

a 50-ml vessel equipped with a Kontes high vacuum stopcock. The solution was frozen at -196°C and evacuated. One atmosphere of hydrogen was added to the cooled tube, the stopcock was closed, and the tube allowed to warm to room temperature. The solution was stirred for 12 h. Excess hydrogen and the solvent were removed in vacuo leaving the pale yellow-brown complex. Efforts to recrystallize the product resulted in some decomposition of the complex to $\text{HCo}[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_4$. Anal. Calcd: C, 47.23; H, 9.62; Co, 8.60. Found: C, 47.11; H, 9.64; Co, 8.47. NMR: δ -4.98 ppm (doublet of septets, 9) ($J_{\text{H-H}} = 5.9$ Hz) ($J_{\text{P-H}} = 3.0$ Hz), -1.44 ppm (doublet, 54) ($J_{\text{H-H}} = 6$ Hz), $+12.97$ ppm (quartet) ($J_{\text{H-P}} = 29$ Hz). IR: $\nu_{\text{C-O-H}}$ 1950 cm^{-1} (weak broad), 1830 cm^{-1} (sharp); $\text{D}_3\text{Co}[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_3$, $\nu_{\text{C-O-D}}$ 1330 cm^{-1} , others obscured.

$\text{H}(\text{N}_2)\text{Co}[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_3$. Two hundred milligrams of $\text{H}_3\text{Co}[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_3$ (0.29 mmol) was dissolved in 5 ml of diethyl ether in a 50-ml vessel equipped with a Kontes high vacuum stopcock. The solution was frozen at -196°C and evacuated, and 1 equiv (0.29 mmol) of carbon monoxide was added. The stopcock was closed and the solution was allowed to warm to room temperature with rapid stirring. After 3 h, the evolved hydrogen and the solvent were removed in vacuo leaving a pale yellow product. Anal. Calcd: C, 47.19; H, 8.99; Co, 8.28. Found: C, 46.92; H, 9.02; Co, 8.13. NMR: δ -1.40 (doublet, 54) ($J_{\text{H-H}} = 6.3$ Hz), -4.91 (doublet of septets, 9) ($J_{\text{H-H}} = 5.9$ Hz), ($J_{\text{P-H}} = 2.7$ Hz), $+14$ ppm (quartet, 1) ($J_{\text{P-H}} = 45.5$ Hz). IR: $\nu_{\text{C-O}}$ 1930 cm^{-1} .

$\text{H}(\text{N}_2)\text{Co}[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_3$. Purified nitrogen (99.998%) was passed through columns of CaCl_2 and "BTS Catalyst" (BASF Corp.) and then bubbled through a hexane solution of $\text{H}_3\text{Co}[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_3$ (25 ml, 2.8×10^{-2} M) for 3 h. The solution changed in color from yellow brown to nearly colorless. Attempts to isolate the complex were unsuccessful. IR: (hexane solution) $\nu_{\text{N-N}}$ 2130 cm^{-1} (sharp); $\nu_{\text{C-O-H}}$ 1950 cm^{-1} . Bubbling hydrogen through the solution re-formed $\text{H}_3\text{Co}[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_3$ within 30 min.

Catalytic Reactions—Procedure. Experimental conditions for the catalytic hydrogenation reactions are summarized in Table I. The reaction scale was typically 10^{-2} mol of the unsaturated molecule with 10^{-4} mol of cobalt catalyst. Reactions were run at 20 or 70°C and an average hydrogen pressure of 1 atm. A reaction vessel (~ 300 ml volume) fitted with a Teflon stopcock was charged with a catalyst and the unsaturated organic compound (if this compound was not easily vacuum transferred) and with a Teflon stirring bar; the operation was effected in the Dri Lab in a nitrogen or argon atmosphere. The stopcock was closed. Then the reaction vessel was removed and connected to a vacuum train. The reaction vessel was thoroughly evacuated (at -78°C if the organic molecule had an appreciable vapor pressure at

20°C). Volatile organic unsaturated compounds were vacuum transferred to the vessel. Then hydrogen was admitted to the reaction vessel (final pressure was ~ 1.2 – 1.3 atm). The stopcock was closed and the reaction mixture was stirred throughout the reaction period. About 1 ml of diethyl ether was added (vacuum transfer) to all reaction systems that used organic compounds that were solids.

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Metal Clusters in Catalysis. 6.¹ Synthesis and Chemistry of $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ and Related Clusters

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Abstract: Reaction of alkyl isocyanides with bis(cyclooctadiene)nickel in ~ 1.75 to 1 molar ratio gave in high yield a nickel cluster, $\text{Ni}_4(\text{CNR})_x$, in which the four nickel atoms describe the vertices of a highly compressed tetrahedron. The $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ molecule was stereochemically nonrigid and underwent a two-step intramolecular rearrangement at high rates in the 10 – 100°C range that may have been accompanied at 80 – 120°C by a fast dissociative process ($\text{Ni}_4\text{L}_7 \rightleftharpoons \text{Ni}_4\text{L}_6 + \text{L}$). Ligand dissociation from solid Ni_4L_7 was demonstrated at 60°C . These nickel clusters are catalysts for a variety of catalytic reactions which include the trimerization of acetylenes to benzenes, butadiene to 1,5-cyclooctadiene, polymerization of allene, and the selective hydrogenation of acetylenes to cis olefins. Possible intermediates in the catalytic acetylene reactions that have been identified include $\text{Ni}_4\text{L}_{7-x}(\text{acetylene})_x$.

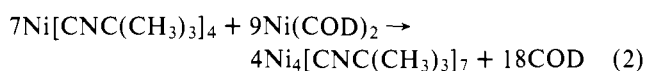
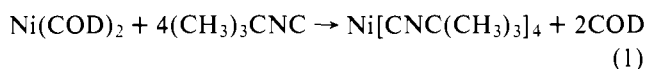
We pursue the thesis² that metal cluster molecules or ions can in some instances serve as plausible models of surface modes of chemisorption and heterogeneous catalysis. In known

clusters³ and in devised new clusters, we have sought the elements of catalytic processes that require the intervention of two or more metal atoms in a catalytic transformation. In this ar-

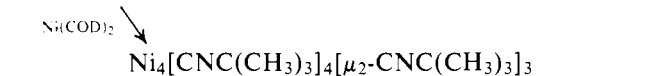
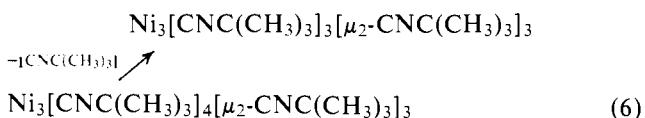
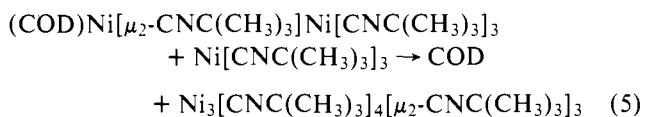
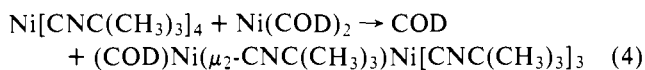
ticle, we describe the synthesis and properties of a unique four-metal-atom cluster class that is catalytically active and provides insight to requisite features of certain catalytic reactions as they may ensue on surfaces. The four-atom cluster is comprised of four nickel atoms with terminal and bridging alkyl isocyanide ligands; the paradigm in this class is $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$.⁴ Full structural characterization of this cluster class will be presented in a following article⁵ and complete characterization of catalysis intermediates in separate articles.^{6,7} We describe here the synthesis and characterization of the parent cluster $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ and the essential elements of its catalytic chemistry.

Results and Discussion

Synthesis. Interaction of an excess of any aryl or alkyl isocyanide with the premier zero-valent nickel reagent, bis(cyclooctadiene)nickel $[\text{Ni}(\text{COD})_2]$, invariably led to the rapid formation of diamagnetic, tetrahedral NiL_4 complexes. With a deficiency of isocyanide reactant, another product was generated. At isocyanide to $\text{Ni}(\text{COD})_2$ molar ratios of about 1.75 to 1, a dark, typically red or reddish brown complex was formed in high yield. In the specific case of *tert*-butyl isocyanide the composition of the resultant complex was $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$. Under synthesis conditions, the isocyanide was completely dissolved and $\text{Ni}(\text{COD})_2$ was only partially dissolved. The fast synthesis reaction and the reaction conditions require the sequence illustrated in eq 1 and 2.



Reaction 2, obviously not a single reaction step, was independently demonstrated. Intermediate steps in reaction 2 could include steps like 3 through 6.



The cyclic trimer Ni_3L_6 has not been detected in our studies but it is the stable form in the palladium⁴ and platinum⁸ systems. Migration of ligand atoms in such reactions should readily proceed by intramolecular processes since these nickel clusters, *vide infra*, are highly fluxional molecules.

Reaction products from analogous reactions with benzyl and isopropyl isocyanides were also dark red or brown solids but solubilities were reduced, especially for the benzyl derivative. Analyses indicated the compositions $\{\text{Ni}_4[\text{CNCH}(\text{CH}_3)_2]_6\}_x$ and $\{\text{Ni}_4[\text{CNCH}_2\text{C}_6\text{H}_5]_4\}_x$ but these must be confirmed and structurally defined by crystallographic analysis. A persistent and frustrating problem here has been the formation of crystalline plates with very small dimension for all these isocyanide clusters.

Structure and Spectral Properties. Crystallographic studies⁴

have established the essential structural features of $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ and a new data set for this cluster in a crystal derived from a different solvent should provide⁵ a more accurate structural assessment. In this cluster, the nickel atoms define the vertices of a highly compressed C_{3v} -tetrahedron (ca. 1 Å separation between the apex and the unique basal plane). Each nickel atom bears a terminally bound isocyanide ligand. Bridging about the basal edges in a four-electron donor and unsymmetric mode are the remaining three isocyanide ligands. The structure is shown in qualitative form in Figure 1. It should be noted that the crystal used for the initial crystallographic study, obtained from benzene solvent, had large voids which suggested that the crystal initially contained benzene solvate and that the solvate molecules were largely lost in the transfer of the crystal to a capillary.

All nickel isocyanide clusters had two salient infrared spectral features: a strong CN stretching absorption at $\sim 2050 \text{ cm}^{-1}$ characteristic of a terminal isocyanide ligand and a lower energy absorption at $\sim 1600 \text{ cm}^{-1}$ ascribable to some type of bridging isocyanide ligand. Regions typical of simple M-M bridging isocyanide⁹ ligands are in the 1800-cm^{-1} area.

The ^1H NMR spectrum of $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ at 0°C consisted of three methyl resonances of relative intensities 3, 3, and 1 which was fully consistent with the solid state structure. Temperature dependency of the spectrum established the cluster as a stereochemically nonrigid molecule. As the temperature was raised, the two high field methyl resonances of intensities 3 and 1 broadened and began to merge (LTP for low temperature process). Before the collapse of the two high field resonances into a sharp singlet was complete, a second exchange process (HTP for high temperature process) was evident, and the low field resonance began to broaden and merge with the other exchange collapsed singlet. Complete collapse into a single proton resonance occurred above 100°C . All spectral features were completely reversible between the temperature extremes of -20 and $+120^\circ\text{C}$ although extensive residence times at 100°C very slowly led to formation of $\text{Ni}[\text{CNC}(\text{CH}_3)_3]_4$ and an intractable nickel containing solid. Simulation of the NMR line shapes between -10 and $+80^\circ\text{C}$ required, for agreement between experimental and calculated spectra, treatment (Figure 2) of this dynamic process as a two-step process. Experimental and calculated spectra differed slightly between ~ 80 and 120°C . This is tentatively attributed to the onset of a third exchange process although an alternative of nonlinear temperature dependence of chemical shifts in this temperature range cannot be dismissed. Activation parameters for the first two exchange processes are shown below.

	E_a	ΔH^\ddagger	ΔS^\ddagger
LTP	16.5 kcal/mol	15.9 kcal/mol	-1 eu/mol
HTP	17.3 kcal/mol	16.5 kcal/mol	-5 eu/mol

Lacking a metal spin label in the Ni_4L_7 system, an intramolecular rearrangement process cannot be differentiated unequivocally from a bond breaking dissociative process (e.g., $\text{Ni}_4\text{L}_7 \rightleftharpoons \text{Ni}_4\text{L}_6 + \text{L}$). The possibility of a fast, solution phase dissociative process was suggested by an experiment in which isocyanide was removed from $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ by vacuum action on crystals heated to 60°C . This process would be operative in solution and it might account for the apparent exchange process in the $80\text{-}120^\circ\text{C}$ range. Alternatively, the third apparent process may involve ligand exchange between $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ and $\text{Ni}[\text{CNC}(\text{CH}_3)_3]_4$ (an ubiquitous impurity in all our studies). We independently established that this latter exchange occurred at rates rapid on the NMR time scale above 50°C for 1:1 Ni_4L_7 : NiL_4 mixtures. The rate *may be* too low to account for the putative third process for the Ni_4L_7 cluster.

The first or LTP process averages ligand environments between the unique apical site and either the terminal basal or

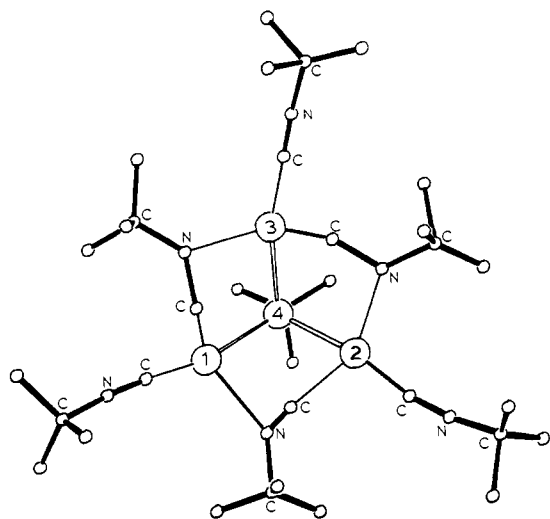


Figure 1. A representation of the structure of $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ using one of the two idealized⁴ bonding modes for the bridging isocyanide ligands.

the bridging sites. After consideration of many possible mechanisms, we propose that the most plausible LTP equilibration process involves the terminal apical ligand and the terminal basal ligand environments. Specifically, we suggest that there is a thermally accessible excited state in which the nickel atoms describe the vertices of a more nearly regular tetrahedron with each nickel atom bearing one terminal ligand and with three tetrahedral edges (common face) or three faces bridged by the carbon atoms of the isocyanide ligands. This proposed excited state would have the same number of cluster framework electrons as does the ground state structure. If in the ground to excited state traverse, the isocyanide carbon atoms can migrate to different edges, then the net effect would be an equilibration of *terminal* ligand atom environments even if an unsymmetric CN bridging mode were maintained. An alternative to an intramolecular rearrangement process in the LTP is a dissociative process but we have discerned no reasonable schemes based on such a process to explain the qualitative features of the ¹H DNMR spectra. In the HTP process, terminal-bridge exchange of ligands analogous to that operative¹⁰ in $\text{C}_{30}\text{-Rh}_4(\text{CO})_{12}$ is a plausible physical process.

The solid state structure of the (isopropyl isocyanide) nickel cluster, whose composition as indicated by analysis is $\text{Ni}_2[\text{CNCH}(\text{CH}_3)_2]_3$, has not been established because the single crystals (plates) obtained to date have consistently been too thin for a crystallographic study. Color and infrared spectral features are suggestive of a structural form analogous to the *tert*-butyl isocyanide cluster. One possibility is a Ni_8L_{12} species consisting of two Ni_4L_6 compressed tetrahedra joined through the unique apical or the basal nickel atoms or a monomeric tetrahedral form with only two bridging ligands as outlined in **1** where heavy connectors indicate possible NiNi

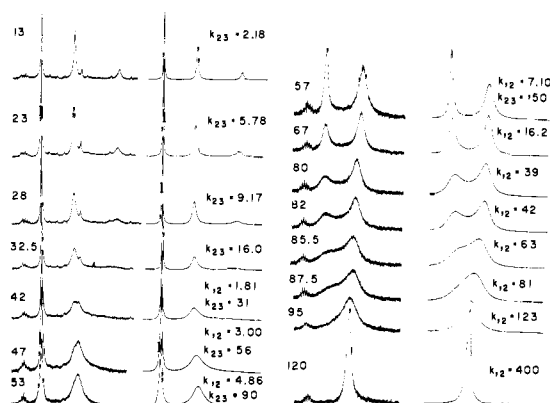
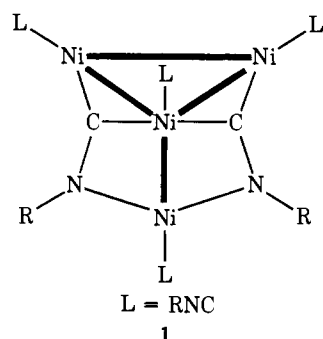
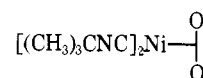


Figure 2. Observed and simulated ¹H NMR spectra for $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ over the temperature range of 13 to 120 °C. Temperatures are noted to the left of each observed spectrum. The small multiplet is the $\text{CH}_x\text{D}_{3-x}$ resonance of toluene-*d*₈. Spectra are artificially aligned here with respect to the low field $\text{C}(\text{CH}_3)_3$ resonance rather than the reference signal of the CHD_2 quintet of residual methyl protons in toluene-*d*₈ solvent.

double bonds. Solubility of the cluster is too low for accurate solution molecular weight measurements. Proton NMR spectra (60, 90, and 220 MHz) of this cluster proved too complex for any structural conclusions to be reached. For example, the 220-MHz spectrum showed the presence of at least three environmentally distinct isopropyl CH multiplets and a multitude of distinct isopropyl CH_3 doublets. The latter observation suggests that there may be a slow (NMR time scale) rotation about the N-C (isopropyl) bond. The search for an adequate single crystal continues. The benzyl isocyanide and methyl isocyanide clusters were not amenable to similar NMR studies because of their insolubility.

General Properties of $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$. Crystals or solutions of $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ were very air sensitive; the dominant reaction was with oxygen to form

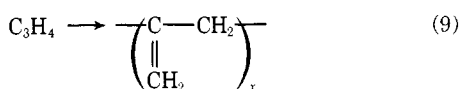
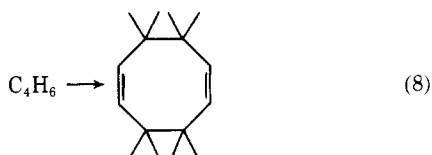
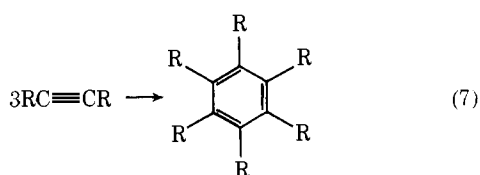


a structurally defined molecule.¹² In reaction with other donor ligands and with $(\text{CH}_3)_3\text{CNC}$, the only products produced were the conventional tetrahedral $\text{d}^{10} \text{ML}_x\text{L}'_{4-x}$ and ML_4 complexes. No intermediate species were detected in contrast to the palladium system in which the fluxional trimer $\text{Pd}_3[\text{CNC}(\text{CH}_3)_3]_3[\mu_2\text{-CNC}(\text{CH}_3)_3]_3$ was the only isolable species from the reaction of $[\text{C}_3\text{H}_5\text{PdC}_5\text{H}_5]_2$ ^{4,11} with isocyanide.

$\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ had essentially no solubility in pentane but the addition of 1 mol of benzene, of most acetylenes, or of dienes per mole of cluster was sufficient to promote a relatively high solubility of the cluster in pentane or other aliphatic hydrocarbon solvents. Although infrared data indicated that the basic cluster framework was unaltered in the presence of these unsaturated molecules, the solubilization experiments provided a clear indication of complex formation. Complex formation was fully reversible because the donor molecules were completely recovered by thorough evacuation of the solutions leaving behind the intact Ni_4L_7 cluster. Evidence was earlier advanced⁴ to support a thesis that the clusters formed a complex with benzene. The single crystal employed for the initial crystallographic studies had been obtained from a benzene solution, and the x-ray analysis indicated large voids in the crystals that may have been generated by solvent loss before the crystal was sealed in a capillary.⁴ NMR data for various solutions of the cluster were also suggestive of cluster-donor molecule interaction. There was a substantial alteration in cluster ligand proton NMR chemical shifts between the ben-

zene and the tetrahydrofuran solution cases. In tetrahydrofuran, the ligand methyl spectrum consisted of two resonances in a 6:1 relative intensity ratio. This was simply a case of accidental degeneracy for terminal (basal) and bridge ligand resonance since the line shape changes with temperature increase showed that the peak of intensity six comprised two distinct sets one of which rapidly exchanged with the apical ligand set associated with the high field resonance (intensity 1) and the other set initially remained sharp. Similar results were obtained with donor molecules like nitriles, pyridine, and dimethoxymethane. These donor solvents primarily affect the chemical shift of the peaks ascribed to the terminal isocyanide ligand protons of Ni_4L_7 . Activation parameters for the LTP and HTP exchanges do not seem to substantially change with solvent changes. The genesis of this weak cluster interaction¹³ with these unsaturated or donor molecules can be ascribed to the electronic character of Ni_4L_7 wherein there is an apparent¹⁴ six-electron deficiency. Complex formation for the cluster must be the first step in the catalysis chemistry described below.

Catalytic Chemistry. A number of relatively simple organic transformations have been examined at 17–20 °C for catalysis by $Ni_4[CNC(CH_3)_3]_7$; these include those enumerated in eq 7 through 11. Reaction 7, fully selective, was fast with acety-



lene and very slow for dialkylacetylenes at 17 °C. Catalyst life was very short in acetylene trimerization and this was ascribed to impurities in the acetylene. Trimerization rates for the alkylacetylenes rose sharply with temperature increase and this was not accompanied by a significant loss in catalyst life. Catalysis of the butadiene oligomerization was also stereoselective; only 1,5-cyclooctadiene and a small amount of the 1,3 isomer were detected in the reaction products. In this case, catalyst life was very long; the cyclodimerization reaction was run for 2 weeks without rate diminution. The order of this dimerization reaction (20 °C) in $Ni_4[CNC(CH_3)_3]_7$ was established to be one. These kinetic data are consistent with but do not establish a cluster catalyzed reaction as distinguished from one catalyzed by a mononuclear complex fragment. Alkene polymerization by the nickel cluster was slow as compared with $[\eta^3-C_3H_5Fe(CO)_3]_2$.^{16a} Also slow was the hydrogen-deuterium exchange reaction between H_2 and D_2 ; equilibrium in this system required several days at 17 °C. Attempts to detect cluster hydrides in the $Ni_4L_7-H_2$ system were unsuccessful.

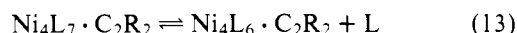
$Ni_4[CNC(CH_3)_3]_7$ did not catalyze the hydrogenation of olefins. This is ascribed to the absence of olefin- Ni_4L_7 interaction analogous to that of acetylenes with the cluster (vide infra). Separate reactions of the cluster with 1-, 2-, and 3-

hexenes in a hydrogen atmosphere (3 atm) gave no detectable amounts of hexane nor any hexene isomerization within 6 days at 20 °C. Similarly, 1,3- and 2,4-hexadienes showed no evidence of hydrogenation or isomerizations under analogous conditions. However, this cluster cleanly catalyzed the hydrogenation of terminal and internal acetylenes to olefins. Selectivity was a distinctive feature of these catalytic hydrogenations. No alkanes were produced—provided no degradation of the cluster occurred. The cluster seemed indefinitely stable in solution either in the presence of hydrogen or in the presence of the acetylene but the cluster did slowly decompose, with the formation of intractable solids, in the presence of hydrogen and an acetylene. Clear visual evidence of decomposition usually appeared after about 2 days. For the 3-hexyne hydrogenation system, the only product detected was *cis*-3-hexene for about a 1 day reaction period and the Ni_4L_7 catalyst was recovered without change. After 2 days, the only reaction products were 3-hexenes with a *cis*:*trans* ratio of ~20:1. Beyond 2-day reaction periods (where cluster decomposition was clearly evident), the *cis*:*trans* ratio dropped drastically to as low as 4:1 and *n*-hexane was a coproduct. The nature of the insoluble cluster-decomposition products was not definitely established but the intractable solids were believed to contain nickel metal. We established that nickel metal, obtained from the solution phase hydrogenation of $Ni(COD)_2$, catalyzed the hydrogenation of 3-hexyne to give *cis* and *trans* hexenes as well as *n*-hexane. Thus, the intact cluster is a selective catalyst for the formation of *cis* olefins but its instability in the reaction system places constraints on its use in synthesis.

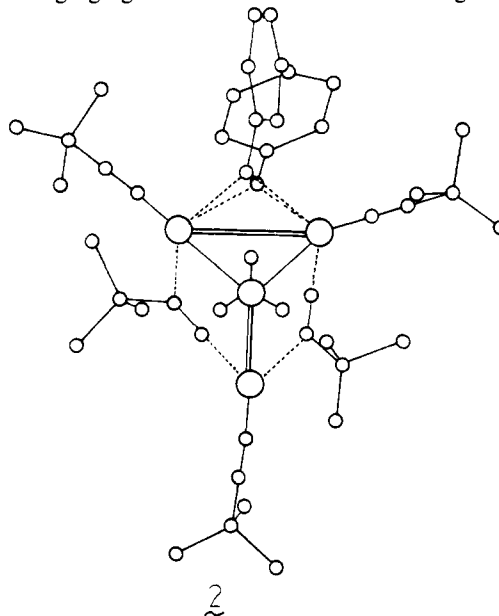
Mechanistic features of the butadiene dimerization reaction are to be further examined by possible isolation and crystallographic characterization¹³ of the butadiene- Ni_4L_7 complex; the structural features of the complex may show reasonable pathways by which dimerization might occur. Most amenable to mechanistic analysis is the catalytic hydrogenation of acetylenes to *cis* olefins. The solubilization of Ni_4L_7 in pentane by unsaturated molecules (vide supra) suggests an initial fast step (eq 12) of a 1:1 complex formation.



A second step, slow on the NMR time scale, may be the loss of isocyanide ligand (eq 13)

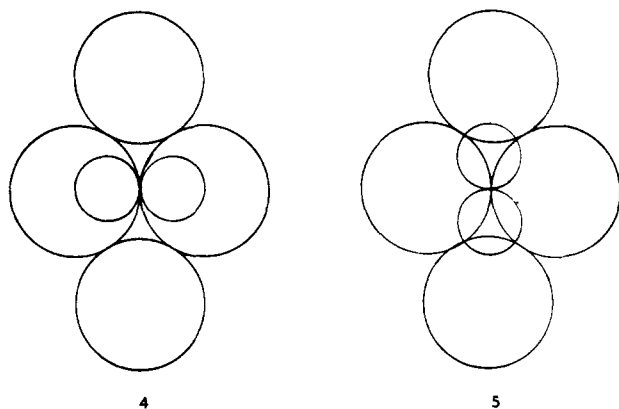


wherein the new complex would have the acetylene bound as an η^2 bridging ligand as in **2** with the RNC bridge ligands in



unsymmetric (**2**) or symmetric η^2 form. The $\text{Ni}_4\text{L}_6(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ complex has been prepared and isolated by alternative schemes and it has an NMR spectrum fully consistent with **2**.¹⁵ Hydrogen addition to the electron deficient nickel framework structure could comprise the second step which would be followed by hydrogen atom migration from nickel to the acetylenic carbon atoms to give the *cis*-olefin product. As reported in paper 5,¹ diphenylacetylene reacts with $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ to give $[(\text{CH}_3)_3\text{CNC}]_2\text{NiC}_6\text{H}_5\text{-C}\equiv\text{CC}_6\text{H}_5$ (catalytically inactive) and **3**, $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_4[\mu_3\text{-}\eta^2\text{-C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5]_3$, an active catalyst for acetylene hydrogenation. Crystallographic studies¹ of **3** established the mode of bonding of diphenylacetylene to the Ni_4 cluster to be precisely that represented for **2**. NMR studies showed that the reaction of Ni_4L_7 with dialkylacetylenes is fully reversible and yields $\text{L}_2\text{Ni}\cdot\text{RC}\equiv\text{CR}$ and $\text{Ni}_4\text{L}_{7-x}(\text{RC}\equiv\text{CR})_x$.

Collectively,^{1,6,7} our cluster studies are beginning to reveal the intimate mechanistic details of the catalytic hydrogenation process, and full kinetic and spectroscopic study is underway. We note that the acetylene bonding mode in **2** and **3** substantially reduces the acetylenic carbon-carbon bond order. Analogous structural and electronic features probably prevail in acetylene reduction on metal surfaces. Unmodified nickel metal as generated by hydrogen reduction of $\text{Ni}(\text{COD})_2$ proved active in the hydrogen reduction of acetylenes but was not selective and produced alkenes and alkanes. Sulfur or amine treatment of nickel tends to yield a surface on which the alkene hydrogenation step is strongly inhibited.^{16b} Surface modeling of this ccp-metal and of its sulfur or amine modified form is in progress—at this early stage we note that the surface sulfur “ligands” may shift^{16c} the surface acetylene bonding mode from a σ^2 to a π^2 form, **4** and **5**, respectively; the latter



form is more closely analogous to the acetylene binding mode¹ in **3**.

Experimental Section

General. All manipulations were performed using standard vacuum techniques or a Vacuum Atmosphere Dri-Lab in a N_2 or argon atmosphere. Solvents were purified by refluxing over sodium and benzophenone and distillation under vacuum (due to the sensitivity of the compounds, scrupulous exclusion of O_2 was necessary). The ^1H NMR spectra were recorded on a Varian A60-A instrument, equipped with a variable temperature probe. Infrared spectra were recorded on a Perkin-Elmer IR 337 instrument with KBr windows. Routine separation and identification of volatile compounds in catalytic reactions were effected with a Perkin-Elmer 990 gas chromatograph. Positive identification of compounds was obtained by analysis with a Finnigan Gas Chromatograph/Mass Spectrometer Model # 3300 with a System Industries-150 interface. Column material was squalane (3%, 12 ft) and ethyl *N,N*-dimethylxamate (20%, 7 ft) joined in series which is especially effective for the separation of hexane, the isomeric hexenes, and *cis*- and *trans* 2-hexene. A silver nitrate column was used for the separation of *cis*- and *trans* 3-hexene. *tert*-Butyl isonitrile and

3-hexyne, 2-butyne, and benzyl isocyanide were dried by vacuum distillation from 4A molecular sieves. The preferred purification procedure for dialkylacetylenes and for olefins comprised treatment with CaH_2 , vacuum distillation, and passage down an activated alumina (grade 1) column. Diphenylacetylene was sublimed before use. $\text{Ni}(\text{COD})_2$ was prepared as described by Schunn,¹⁷ and stored under argon. Isopropyl isocyanide was prepared by the dehydration of isopropyl formate¹⁸ as described by Ugi¹⁹ with the following modifications: after reaction and hydrolysis the aqueous layer was extracted with pentane and all the pentane fractions were combined and washed with 1% HCl solution to remove pyridine. The pentane solution was then extracted 2X with water, dried with MgSO_4 , and further dried with CaH_2 . Pentane and isopropyl isocyanide were separated by fractional distillation at reduced pressure to avoid polymerization.

Variable Temperature NMR Studies. $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ was dissolved in toluene- d_8 in a drybox and sealed under vacuum in a 5-mm NMR tube. Chemical shifts were measured in hertz relative to the center of the quintet due to residual methyl protons in the toluene- d_8 solvent. Temperatures were calibrated using the chemical shift separation obtained from a methanol solution at low temperatures and from an ethylene glycol solution at high temperatures.²⁰ The $\text{Ni}_4\text{L}_7\text{-NiL}_4$ system in toluene- d_8 was studied at a 1:1 molar ratio in the +20 to +100 °C range; apparent intercomplex ligand exchange became detectable on the NMR time scale somewhere above 50–60 °C.

Upfield from the toluene CHD_2 quintet, the first peak (intensity 3) was assigned to the bridging isocyanides, the second peak (intensity 3) was assigned to the terminal basal isocyanides, and the third peak (intensity 1) was assigned to the unique terminal isocyanide on the apical Ni atom. Computer simulations were carried out using Binsch's DNMR 3 program.²¹ Input parameters included the rate constants k_{23} (apical terminal-basal terminal exchange rate) and k_{12} , k_{13} (the bridging-terminal exchange rates). Line widths at half height in the no exchange limit were taken as 1 Hz for peak number 1, and 1.5 Hz for peaks 2 and 3. The three peaks moved towards each other, independent of the exchange process, with increasing temperature. To compensate for this, the chemical shift of peak 1 was increased 1 Hz per 10 °C and the chemical shift of peak 3 was decreased 1 Hz per 10 °C temperature rise from the no exchange limit. The k_{12} and K_{23} values were varied until the simulated spectra matched the experimental spectra. A least-squares fitting program of $\ln k$ vs. $1/T$ and $\ln k/T$ vs. $1/T$ was used to refine activation parameters.

Preparation of $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$. A mixture of 3.29 g of *tert*-butyl isocyanide (0.04 mol) and 50 ml of pentane was added to a slurry of 5.5 g of bis(1,5-cyclooctadiene)nickel(0) (0.02 mol) in 50 ml of pentane at 20 °C. After 3 h the reaction solution produced a red microcrystalline product which was removed by filtration, washed with five portions (30 ml) of pentane, and then vacuum dried (95% yield). Crystals were obtained by the diffusion of heptane into saturated cluster solutions in tetrahydrofuran (THF), benzene, or pyridine. IR: (benzene solution) $\text{CN}_{\text{bridge}}$ 1604 (m), 1620 (sh); $\text{CN}_{\text{terminal}}$ 2040 (s), 2085 (sh). ^1H NMR (60 MHz, 0 °C, Me_4Si reference) δ -2.08 (s, 9), -1.41 (s, 9), -0.63 (s, 3). Anal. Calcd for $\text{Ni}_4\text{C}_{35}\text{N}_7\text{H}_{63}$: C, 51.48; H, 7.72; N, 12.01. Found: C, 51.61; H, 7.94; N, 11.98.

$\text{Ni}[\text{CNC}(\text{CH}_3)_3]_4$ (1 mmol) and $\text{Ni}(\text{COD})_2$ (1 mmol) were added to 25 ml of pentane, and the mixture was stirred for ~5 min. After 24 h the slurry was filtered to give insoluble $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ and a yellow filtrate that contained a small amount of NiL_4 . The former was obtained in greater than 70% yield based on the equation: $7\text{NiL}_4 + 9\text{Ni}(\text{COD})_2 \rightarrow 4\text{Ni}_4\text{L}_7 + 18\text{COD}$.

Preparation of $\text{Ni}_8[\text{CNCH}(\text{CH}_3)_2]_{12}$. A mixture of 208 mg of isopropyl isocyanide (3 mmol) and 50 ml of pentane was added to a slurry of 550 mg of bis(1,5-cyclooctadiene)nickel(0) (2 mmol) in 50 ml of pentane at 20 °C. The mixture was allowed to stand for 4 h after which time a brown-black microcrystalline product was recovered by filtration and was washed with five portions (30 ml) of pentane and then vacuum dried. Crystals (plates) were obtained by the diffusion of pentane into concentrated THF solutions. IR: (mull) $\text{CN}_{\text{bridge}}$ 1600 (m), 1670 (w); $\text{CN}_{\text{terminal}}$ 2100 (s), 2140 (sh). ^1H NMR (60 MHz, 0 °C, Me_4Si reference) δ -1.1 (broad, 1), -2.0 (broad, 1). Anal. Calcd for $\text{Ni}_8\text{C}_{48}\text{N}_{12}\text{H}_{84}$: C, 44.5; H, 6.6; N, 12.9; Ni, 36.2. Found: C, 44.4; H, 6.5; N, 12.5; Ni, 35.8.

Preparation of $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_6[\text{C}_6\text{H}_5\text{CCC}_6\text{H}_5]$. A solution of *tert*-butyl isocyanide (0.125 g, 1.5 mmol) in 3 ml of pentane was added to a slurry of bis(1,5-cyclooctadiene)nickel (0.275 g, 1 mmol) in 20 ml of pentane at 20 °C. After allowing the red-brown solution to stand

Table I

Total elapsed time in h	Relative concn of cyclooctadiene at x Molar Ni ₄ L ₇ soln in C ₄ H ₆			
	0.006	0.012 (calcd) ^a	0.018 (calcd) ^a	0.024 (calcd) ^a
3	2	4 (4)	6 (6)	8 (8)
6	3.6	7 (7.2)	13 (11)	15 (14.5)
8.5	6.5	11.5 (13)	18 (19.5)	29 (26)
17	11	23 (22)	38 (33)	52 (44)
27.3	20	35 (40)	63 (60)	80 (80)

^a Calculated for first order in cluster.

10 min, diphenylacetylene (0.045 g, 0.25 mmol) was added and the solution stirred for several minutes and then allowed to stand 4 h. The brown-black microcrystalline fibers were recovered by filtration, washed with five 5-ml portions of pentane, and vacuum dried. IR (Nujol mull): CN_{terminal} 2090 (s), 2051 (vs); and CN_{bridge} 1585 (m) cm⁻¹. ¹H NMR (60 MHz, 38 °C, benzene-*d*₆ solvent, internal Me₄Si reference): δ -1.10 (s, 18), -1.20 (s, 18), -1.61 (s, 9), -1.93 (s, 9), -6.2 (br, 10).

Exchange of *tert*-Butyl Isocyanide with Ni[CNC(CH₃)₃]₄ and Ni[CNC(CH₃)₃]₄ with Ni₄[CNC(CH₃)₃]₇. Three solutions of Ni[CNC(CH₃)₃]₄ with CNC(CH₃)₃, and Ni[CNC(CH₃)₃]₄ with Ni₄[CNC(CH₃)₃]₇ at molar ratios of 1/2:1, 1:1, and 1:1/2 in each case were prepared. The solution ¹H NMR spectra in toluene-*d*₈ were then recorded between 20 and -120 °C. Only one resonance was observed at all temperatures for the CNC(CH₃)₃-Ni[CNC(CH₃)₃]₄ solution. Distinct resonances for each complex were observed for the Ni[CNC(CH₃)₃]₄-Ni₄[CNC(CH₃)₃]₇ solution up to 55 °C but these merged at higher temperatures to give a single sharp resonance at 100 °C.

Preparation of Ni₄(CNCH₂C₆H₅)₄. A solution of 0.206 g (2 mmol) of C₆H₅CH₂NC in 50 ml of pentane was added to a slurry of 0.275 g of Ni(COD)₂ (1 mmol) in 50 ml of pentane at 20 °C. The mixture was allowed to stand for 8 h, after which time a red product was removed by filtration and washed with 50 ml of diethyl ether. IR: CN_{terminal} 2040 s, 2065 sh; CN_{bridge} 1065 m, 1580 sh. Anal. Calcd for Ni₄C₃₂H₂₈N₄: C, 54.64; H, 3.98; N, 7.97. Found: C, 54.12; H, 4.06; N, 7.72.

Catalytic Reactions. The dimerization of 1,3-butadiene by Ni₄[CNC(CH₃)₃]₇ was charted at 20 °C by integration of the ¹H NMR signals for 1,5-cyclooctadiene vs. 1,3-butadiene with 0.006, 0.012, 0.018, and 0.024 M solutions of cluster in butadiene solutions. The rate of dimerization was twice (essentially identical results) followed by this technique with the four different concentrations over one half-life of the reaction. GC-MS analysis indicated three different cyclooctadienes and GC-MS analysis and ¹H NMR integration indicated the amounts of isomers present were approximately 95% 1,5-COD, 5% 1,3-COD, and a possible trace of 1,4-COD (Table I). The reaction of acetylene with a benzene solution of Ni₄[CNC(CH₃)₃]₇ was followed tensimetrically at 17 °C and by NMR; trimerization was very fast with initial turnovers of 30/min but this was accompanied by decomposition of the nickel cluster. The only product detected by GC and GC-MS was C₆H₆. The polymerization of allene was followed tensimetrically at 17 °C and 1 atm pressure of allene over a 5-ml benzene solution of 2.0 mg of cluster. The rate was approximately 14 turnovers/h which did not vary over a 72-h period.

All acetylene hydrogenation reactions were effected at 20 °C and a hydrogen pressure of about 3 atm. In the 2-butyne reaction, 0.03 mol of butyne and 0.5 × 10⁻⁵ mol of Ni₄[CNC(CH₃)₃]₇ were allowed to react with hydrogen for 3 days. Mass spectral analysis of the products showed only butene and 2-butyne to be present. ¹H NMR analysis established the butene to be *cis*-2-butene. At 60 °C, the hydrogenation rate was higher but trimerization of the butyne became a significant competing reaction.

Solutions of 2 ml of 3-hexyne and 0.01 g of cluster in 5 ml of benzene were allowed to react with hydrogen (3 atm) for 1-6 days. The conversion to 3-hexene was about 3-5% after 3 days. ¹H NMR, GC-MS, and GC analysis established the product to be *cis*-hexene. GC analysis with the coupled squalane-oxamate column failed to detect either

hexane or hexenes other than 3-hexene with reaction periods of 2-3 days or less. Analysis with a silver nitrate column was used to establish the *cis* to *trans* ratio. Turnover rate was 33-50/day. The cluster was recovered nearly quantitatively after 2-day reaction periods; beyond this time period, decomposition of the cluster was visually evident (formation of solids). In separate reactions, 1-, 2-, and 3-hexene were similarly allowed to react for 6 days, and no hexane was detected by GC analysis (at least 0.1% sensitivity); there was no evidence of olefin isomerization in these reactions as judged by GC analysis with the squalane-oxamate column. In the olefin-H₂ reaction systems, there was no visual evidence for decomposition of the Ni₄L₇ catalyst within a period of 10 days.

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- Low temperature crystallization of nickel cluster from donor solvents gives promise of yielding single crystals of the cluster complex. A low temperature crystallographic study would appear to be the only method whereby a stereochemical definition of the interaction could be defined.
- In Ni₄L₇, there are three short Ni-Ni distances. If these are formally construed as NiNi double bonds, then the cluster is formally a saturated complex. Structure 1 would be saturated if all Ni-Ni interactions were NiNi double bonds. In structure 2, the complex would be saturated if all nickel interactions, as noted by heavy lines, were double bonds.
- Single crystals of this complex are being sought so that a full structural characterization can be achieved at least for the solid phase.
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