (1)
Ni(1)	0.0972 (2)	−0.0972 (2)	0	0.058 (1)	0.058 (1)	0.047 (1)	0	0	0.011 (1)
C(11)	0.248 (4)	−0.207 (4)	0.072 (1)	0.03 (3)	0.05 (3)	0.10 (3)	0.04 (3)	0.00 (3)	0.01 (3)
C(12)	0.169 (4)	−0.302 (4)	0.021 (1)	0.03 (2)	0.03 (2)	0.09 (4)	0.01 (2)	−0.02 (3)	0.02 (2)
C(13)	0.199 (4)	−0.266 (4)	−0.062 (1)	0.07 (4)	0.08 (4)	0.04 (2)	−0.02 (3)	−0.01 (3)	0.00 (3)
C(14)	0.297 (4)	−0.150 (4)	−0.062 (1)	0.02 (2)	0.08 (4)	0.11 (4)	0.02 (3)	0.01 (2)	0.02 (3)
C(15)	0.327 (4)	−0.113 (4)	0.021 (1)	0.04 (2)	0.08 (3)	0.08 (4)	−0.03 (3)	−0.04 (2)	−0.00 (2)
C(21)	0.317 (2)	0.125 (1)	0.177 (1)	0.06 (2)	0.03 (1)	0.20 (3)	0.00 (2)	−0.07 (2)	−0.02 (1)
C(22)	0.318 (2)	0.251 (1)	0.128 (1)	0.06 (1)	0.02 (1)	0.10 (1)	−0.009 (9)	−0.03 (1)	−0.02 (1)
C(23)	0.189 (2)	0.326 (1)	0.143 (1)	0.02 (2)	0.07 (1)	0.15 (2)	−0.02 (2)	−0.01 (1)	−0.02 (1)
C(24)	0.107 (2)	0.246 (1)	0.200 (1)	0.15 (3)	0.06 (2)	0.12 (2)	−0.06 (2)	−0.01 (2)	−0.06 (2)
C(25)	0.187 (2)	0.122 (1)	0.221 (1)	0.10 (2)	0.14 (3)	0.06 (1)	−0.01 (2)	−0.04 (1)	−0.00 (2)

Table III. Selected Geometrical Parameters[a]

Bond Distances (Å)

Zn(1)-Ni(1)	2.398 (2)	Zn(1A)-Zn(1B)	4.050 (2)
Zn(1)-Zn(1A)	2.854 (1)	Ni(1)-Ni(1A)	2.571 (2)
Zn(1)-Zn(1B)	2.873 (2)		

Perpendicular Metal-Cyclopentadienyl Distances (Å)

Ni-Cp	1.74	Zn-Cp	2.02

Bond Angles (deg)

Zn(1)-Ni(1)-Zn(1A)	73.0 (1)
Zn(1)-Ni(1)-Zn(1B)	73.6 (1)
Zn(1A)-Ni(1)-Zn(1B)	115.2 (1)
Ni(1)-Zn(1)-Ni(1A)	64.8 (1)

[a] Symmetry code: A = $-x, -y, z$; B = $x, y, -z$.

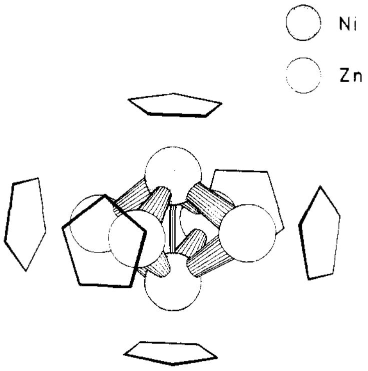

Figure 1. PLUTO drawing of $Cp_6Ni_2Zn_4$, showing only one orientation for each disordered Cp ring.

Structure and Properties. $Cp_6Ni_2Zn_4$ crystallizes in the tetragonal system, space-group $P4_2/mnm$, with 2 molecules in a cell of dimensions a = 9.352(5) Å and c = 16.32(1) Å. The molecule consists of an octahedral arrangement of two apical nickel atoms and four equatorial zinc atoms, each having an η^5-bound Cp group attached to it. The octahedron is compressed along the Ni-Ni axis, giving 8 Ni-Zn bonds of 2.398(2) Å, one long Ni-Ni bond of 2.571(1) Å and 4 nonbonded distances of (2.854(1) and 2.873(2) Å). Fractional atomic ccordinates are given in Table II, and some relevant geometrical parameters in Table III. The metal core has an almost perfect $4/mnm$ (D_{4h}) symmetry, although the site symmetry is only mmm (D_{2h}). All Cp groups are disordered; the PLUTO drawing (Figure 1) shows only one orientation for each Cp ring. The bonding situation in this cluster, i.e., zinc atoms bridging between transition metal atoms, can be compared to that in the $Zn_2Co_4(CO)_{15}$ cluster[12] in which two Zn-$(Co(CO)_4)$ atoms form bridges between two Co atoms which themselves are weakly bonded together. In the latter case, the Zn-Co bridges (2.478 Å) are appreciably longer than the terminal Zn-Co bonds (2.352 Å). The Zn-Ni bonds in our case (2.398 Å) are intermediate between these values and, therefore, have reasonable lengths in view of the close similarity between nickel and cobalt covalent radii. The zinc-zinc distances (2.854 and 2.873 Å) preclude direct zinc-zinc bonding (cf. the nonbonding Zn-Zn distance in $(CpZn)_2Co(Cp)PPh_3$[11] (2.783 Å)). The Ni-Ni distance (2.571 Å) is appreciably shorter than the shortest trans Ni-Ni distance in the Cp_6Ni_6 cluster (3.373 Å),[6] but only slightly longer than the mean Ni-Ni distances in $Ni_4(\eta^5\text{-}C_5H_5)_4(\mu_3\text{-}H)_3$.[13]

$Cp_6Ni_2Zn_4$ is a dark-green compound, which shows a poor to moderate solubility in most organic solvents, giving grass-green solutions. It is sensitive to air and moisture, especially in solution, and rapidly turns brown on hydrolysis. It also turns brown with nitrogen bases, which presumably disrupt the cluster structure. In the solid state, the compound has a high thermal stability, and in an inert atmosphere it can be heated to 250 °C without decomposition. It is diamagnetic, and its ^1H and $^{13}C\{^1H\}$ spectra show singlets for the Cp(Zn) and Cp(Ni) resonances in the ratio 2:1.

Bonding in $Cp_6Ni_2Zn_4$. As discussed by Mingos[14] and Lauher,[15] most stable octahedral cluster compounds have a total of 86 valence electrons, corresponding to a closed-shell configuration with a relatively large HOMO-LUMO separation. The compounds Cp_6Ni_6 and $Cp_6Ni_6^+PF_6^-$ recently synthesized by Paquette and Dahl[6] are electron-rich, having 90 and 89 valence electrons, respectively. The latter compound has 3 unpaired electrons, which corresponds to a half-filled t_{2u} HOMO as proposed by Mingos. In Cp_6Ni_6, the t_{2u}^4 configuration should give rise to a Jahn-Teller distortion; indeed, a slight compression along one Ni-Ni axis was observed.[6]

The treatment of octahedral clusters by Mingos[14] was based on an MO calculation on a naked Co_6 cluster; interaction with ligands was considered separately at a later stage. If one treats the $Cp_6Ni_2Zn_4$ cluster in the same way, one finds that 6 electrons have to be placed in the metal-metal antibonding t_{2u} and in the strongly antibonding t_{1g} cluster orbitals (disregarding the deviations from octahedral symmetry for the moment). Accordingly, such a treatment does not seem very realistic.

For the later transition metals like Ni and especially Zn, the 3d orbitals are very low in energy and will be completely filled; they will contribute little to the metal-metal and metal-ligand bonding. The next lowest set of orbitals are the Cp π orbitals. These give rise to the symmetry combinations $a_{1g}e_gt_{1u}$ (π_σ) and $t_{1g}t_{2g}t_{1u}t_{2u}$ (π_π) which will also be completely occupied. We are then left with the

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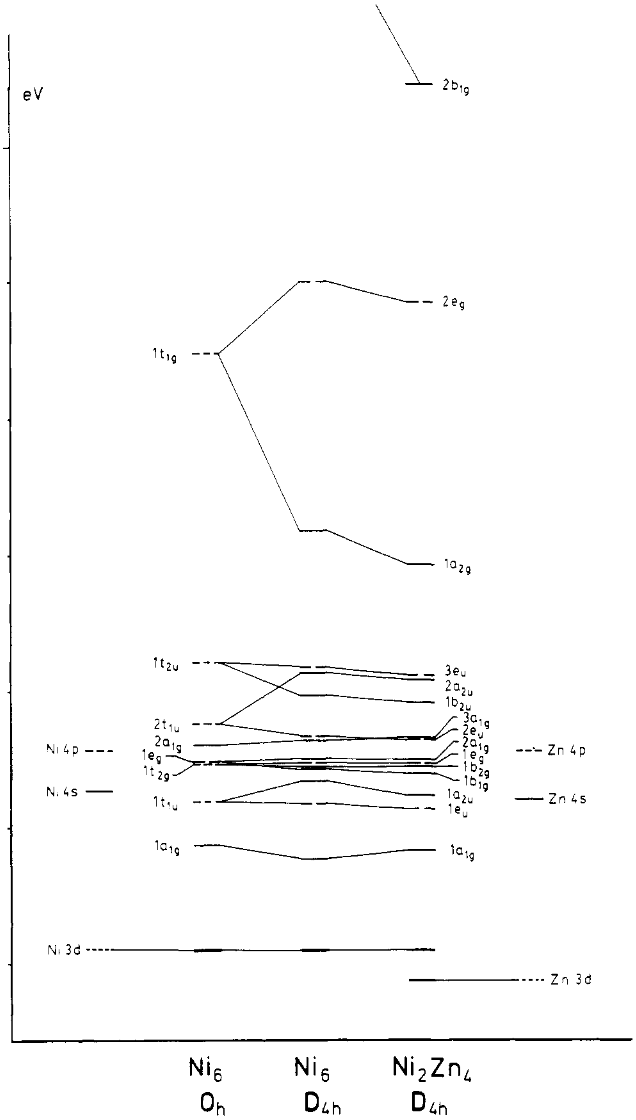

Figure 2. One-electron levels for Ni_6 and Ni_2Zn clusters from an EHT calculation. The metal 3d, 4s, and 4p atomic levels are also indicated.

metal 4s and 4p orbitals, which give rise to the symmetry combinations $1a_{1g}1t_{1u}1t_{2g}1e_g2a_{1g}2t_{1u}1t_{2u}1t_{1g}$... The lowest a_{1g} orbital, which is mainly a combination of metal 4s orbitals, can receive the last two valence electrons, and the remaining symmetry combinations are perfectly matched for interaction with the Cp ligand orbitals of the same symmetry, giving MO's of mainly metal-ligand bonding character. Of course, the $1t_{2u}$ and $1t_{1g}$ cluster orbitals are much too high in energy to contribute appreciably, and the resulting MO's will have predominantly ligand character. Nevertheless, it is clear that it is possible to accommodate the 98 valence electrons without occupying high-lying antibonding orbitals. On lowering the symmetry from O_h to D_{4h}, by compression along the Ni–Ni axis, the lower M_6 cluster orbitals become more Ni–Ni bonding and less Zn–Zn bonding, as expected. Of course, the cluster and ligand orbitals still remain matched in symmetry. The M_6 cluster orbitals from an extended Hückel calculation[16] are shown in Figure 2.

The resulting picture of the bonding in $Cp_6Ni_2Zn_4$ is as follows. The metal d levels are completely filled and contribute little to metal–metal or metal–ligand bonding. One orbital, consisting mainly of metal 4s orbitals, is predominantly metal–metal bonding; the remaining valence orbitals have mostly metal–ligand bonding character, while the lower of these also contribute somewhat to the metal–metal bonding. This description is in accord with partial bond orders for the Ni–Zn and N–Ni bonds and also with the observed diamagnetism of the compound.

A listing of structure factor amplitudes can be obtained from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany, by quoting the number CSD 50328 and reference 2.

Acknowledgment. Part of this work (A.L.S.) was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research.

Registry No. $Cp_6Ni_2Zn_4$, 94800-12-1; Cp_6Ni_6, 75349-30-3; Cp_2Ni, 1271-28-9; Cp_2Zn, 11077-31-9; $N_1(COD)_2$, 1295-35-8.

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[17] The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.