1552 *Inorg. Chem.* **1980**, *19*, 1552-1560

Contribution from the Department of Chemistry,
University of California, Berkeley, California 94720

Metal Clusters. 23.[1] Tetranuclear Nickel Alkyl Isocyanide Clusters

E. L. MUETTERTIES,* E. BAND, A. KOKORIN, W. R. PRETZER, and M. G. THOMAS

Received October 12, 1979

The basic structural and spectral features of a family of nickel isocyanide clusters are described in this paper. This family is presently comprised of tetrahedral nickel clusters with the forms $Ni_4(CNR)_6$, $Ni_4(CNR)_7$, $Ni_4(CNR)_6L$, $Ni_4(CNR)_4(RC{\equiv}CR)_3$, and $Ni_4(CNR)_6(RC{\equiv}CR)$. All are active catalyst precursors for the hydrogenation of acetylenes and some are active for the hydrogenation of isocyanides and nitriles. Experimental details of the latter hydrogenation are presented. A comprehensive study of the interactions between clusters and simple molecules such as acetylenes is presented in an attempt to delineate mechanistic features of these cluster-catalyzed reactions.

Introduction

An essential feature in the development of a useful analogy between metal clusters and metal surfaces in chemisorption and catalytic processes is a definition of boundary conditions since the simple, small metal cluster model cannot possibly emulate a metal surface in all facets of these processes,[2] especially of catalytic processes that involve coordinately saturated clusters. We have attempted a critical assay of this analogy in the stereochemistry and catalytic chemistry of a family of tetrahedral nickel clusters comprised of the following classes: $Ni_4(CNR)_6$, $Ni_4(CNR)_7$, $Ni_4(CNR)_6L$, $Ni_4(CNR)_4(RC{\equiv}CR)_3$, and $Ni_4(CNR)_6(RC{\equiv}CR)$.[3-5] These clusters share a capability to catalytically hydrogenate molecules with triple bonds; in fact, these clusters exhibit a selectivity to molecules that have triple bonds. The catalytic hydrogenation of acetylenes was described in earlier papers.[5] Fully described here are the hydrogenations of isocyanides and nitriles.[6] The results of a comprehensive study of the cluster solution behavior and their interaction with organic molecules like acetylenes are presented in an attempt to delineate mechanistic features of the catalytic chemistry.

Results and Discussion

The Nickel Cluster Family. Isocyanides that have very bulky alkyl substituent groups react with bis(1,5-cyclooctadiene)nickel(0), $Ni(COD)_2$, to form the molecular complexes $Ni(CNR)_4$ and $Ni_4(CNR)_7$ in the molar ratios represented in (1). Isolation and NMR studies gave no evidence of other

$$Ni(COD)_2 + x\mathrm{RNC} \rightarrow 2\mathrm{COD} + ((4-x)/9)Ni_4(CNR)_7 + ((4x-7)/9)Ni(CNR)_4 \tag{1}$$

mononuclear nickel complexes such as $Ni(CNR)_3$, a type of complex known in nickel phosphine and phosphite chemistry, although a Beer's law study of $[(CH_3)_3CNC]_4Ni$ showed a departure from linearity at low concentrations which strongly implicated an $NiL_4 \rightleftharpoons NiL_3 + L$ equilibrium. The class of Ni_4L_7 clusters has been established unambiguously for $(CH_3)_3CNC$ and $C_6H_{11}CNC$ (cyclohexyl isocyanide). NMR and infrared data established a cluster form in which there are three different RNC environments of which one represents a bridging isocyanide environment. An X-ray diffraction study[3] of a disordered crystal of $Ni_4[CNC(CH_3)_3]_7$ showed that the nickel atoms form a tetrahedron, compressed along a threefold axis, with each nickel atom bearing a terminally bonded isocyanide ligand and the unique basal edge unsymmetrically bridged by isocyanide ligands (Figure 1). These $Ni_4(CNR)_7$ clusters were stereochemically nonrigid (vide infra).

Two derivatives of the parent $Ni_4[CNC(CH_3)_3]_7$ cluster were prepared by reaction, (2), of $Ni(COD)_2$ with the ap-

$$4Ni(COD)_2 + 6CNC(CH_3)_3 + L \rightarrow 8\mathrm{COD} + Ni_4[CNC(CH_3)_3]_6L \tag{2}$$

propriate equivalents of *tert*-butyl isocyanide and a second donor ligand, trimethyl phosphite or methyl isocyanide. These derivatives, $Ni_4[CNC(CH_3)_3]_6P(OCH_3)_3$ and $Ni_4[CNC(CH_3)_3]_6CNCH_3$, had NMR spectra that were consistent with the Ni_4L_7 structure (Figure 1) in which the unique ligand is bound to the apical nickel atom of the cluster. Because the activity of the two clusters in the catalytic hydrogenation of acetylene was substantially lower than for the parent Ni_4L_7 clusters and because they slowly decomposed in solution, their chemistries were not further explored.

Vacuum thermolysis of crystalline $Ni_4[CNC(CH_3)_3]_7$ at 60 °C led to loss of isocyanide. Consistent with this finding, high-temperature ^1H NMR studies of this complex suggested the facile equilibrium (3). Apparent isolation of $Ni_4[CNC(CH_3)_3]_6$

$$Ni_4(CNR)_7 \rightleftharpoons Ni_4(CNR)_6 + \mathrm{RNC} \tag{3}$$

was achieved through the reaction sequence illustrated in (4) and (5).[5] This Ni_4L_6 cluster showed CN infrared

$$2Ni(COD)_2 + 6\mathrm{RNC} + (CH_3)_2C{=}CHCH{=}C(CH_3)_2 \rightarrow 4\mathrm{COD} + Ni_4(CNR)_6[(CH_3)_2C{=}CHCH{=}C(CH_3)_2] \tag{4}$$

$$Ni_4(CNR)_6[(CH_3)_2C{=}CHCH{=}C(CH_3)_2] + H_2 \rightarrow C_8H_{16} + Ni_4(CNR)_6 \tag{5}$$

stretching frequencies at 2050–2095 and 1715–1750 cm^{-1} and a single *tert*-butyl proton NMR resonance from +50 to −50 °C [below −50 °C, the resonance progressively broadened due to relaxation (viscosity) effects].[5] Clearly a high degree of stereochemical nonrigidity is extant in $Ni_4[CNC(CH_3)_3]_6$. Crystals of this cluster with requisite dimensions and X-ray diffraction quality have not been isolated to date.[7]

The $Ni_4[CNC(CH_3)_3]_6$ cluster was also obtained from the direct reaction of $Ni(COD)_2$ with an appropriate amount of isocyanide but also formed in such reactions of $Ni(COD)_2$, and limited amounts of isocyanide was a species (or more than one species) with a very complex *tert*-butyl ^1H NMR spectrum. This latter cluster may be related to one derived from isopropyl isocyanide which had the empirical composition $Ni_2[CNCH(CH_3)_2]_3$ and also a very complex ^1H NMR spectrum. Single crystals of the isopropyl isocyanide cluster have been obtained easily, but all these crystals (plates) have

---

(1) Preceding paper in this series: Muetterties, E. L.; Sivak, A. J.; Brown, R. K.; Williams, J. W.; Fredrich, M. F.; Day, V. D. *Fundam. Res. Homogeneous Catal.* [*Proc. Int. Workshop*] *2nd*, **1979**.

(2) Muetterties, E. L.; Rhodin, T. N.; Band, A.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91.

(3) Day, V. W.; Day, R. O.; Kristoff, J. S.; Hirsekorn, F. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1975**, *97*, 2571.

(4) Thomas, M. G.; Muetterties, E. L.; Day, R. O.; Day, V. W. *J. Am. Chem. Soc.* **1976**, *98*, 4645.

(5) Thomas, M. G.; Pretzer, W. R.; Beier, B. F.; Hirsekorn, F. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 743.

(6) Band, E.; Pretzer, W. R.; Thomas, M. G.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 7380.

(7) An intermittent 4-year attempt yielded at best crystals with a small dimension of ~0.02 mm.

0020-1669/80/1319-1552$01.00/0

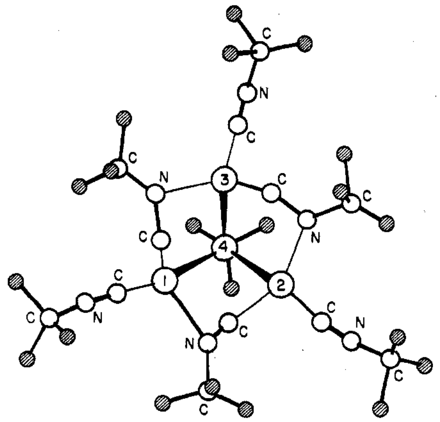


Figure 1. A representation of the structure of $Ni_4[CNC(CH_3)_3]_7$ looking down the threefold axis of the compressed tetrahedron. The unique apical nickel atom is labeled 4, and the basal nickel atoms are numbered 1 through 3. Hydrogen atoms of the *tert*-butyl groups are not depicted. The three isocyanide ligands that bridge the basal edges of the tetrahedron are effectively four-electron donors whereas the four terminally bound isocyanide ligands are two-electron donors. Because there was a disorder in the crystal used in the crystallographic study, a precise characterization of the unique bridging isocyanide ligand atom positions was not feasible.[3]

been too thin for a crystallographic study.[7] In the proton NMR spectrum of the isopropyl derivative, there was a myriad of CH and CH_3 isopropyl resonances (220 and 270 MHz). The multiplicity of isopropyl environments was too large for any highly symmetrical Ni_4L_6 cluster form.

Isocyanides with nonbulky alkyl substituents (e.g., n-C_4H_9, $C_6H_5CH_2$, and CH_3) reacted with $Ni(COD)_2$ to form $Ni(CNR)_4$, which typically possessed low solubilities in organic solvents, as well as deep red to black or black-brown solids which were essentially insoluble in nonreactive solvents and which had varying empirical compositions that ranged from NiCNR to $Ni(CNR)_{1.25}$. Since the latter complexes all showed a low-energy CN stretch indicative of a bridging RNC group, they may be related in a structural context to the $Ni_4(CNR)_6$ and $Ni_4(CNR)_7$ clusters.[5]

The Nickel Isocyanide Acetylene Family. Reaction of bis(1,5-cyclooctadiene)nickel with 1 equiv of an isocyanide and of a diarylacetylene yielded clusters of the composition $Ni_4(CNR)_4(RC{\equiv}CR)_3$ (eq 6). Isolation of the clusters was

$$4Ni(1,5\text{-}C_8H_{12})_2 + 4RNC + 3ArC{\equiv}CAr \rightarrow Ni_4(CNR)_4(ArC{\equiv}CAr)_3 + 8(1,5\text{-}C_8H_{12}) \quad (6)$$

successful only in those reaction systems based on diarylacetylenes in combination with an isocyanide having a bulky alkyl substituent, e.g., $Ni_4[CN(CH_3)_3]_4(ArC{\equiv}CAr)_3$, and $Ni_4(CNC_6H_{11})_4(ArC{\equiv}CAr)_3$ with Ar = phenyl or p-tolyl. When a nonbulky isocyanide like CH_3NC was a coreactant in (6), the insoluble $Ni_x(CNR)_y$ cluster was formed. Reaction 6 was reversible when the acetylene was a dialkylacetylene; attempts to isolate the mixed cluster led to isolation of the reactants $Ni(1,5\text{-}C_8H_{12})_2$ and $Ni_4(CNR)_7$.

An NMR study of the reaction, (7), of diphenylacetylene

$$4Ni_4[CNC(CH_3)_3]_7 + 15ArC{\equiv}CAr \rightarrow 12[(CH_3)_3CNC]_2Ni(ArC{\equiv}CAr) + Ni_4[CNC(CH_3)_3]_4(ArC{\equiv}CAr)_3 \quad (7)$$

with $Ni_4(CNR)_7$ showed no evidence of any other species than those depicted in (7) over a wide range of $Ni_4L_7{:}ArC{\equiv}CAr$ reactant ratios. In contrast, the reversible reaction of the cluster with dialkylacetylenes gave NMR evidence of three clusters, $Ni_4(CNR)_{7-x}(RC{\equiv}CR)_x$ with x = 1, 2, or 3. A cluster of the form $Ni_4(CNR)_6(RC{\equiv}CR)$ was apparently isolated with diarylacetylenes by appropriate adjustment of reactant ratios in reaction 6, but this cluster was always contaminated with the $Ni_4(CNR)_4(RC{\equiv}CR)_3$ cluster.

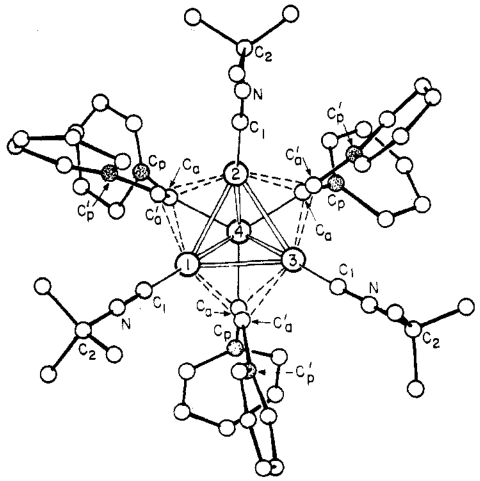


Figure 2. Perspective drawing (adapted from an ORTEP plot) of the $Ni_4[CNC(CH_3)_3]_4[\mu_3\text{-}\eta^2\text{-}C_6H_5C{\equiv}CC_6H_5]_3$ molecule viewed normal to the triangular base along the idealized threefold axis. Nickel atoms are represented by large numbered open circles and carbon and nitrogen atoms by small open circles. Ni(4) is the unique apical nickel atom which lies on the pseudo-threefold axis.

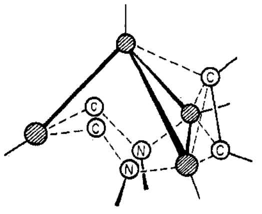


Figure 3. A possible structure for $Ni_4[CNC(CH_3)_3]_6(C_6H_5C{\equiv}CC_6H_5)$. Each nickel atom has a terminal isocyanide ligand shown only by a line projection from the nickel atoms. Two edges of the Ni_4 tetrahedron are bridged by isocyanide ligands in a manner analogous to that of the bridging isocyanides in $Ni_4[CNC(CH_3)_3]_7$ (Figure 1), and one edge is bridged by the μ_3-η^2-diphenylacetylene ligand (the phenyl groups are shown only as line projections from the acetylenic carbon atoms).

The structure of $Ni_4[CNC(CH_3)_3]_4(C_6H_5C{\equiv}CC_6H_5)_3$ is shown in Figure 2;[4] the full crystallographic investigation of this cluster and a closely related one, $Ni_4[CNC(CH_3)_3]_4(p\text{-}CH_3C_6H_4C{\equiv}CC_6H_4\text{-}p\text{-}CH_3)_3$ will be described in a separate article. In these acetylene clusters, there was no evidence of fast intramolecular ligand exchange as was established for Ni_4L_7 by NMR studies; the proton NMR spectra were invariant from −80 to +80 °C. The apparent derivative cluster, $Ni_4[CNC(CH_3)_3]_6(C_6H_5C{\equiv}CC_6H_5)$, consistently exhibited an ^1H NMR spectrum that was difficult to *fully* rationalize. There was a broad phenyl resonance and four *tert*-butyl methyl resonances in the ratios 9:9:18:18 which in principle is consistent with the structure shown in Figure 3, but the *tert*-butyl hydrogen chemical shift positions would not be analogous to those in $Ni_4[CNC(CH_3)_3]_7$ because such a structural assignment would require the protons of the two bridging isocyanides to have a relatively higher field chemical shift than those of some of the terminal isocyanide ligands. This monoacetylene cluster slowly decomposed in solution at 25 °C and single crystals were not obtained.[5]

Solution Properties of Ni_4L_7 Clusters. The visible spectrum of $Ni_4[CNC(CH_3)_3]_7$ consisted of a maximum of 4370 Å (ϵ 20 000). A concentration study of benzene solutions of this cluster down to 10^{-6} M showed no departure from Beer's law behavior (Figure 4). This result was somewhat unexpected; we had presumed that $Ni_4[CNC(CH_3)_3]_6$ was a key, reactive intermediate in catalytic reactions of the parent Ni_4L_7 cluster

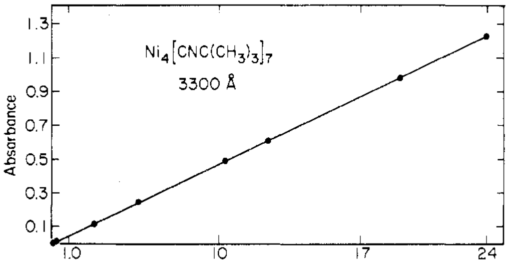


Figure 4. Beer's law plot for $Ni_4[CNC(CH_3)_3]_7$ in toluene at 20 °C.

Table I. Chemical Shifts (δ) of $(CH_3)_3CNC$ Protons in $Ni_4[CNC(CH_3)_3]_7$ in Various Organic Solvents at 0 °C

					solvent properties	
solvent	δ_B	δ_{BT}	δ_{AT}	δ_M[a]	ϵ[b]	Z[c]
C_6D_6[d]	2.07	1.32	0.43	1.17	2.36	54.0
$C_6D_5CD_3$	1.99	1.34	0.47	1.20	2.44	
$(CD_2)_4O$	1.67	1.64	1.12	1.46	7.6[d]	58.8
C_5H_5N	1.94	1.54	0.53	1.29	12.5[e]	64.0
$(CD_3)_2CO$	1.68	1.68	1.15	1.50	23.3	65.5
CD_3CN	1.65	1.66	1.14	1.52	42.0	71.3
C_6H_5CN	1.83	1.53	0.38	1.27	28.5	65.0
$C_6H_5CH_2CN$	1.82	1.43	0.30	1.18	20.1	

[a] Chemical shift for the ubiquitous $Ni[CNC(CH_3)_3]_4$ impurity. [b] Solvent dielectric constant. [c] Kosower Z constant. [d] At 3 °C. [e] At 20 °C.

because free isocyanide was recovered from the high vacuum pyrolysis of the crystalline parent cluster at 60 °C. However, because of similarities in the electronic spectra, minor dissociation of Ni_4L_7 into Ni_4L_6 and L would probably not be detected by this procedure.

Earlier we noted the solubilization of $Ni_4[CNC(CH_3)_3]_7$ in pentane by the addition of equimolar quantities of π donors such as aromatic hydrocarbons and dienes.[3,4] Definition of this cluster–donor ligand interaction was sought in an NMR study. The cluster exhibited three *tert*-butyl proton resonances of relative 3:3:1 intensities that represent the bridging (δ_B), basal terminal (δ_{BT}), and apical terminal (δ_{AT}) isocyanide ligands, respectively. Donor solvent interactions were found to affect only the chemical shifts; there was no perturbation of the basic 3:3:1 resonance set within the temperature range of −50 to 0 °C, although one accidental degeneracy (in acetone-d_6) for δ_B and δ_{BT} was noted. There was no simple correlation of the chemical shift values and solvent properties although δ_B tended to shift to higher magnetic field and δ_{BT} and δ_{AT} to lower fields with increasing polarity of the solvent. Sample data are presented in Table I along with values for the solvent dielectric constant and the Kosower Z constant. For solvent mixtures, the chemical shifts varied linearly with solvent composition; see Figure 5. Acetylenes formed discrete cluster complexes in the interaction with $Ni_4[CNC(CH_3)_3]_7$ as discussed below. Strong σ-donor and π-acceptor molecules like phosphines, phosphites, and carbon monoxide converted Ni_4L_7 to mixtures of mononuclear $NiL_2L'_2$ and $NiLL'_3$ complexes.

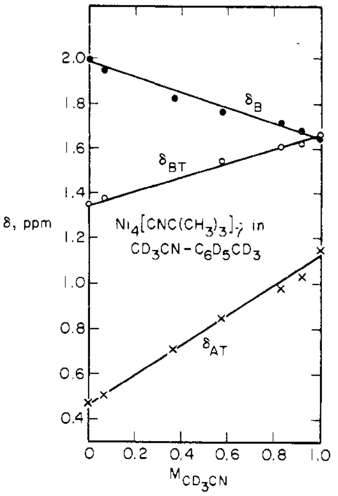


Figure 5. Chemical shifts for $Ni_4[CNC(CH_3)_3]_7$ at 0 °C presented as a function of the molar fraction of CD_3CN in a CD_3CN–$C_6D_5CD_3$ solution. δ_B, δ_{BT}, and δ_{AT} refer to the resonances associated with the bridging, basal terminal, and apical terminal isocyanide proton resonances, respectively.

$Ni_4[CNC(CH_3)_3]_7$ is a stereochemically nonrigid molecule.[3] Intramolecular ligand exchange in this cluster proceeds in two discrete steps as analyzed in paper 6 of this series. In the low-temperature process (LTP), an exchange effects the equilibration of the two types (δ_{BT} and δ_{AT}) of terminal isocyanide ligand resonances. In the high-temperature process (HTP), all isocyanide environments are rendered environmentally equivalent on the NMR time scale. This exchange process has been evaluated as a function of the medium with the determination of exchange parameters; the calculated parameters are presented in Table II. Variations with medium in E_a, $\Delta H^‡$, and $\Delta S^‡$ are significant, but $\Delta G^‡$ values are nearly invariant; the average $\Delta G^‡$ values are 16.2 ± 0.5 and 18.9 ± 0.7 kcal/mol for the LTP and HTP, respectively. The near constancy in the two $\Delta G^‡$ values suggests that these reflect the thermodynamic features of the two transitional states. For the $\Delta H^‡$ and $\Delta S^‡$ values there is a cooperativity effect; the graph of $\Delta S^‡$ vs. $\Delta H^‡$ is for both the LTP and HTP a near

Table II. Activation Parameters for Intramolecular Ligand Exchange in $Ni_4[CNC(CH_3)_3]_7$

solvent	process	temp interval, °C	$E_a^{‡}$ [a]	$\Delta H^{‡}$ [a]	$\Delta S^{‡}$ [b]	$\Delta G^{‡}$ [a]
C_6D_6	LTP	0–40	15.1 ± 0.6	14.5 ± 0.6	−6.5 ± 0.2	16.4 ± 0.7
	HTP	40–80	15.4 ± 1.4	14.8 ± 0.4	−13.3 ± 0.3	18.8 ± 1.5
$C_6D_5CD_3$	LTP	13–57	16.5	15.9	−1.0	16.2
	HTP	42–120	17.3	16.5	−5.0	18.0
$(CD_2)_4O$	LTP	−17–37	14.5 ± 0.4	13.9 ± 0.4	−5.4 ± 0.2	15.5 ± 0.5
	HTP	37–78	17.8 ± 0.2	17.1 ± 0.2	−4.9 ± 0.1	18.6 ± 0.3
C_5H_5N	LTP	18–47	16.5 ± 0.5	15.8 ± 0.4	−2.5 ± 0.3	16.5 ± 0.5
	HTP	47–110	18.6 ± 0.7	18.0 ± 0.6	−4.8 ± 0.4	19.4 ± 0.7
$(CH_3)_2CO$	LTP	−13–81	16.1 ± 0.6	15.2 ± 0.2	−1.3 ± 0.3	15.6 ± 0.6
	HTP	32–81	16.5 ± 0.8	15.9 ± 0.7	−8.2 ± 0.4	18.3 ± 0.8
CD_3CN	LTP	−5–30	12.9 ± 0.7	12.2 ± 0.5	−12.3 ± 0.3	15.9 ± 0.6
	HTP	30–69	16.6 ± 1.2	16.0 ± 1.2	−8.2 ± 0.5	18.4 ± 1.3
C_6H_5CN	LTP	14–32	15.3 ± 0.3	14.7 ± 0.2	−6.3 ± 0.2	16.6 ± 0.3
	HTP	31–92	19.3 ± 0.7	18.6 ± 0.6	−3.4 ± 0.2	19.6 ± 0.7
$C_6H_5CH_2CN$	LTP	14–47	18.1 ± 0.9	17.5 ± 0.9	+2.9 ± 0.5	16.8 ± 1.0
	HTP	47–102	19.6 ± 0.9	19.0 ± 0.8	−3.7 ± 0.4	20.1 ± 1.0

[a] kcal/mol. [b] cal/(mol deg).

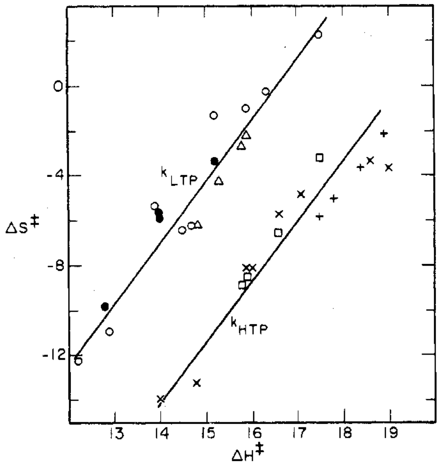


Figure 6. Plot of $\Delta S^{\ddagger}$ (cal mol^{-1} deg^{-1}) vs. $\Delta H^{\ddagger}$ (kcal mol^{-1}) for the LTP exchange process for $Ni_4[CNC(CH_3)_3]_7$ in pure solvents (○), mixtures of CD_3CN and $CD_3C_6D_5$ (●), and mixtures of C_6H_5CN and C_6D_6 (△) and for the HTP process in pure solvents (×), mixtures of CD_3CN and $CD_3C_6D_5$ (□), and mixtures of $C_6H_5CN + C_6D_6$ (+).

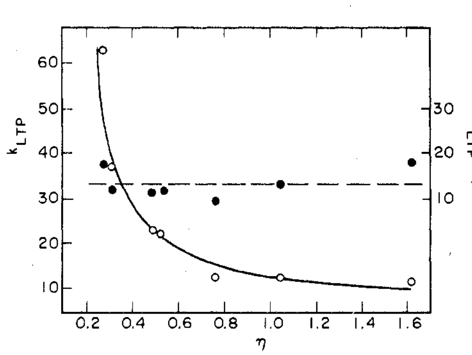


Figure 7. Plot of k_{LTP} vs. viscosity (η) and of $k_{LTP}\eta$ vs. viscosity for $Ni_4[CNC(CH_3)_3]_7$ in various solvents.

straight line for a variety of solvents (Figure 6). A similar effect upon exchange parameters was observed for acetonitrile-d_3–toluene-d_8 mixtures; $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ varied nearly monotonically with composition, while $\Delta G^{\ddagger}$ was essentially invariant. The primary correlation between the activation parameter and the solvent seems to be best based or at least summarized in the solvent viscosity. This correlation is shown in Figure 7 where k_{LTP} and $k_{LTP}\eta$ are plotted against η, the medium viscosity; the $k_{LTP}\eta$ vs. η plot is essentially a horizontal straight line. These correlations are explicable in that an intramolecular isocyanide ligand-exchange process, where the *tert*-butyl proton (isocyanide substituent) interactions with solvent must be substantial, should be sensitive to solvent viscosity. This viscosity effect is more marked for the high-temperature process which involves bridge–terminal exchange; consistent with this result was the low-termperature (−30 to −50 °C) observation that viscosity broadening appeared first for the bridge isocyanide resonance.

A nearly ubiquitous impurity in solutions of $Ni_4[CNC(CH_3)_3]_7$ was $Ni[CNC(CH_3)_3]_4$. Exchange broadening of the very weak resonance line associated with this mononuclear complex was evident in the 30–70 °C temperature range. Hence, a contributing *intermolecular*-exchange process to the Ni_4L_7 exchange phenomena must be based on reactions like (8) through (10). Crude estimates of $\Delta G^{\ddagger}$ for intermolecular

$$NiL_4 \rightleftharpoons NiL_3 + L \qquad (8)$$

$$\text{“L”} + Ni_4L_7 \rightleftharpoons Ni_4L_6\text{“L”} + L \qquad (9)$$

$$Ni_4L_7 \rightleftharpoons Ni_4L_6 + L \qquad (10)$$

exchange between Ni_4L_7 and NiL_4 impurity were 17.4, 16.6, and 17.9 kcal/mol for benzene, acetone, and benzyl cyanide solutions.

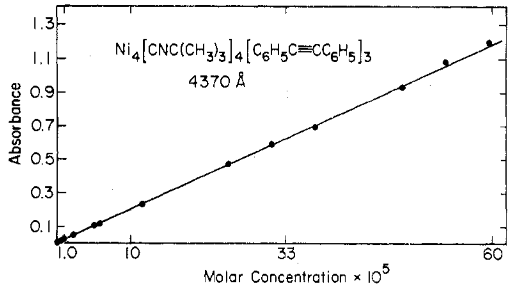


Figure 8. Beer's law plot for $Ni_4[CNC(CH_3)_3]_4(C_6H_5C{\equiv}CC_6H_5)_3$.

The cyclohexyl isocyanide Ni_4L_7 cluster was not subject to an incisive NMR analysis because of the overlap of the cyclohexyl protons. The ^1H spectrum showed a slight dependence upon temperature consistent with, but not definitive for, a stereochemical nonrigid molecule.

Interaction of $Ni_4[CNC(CH_3)_3]_7$ with $(CH_3)_3CNC$ in benzene-d_6 was monitored by ^1H NMR spectroscopy at 0 °C. Addition of the isocyanide to the solution of the cluster gave rise to the resonance of $Ni[CNC(CH_3)_3]_4$. The only resonances observed were those characteristic of the cluster and the mononuclear complex between the isocyanide to nickel cluster ratios of 7:4 to 4:1.

Solution Properties of $Ni_4L_4(RC{\equiv}CR)_3$. The mixed nickel isocyanide diarylacetylene clusters were stable solution species which exhibited no evidence of dissociation. For $Ni_4[CNC(CH_3)_3]_4(C_6H_5C{\equiv}CC_6H_5)_3$, there was no departure from Beer's law behavior down to 10^{-6} M concentrations (Figure 8). Unlike the parent Ni_4L_7 cluster, the acetylene clusters were not stereochemically nonrigid. The proton NMR spectrum of $Ni_4[CNC(CH_3)_3]_4(C_6H_5C{\equiv}CC_6H_5)_3$ consisted of two *tert*-butyl resonances of relative intensities 3 and 1 and two separate phenyl multiplet resonances as fully required in the established crystalline state structure (Figure 2). Other than minor chemical shift changes, the proton NMR spectrum was invariant from −30 to +90 °C. An analogous NMR behavior was observed for $Ni_4[CNC(CH_3)_3]_4(p\text{-}CH_3C_6H_4C{\equiv}CC_6H_4\text{-}p\text{-}CH_3)_3$ and $Ni_4(CNC_6H_{11})_4(C_6H_5C{\equiv}CC_6H_5)_3$. In the presence of either excess diphenylacetylene or 2-hexyne, the cluster showed no evidence of fast (NMR time scale) acetylene ligand exchange up to 80 °C; the spectral composites of cluster and free acetylene were not significantly altered over this temperature range. Acetylene ligand exchange occurred between di-*p*-tolylacetylene and $Ni_4[CNC(CH_3)_3]_4(C_6H_5C{\equiv}CC_6H_5)_3$ as evidenced by the diminution of the methyl NMR resonance of the free tolylacetylene and the appearance of a new methyl resonance in the region of the tolyl methyl resonance in $Ni_4[CNC(CH_3)_3]_4(C_7H_7C{\equiv}CC_7H_7)_3$. This exchange was very slow at 20 °C; only about 10% exchange in the cluster was observed after 5 days. Solutions of the cluster reacted immediately with *tert*-butyl isocyanide to form the mononuclear $M(CNR)_4$ complex, (11), but the rate for the analogous reaction (12) with phosphines and phosphites was lower.

$$Ni_4(CNR)_4(RC{\equiv}CR)_3 + 6RNC \rightarrow 3(RNC)_2Ni(RC{\equiv}CR) + Ni(CNR)_4 \qquad (11)$$

$$Ni_4(CNR)_4(RC{\equiv}CR)_3 + 3L \rightarrow 2(RNC)_2Ni(RC{\equiv}CR) + RC{\equiv}CR + 2Ni(CNR)L_3 \qquad (12)$$

Hydrogen reacted rapidly with $Ni_4[CNC(CH_3)_3]_4(C_6H_5C{\equiv}CC_6H_5)_3$ at 20 °C to initially form *cis*-stilbene.[5] As this hydrogenation progressed toward completion, nickel metal separated out. In the presence of excess diphenylacetylene, the hydrogenation reaction was catalytic and the catalyst could be quantitatively recovered. The cluster was also a catalyst for dialkylacetylene hydrogenation. For 3-hexyne, the turnover rate was about 0.3/min although after about 15 h, catalyst degradation was evident (solids were present). Product analysis after 20 h showed *cis*-3-hexene, hexane and *trans*-3-hexene to be present in 128:2.7:1 proportions, respectively. The relative concentrations of the latter two were respectively lower and higher at shorter and longer reaction periods; apparently these two products were largely derived from a hydrogenation catalyzed by a cluster degradation product as was observed earlier for Ni_4L_7-catalyzed hydrogenation of acetylenes.[5]

There was no interaction between the Ni_4L_7 cluster and olefins, and this parent cluster did not catalyze the hydrogenation of olefins. In addition, the acetylene derivative cluster did not interact with olefins; an olefin does not possess the requisite electronic features to bind as a ligand in the cluster and is not a sufficiently strong σ-donor–π-acceptor ligand to displace the terminally bound isocyanide ligand. However, the acetylene clusters did "catalyze" the hydrogenation of olefins. In the first stages of the hydrogen–1-hexene reaction at 20 °C, *cis*-stilbene was formed, (13). Then the nickel

$$Ni_4(CNR)_4(C_6H_5C{\equiv}CC_6H_5)_3 + 3H_2 \rightleftharpoons \text{“}Ni_4(CNR)_4\text{”} + 3C_6H_5CH{=}CHC_6H_5 \quad (13)$$

isocyanide fragment which was not stabilized substantially by the interaction with 1-hexene decomposed to form a nickel mirror and $Ni_4(CNR)_7$. The nickel mirror was responsible for the observed hexane formation which was relatively rapid (~0.2–1.0 turnover per minute) once the solids formed. Dienes, unlike simple olefins, were catalytically hydrogenated by $Ni_4(CNR)_4(C_6H_5C{\equiv}CC_6H_5)_3$, and these reaction systems were homogeneous over 1- and 2-week periods. The hydrogenation products from 1,3-hexadiene and 2,4-hexadiene were quite different: the 2,4 isomer yielded only hexane whereas the 1,3 isomer gave a gross mixture of hexenes which included 1-hexene, *cis*-3-hexene, *trans*-3-hexene, and *trans*-2-hexene in 1:0.2:1.3:1 proportions. Turnover rates were very low in these hydrogenations, in the ranges of 2–3 turnovers per day at 20 °C. Intermediates of the form $Ni_4L_4(\text{diene})_x$ may have been present in these systems since a complex of the form $Ni_4[CNC(CH_3)_3]_6$(1,3-tetramethylbutadiene) was obtained by reaction 4. In any case, the qualitatively different behavior of the 1,3- and 2,4-hexadiene seems inexplicable. However, since the 2,4-hexadiene system always contained very small amounts of solids, these solids (not nickel metal) may have been responsible for the catalyzed hexane formation.

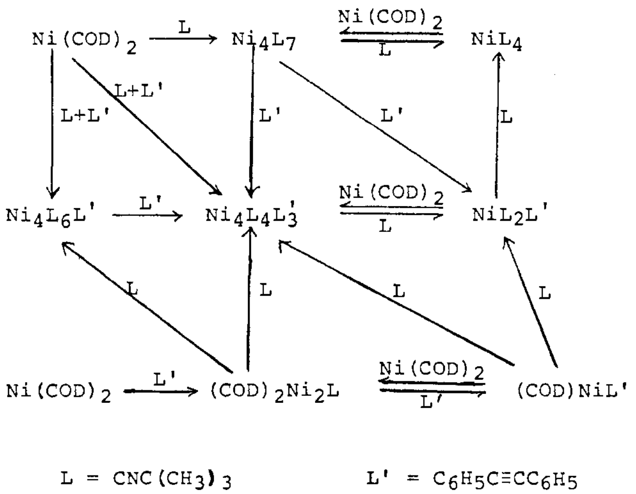
Reactions of Ni_4L_7 and Acetylenes. Chemical isolation and NMR solution studies have established that the $Ni_4[CNC(CH_3)_3]_7$ reaction with diarylacetylenes is precisely represented by eq 14 and that there is no further reaction between excess

$$4Ni_4L_7 + 15RC{\equiv}CR \rightarrow 12L_2Ni(RC{\equiv}CR) + Ni_4L_4(RC{\equiv}CR)_3 \quad (14)$$

diphenylacetylene and $Ni_4L_4(RC{\equiv}CR)_3$ except for a slow intermolecular acetylene exchange which was discussed above. Furthermore, the synthetically useful reaction of $Ni(COD)_2$, *tert*-butyl isocyanide, and diphenylacetylene can be tailored through stoichiometry control to produce all three nickel compounds shown in (14) as well as $Ni_4L_6(C_6H_5C{\equiv}CC_6H_5)$. For completion, the full scope of this reaction system is shown in Scheme I which takes into account the conversion (rapid and quantitative) of the nickel clusters to the mononuclear NiL_4 and $L_2Ni(C_6H_5C{\equiv}CC_6H_5)$ complexes by reaction with isocyanide.

Both Ni_4L_7 and $Ni_4L_4(C_6H_5C{\equiv}CC_6H_5)_3$ catalyzed the hydrogenation of diphenylacetylene to *cis*-stilbene at 20 °C.[3,6] Ni_4L_7 itself underwent no reaction with hydrogen until temperatures of 90 °C were attained (see below). However, the acetylene cluster reacted with hydrogen at room temperature to form *cis*-stilbene. The mononuclear complex $L_2Ni(C_6H_5C{\equiv}CC_6H_5)$, that formed along with acetylene clusters in the Ni_4L_7–diphenylacetylene reaction, did not react with hydrogen nor did it catalyze the hydrogenation of acetylenes at 20–80 °C.[6] These facts coupled with the observation that $Ni_4L_4(C_6H_5C{\equiv}CC_6H_5)_3$ was recovered from the catalytic hydrogenation reactions suggest that clusters may be intermediates in the catalytic cycle. The rate-determining step in the catalytic cycle appears to be the addition of hydrogen to this cluster, but the lifetimes of the presumed hydridonickel intermediates must be very short since we have been unable to detect such intermediates at 1–3 atm and −40 to +40 °C by NMR techniques. Hence, we cannot exclude the possibility of cluster fragmentation in the later hydrogenation steps. It is significant, however, that these diarylacetylene hydrogenations catalyzed by the acetylene cluster do not produce, in a side reaction, hexaarylbenzenes; this fact might be taken as evidence against mononuclear intermediates in the diarylacetylene reaction systems since acetylene trimerizations are reactions characteristic of mononuclear metal complexes.

Scheme I



Reaction of dialkylacetylenes and $Ni_4[CNC(CH_3)_3]_7$ provided no synthetic route to nickel clusters with dialkylacetylene ligands; these reactions yielded only starting reagents through conventional isolation procedures. However, a reversible reaction between the cluster and dialkylacetylenes does occur and is a relatively fast reaction as established through solution NMR studies. Addition of 3-hexyne to solutions of $Ni_4[CNC(CH_3)_3]_7$ gave rise to resonances ascribable to $(RNC)_2Ni(C_2H_5C{\equiv}CC_2H_5)$ and the clusters, $Ni_4(CNR)_{7-x}(C_2H_5C{\equiv}CC_2H_5)_x$ where $x = 1$–3. In the limiting case of a large excess of 3-hexyne, the only detectable species by the NMR technique was $(RNC)_2Ni(C_2H_5C{\equiv}CC_2H_5)$. Undetected but implicated by stoichiometry considerations was $Ni(C_2H_5C{\equiv}CC_2H_5)_2$. Similar results were obtained with 2-butyne and with methylphenylacetylene. Such mononuclear species may be the key intermediates in the trimerization of the dialkylacetylene to hexaalkylbenzenes which is a competing catalytic reaction in the hydrogenation of dialkylacetylenes with a $Ni_4(CNR)_7$ or $Ni_4(CNR)_4(ArC{\equiv}CAr)_3$ catalyst precursor, and, of course, such a mononuclear species could be a key intermediate in the catalytic hydrogenation sequence. Attempts to prepare this species from $Ni(COD)_2$ and acetylene were unsuccessful; the only NMR-detectable and also isolable (in the arylacetylene case) species were $Ni_2(COD)_2(RC{\equiv}CR)$[8] and $Ni(COD)(RC{\equiv}CR)$.[9]

---

(8) Muetterties, E. L.; Pretzer, W. R.; Thomas, M. G.; Beier, B. F.; Thorn, D. L.; Day, V. W.; Anderson, A. B. *J. Am. Chem. Soc.* **1978**, *100*, 2090.

(9) This mononuclear complex has been structurally defined by an X-ray crystallographic study which will be reported separately.

The rather sharply contrasting behavior of diarylacetylenes and dialkylacetylenes (or alkylarylacetylenes) in their interactions with Ni_4L_7 (and with the $Ni(COD)_2$ + RNC reaction mixture) is somewhat difficult to explain. The facile reversibility of the dialkylacetylene reactions is in itself easy to rationalize but the reaction of dialkylacetylenes with the $Ni_4L_4(RC{\equiv}CR)_3$ cluster (R = alkyl) is surprising because there is no reaction between diphenyl acetylene and $Ni_4L_4(C_6H_5C{\equiv}CC_6H_5)_3$. Consistent with these data, Ni_4L_7 was recovered from this cluster's catalyzed hydrogenations of dialkylacetylenes.

The mononuclear complex, $[(CH_3)_3CNC]_2Ni(C_6H_5C{\equiv}CC_6H_5)$, underwent no reaction with hydrogen, or with hydrogen and excess diphenylacetylene, until temperatures in excess of 80–90 °C were attained.[5] Under these conditions, hydrogenation of the acetylene to stilbene was observed, along with a competing trimerization of the acetylene to hexaphenylbenzene, but only with the concomitant formation of a red-brown coloration typical of tetranuclear clusters. In fact, the $Ni_4[CNC(CH_3)_3]_6$ cluster was isolated from such high-temperature reactions.[5] This cluster is presumed to be a key intermediate along with $Ni_4L_6(RC{\equiv}CR)$ in such high-temperature hydrogenations. These experiments definitively establish the low reactivity of the mononuclear complex $(RNC)_2Ni(HC{\equiv}CH)$ to a hydrogenation reaction. However, the competitive acetylene trimerization reaction suggests that mononuclear species of the type $Ni(C_6H_5C{\equiv}CC_6H_5)_2$ or $LNi(C_6H_5C{\equiv}CC_6H_5)$ might be present in the high-temperature hydrogenation reaction. Such complexes, although not detected, could serve as intermediates not only in the trimerization reaction but also in the hydrogenation reactions.

Catalytic Hydrogenation of Isocyanides and Nitriles by Tetranuclear Nickel Clusters. There was no evidence of interaction between $Ni_4[CNC(CH_3)_3]_7$ and hydrogen at 25 °C and 1–3 atm. However, an irreversible interaction occurred at temperatures of 90 °C and above with toluene solutions of the cluster to produce *tert*-butylamine, *tert*-butylmethylamine, and methylcyclohexane in about equimolar amounts and an insoluble solid that contained nickel metal. The recovered solid and also nickel metal itself were shown to catalyze the hydrogenation of *tert*-butyl isocyanide in toluene to produce the two amines and methylcyclohexane in similar proportions.[6] Clearly nickel metal formed in the reduction was responsible for the toluene hydrogenation to methylcyclohexane.

A homogeneous and selective catalytic isocyanide hydrogenation was achieved in a toluene solution by using $Ni[CNC(CH_3)_3]_4$ as the continuing source of isocyanide and $Ni_4[CNC(CH_3)_3]_7$ as the catalyst precursor.[6] The hydrogenation product was *tert*-butylmethylamine with only small amounts of *tert*-butylamine. No solids were evident in the 90–120 °C reaction temperature range and 1–3 atm; most critically, the absence of nickel metal in these reaction systems was clearly shown by the fact that no methylcyclohexane could be detected. Materials balance for reaction 15 was clearly quantitative as judged by (1) hydrogen uptake, (2) a quantitative measure of amine product, and (3) the molar ratio of $Ni(CNR)_4$ to $Ni_4(CNR)_7$ in the product. Turnover rates were 0.1/h and 0.7/h (amine per nickel cluster) at 90 and 127 °C, respectively. These experiments represent the first demonstration of a homogeneous catalytic hydrogenation of an isocyanide. A simpler experimental modification of the catalytic system was based on a 1:3 molar ratio of $Ni(COD)_2$ to *tert*-butyl isocyanide which gave at 125 °C a turnover rate of 0.5/h and a selectivity of 99%. Much lower selectivities were observed with *n*-butyl, isopropyl, and cyclohexyl cyanides which gave selectivities to the corresponding secondary amines of 77, 73, and 35%, respectively.

$$4Ni(CNR)_4 + H_2 \xrightarrow{Ni_4(CNR)_7} 9RNHCH_3 + Ni_4(CNR)_7 \tag{15}$$

Catalytic reactions with *tert*-butyl isocyanide and a second isocyanide yielded results that suggested a cluster complex may actually be an intermediate. The nickel clusters based on methyl isocyanide and benzyl isocyanide are quite insoluble in toluene. Hence, the catalytic systems based on mixtures of $Ni_4[CNC(CH_3)_3]_7$ and either $Ni(CNCH_3)_4$ or $Ni(CNCH_2C_6H_5)_4$ gave the insoluble methyl or benzyl isocyanide clusters. On hydrogenation at 90 °C and 3 atm, no *tert*-butylamines were produced—only dimethylamine and a mixture of benzylmethylamine and benzylamine were produced respectively albeit at a low rate presumably because of the low solubility of the respective clusters.[6]

A hydrogenation of acetonitrile to ethylamine was achieved in a 90 °C homogeneous reaction of hydrogen and an acetonitrile solution of $Ni_4[CNC(CH_3)_3]_7$.[6] Reaction rate was very low and the products were $C_2H_5NH_2$ and $(CH_3)_3CNHCH_3$ in a 5:1 molar ratio, respectively. An alternative reaction system comprising hydrogen and an acetonitrile solution of $Ni_4[CNC(CH_3)_3]_4(C_6H_5C{\equiv}CC_6H_5)_3$ yielded $C_6H_5CH{=}CHC_6H_5$ and $C_2H_5NH_2$; hydrogenation of the isocyanide ligand was not detected. The turnover rate for the amine was about 1/h at 63 °C but the system became visibly heterogeneous after 1 h. In attempts to effect the hydrogenation of $^{15}N_2$ with $Ni_4[CNC(CH_3)_3]_4(C_6H_5C{\equiv}CC_6H_5)_3$ and with $Ni_4[CNC(CH_3)_3]_7$, traces of ammonia were detected. However, we have never detected $^{15}NH_3$ from $^{15}N_2$ reactions and, therefore, conclude that N_2 has not been the source of the NH_3 formed in the reactions. No ammonia was detected in a similar system with the $Ni_4[CNC(CH_3)_3]_7$ cluster at 90 °C.

The mechanisms of these catalytic hydrogenations of CN triple bonds are not defined. In the cluster, the unique bridging isocyanide ligands may be more susceptible to hydrogenation than terminally bound isocyanides since the bond order of the CN bond is lower for the bridging ligands. A plausible active intermediate is $Ni_4(CNR)_6$ which is generated from $Ni_4(CNR)_7$ at elevated temperatures, but an equally plausible one is mononuclear $Ni(CNR)_2$ species which could be formed at higher temperatures through a fragmentation of the cluster.

Hydrogenation of Acetylenes, Olefins, and Isocyanides with Nickel Metal. As a check on relationships between nickel cluster and nickel metal catalyzed reactions, the qualitative features of alkyne, alkene, and alkyl isocyanide hydrogenation reactions with nickel metal and nickel metal treated with alkyl isocyanide were examined.

Samples of nickel metal were generated by hydrogenation of bis(1,5-cyclooctadiene)nickel or by decomposition and hydrogen reduction of $Ni(NO_3)_2{\cdot}6H_2O$. In some cases, the nickel surface was pretreated with *tert*-butyl isocyanide prior to use in catalytic reactions. Both forms of nickel metal functioned similarly and in a qualitatively different fashion from the molecular nickel clusters. In the hydrogenation of *tert*-butyl isocyanide, nickel metal effected a nonselective reduction whereby substantial quantities of *tert*-butylamine, as well as methylcyclohexane from the toluene solvent, were produced in addition to *tert*-butylmethylamine. In the catalytic hydrogenation of acetylenes, the nickel metal obtained from both preparative procedures catalytically functioned quite similarly to the nickel acetylene clusters to produce cis olefins—in fact, the metal was more selective at 20 °C with a cis:trans olefin product ratio of 50:1 compared to ~20:1 for the clusters. This ratio for the metal catalyst dropped to ~30:1 at 80 °C. There was, however, a distinctive difference between the metal and the clusters. The metal effected olefin isomerization whereas none was evident in the cluster system. In addition, some alkane was produced in the metal systems whereas the clusters showed no activity for olefin hydrogenation. Despite the fact that the nickel metal was a very active catalyst for olefin isomerization, it selectively hydrogenated acetylenes when exposed to acetylene–olefin mixtures. This common feature of homogeneous and heterogeneous catalysis may relate to bonding strengths of acetylenes vis-â-vis olefins. Nickel metal pretreated with $(CH_3)_3CNC$ did not function in a qualitatively different manner from "untreated" nickel metal—the only difference was a slight increase in selectivity and a decrease in rates on treatment of the surface with isocyanide.

Experimental Section

General Data. All manipulations were performed by using standard vacuum techniques or a Vacuum Atmospheres 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 No. 3300, with a System Industries 150 interface. Column material was squalene (3%, 12 ft) and ethyl *N,N*-dimethyloxamate (20%, 7 ft) joined in series which was 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. Columns employed for the separation of amines produced in the catalytic hydrogenation of isocyanides are described below.

tert-Butyl isocyanide, 3-hexyne, 2-butyne, and benzyl isocyanide were dried by vacuum distillation from 4A molecular sieves. The 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. $Ni(COD)_2$ was prepared as described by Schunn[10] and stored under argon. Isopropyl isocyanide was prepared by the dehydration of isopropyl formate as described by Ugi[11] 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 two times 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.

The preparations of $Ni_4[CNC(CH_3)_3]_7$, $Ni_2[CNC(CH_3)_2H]_3$, and $Ni_4[CNC(CH_3)_3]_6(C_6H_5C{\equiv}C_6H_5)$ were described in paper 6,[5] but see also the additional experiments for the latter two described below.

Beer's law studies followed the procedure described by Harris[12] and Harris et al.[13] All nickel complexes were freshly prepared and recrystallized prior to use. Solvents were purified by extended refluxing with sodium and benzophenone under a nitrogen atmosphere, distillation under nitrogen, and then degassing by freeze-pumping on a high-vacuum manifold. Glassware was oven dried at 120 °C prior to use, and spectrophotometric cells were vacuum dried in a desiccator for 24 h. Solutions were prepared by standard volumetric techniques under an argon atmosphere in a Vacuum Atmospheres Dri-Lab equipped with a Dri-Train. Samples of the solutions were placed in quartz spectrophotometric cells of path lengths ranging from 0.100 to 10.00 cm, and the cells were sealed with Teflon stopper closures. The integrity of the closure was established by monitoring absorbance vs. time at an arbitrary wavelength for a trial solution. The visible spectra of the solutions were recorded immediately on a Cary 14 recording spectrophotometer equipped with a slide wire for measuring absorbance in the 0–2 range. All absorbance measurements were corrected for residual cell and solvent absorbances. See Figures 9 and 10 for the Beer's law studies for $Ni[CNC(CH_3)_3]_4$ and for $Ni[CNC(CH_3)_3]_4$–$CNC(CH_3)_3$ (1:100).

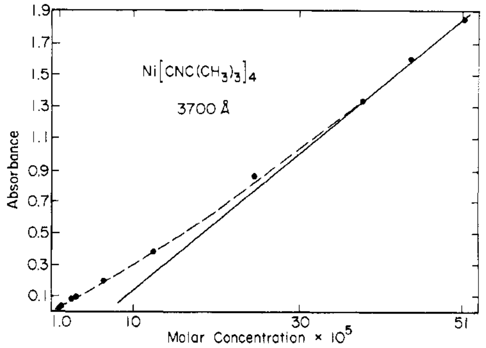


Figure 9. Beer's law plot for $Ni[CNC(CH_3)_3]_4$.

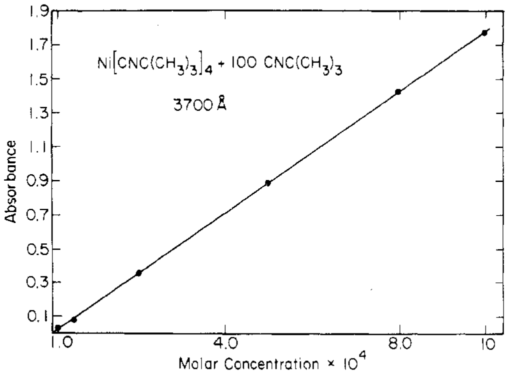


Figure 10. Beer's law plot for 1:100 $Ni[CNC(CH_3)_3]_4$–$CNC(CH_3)_3$.

Hydrogenation of Isocyanides. Procedure. All manipulations were performed by using standard vacuum-line techniques or a Vacuum Atmospheres Dri-Lab under argon atmosphere. Solvents were purified by extended refluxing with sodium and benzophenone under a nitrogen atmosphere followed by distillation of the solvent. All isocyanides were dried over 4A molecular sieves and vacuum transferred or vacuum distilled just prior to use. $Ni_4[CNC(CH_3)_3]_7$ and $Ni[CNC(CH_3)_3]_4$ were prepared from $Ni(COD)_2$ and the appropriate isocyanide as reported previously.[1]

All hydrogenation reactions were carried out by preparation of the toluene (5 mL) solution of 100 mg of $Ni_4(CNR)_7$ and 250 mg of $Ni(CNR)_4$ and filtration through a 2–4 μm porosity glass frit into a glass vessel equipped with a stir bar and a Kontes valve ring seal closure. A portion of the solution reserved to serve as a blank was syringed into a similar reaction vessel. The reaction vessel was charged with ~3 atm of H_2, and the blank vessel was maintained at 1 atm of Ar. Both vessels were heated in an oil bath for 42–48 h at ~90 °C.

For the hydrogenation of isocyanides with decomposed cluster, 250 mg of $Ni_4[CNC(CH_3)_3]_7$ (0.31 mm) was dissolved in ~5 mL of toluene and placed in a reaction vessel. The vessel was charged with 3 atm of hydrogen and heated at 90 °C for 24 h. The volatiles were removed under high vacuum (secondary and primary amines, toluene, and methylcyclohexane), and 0.20 g of *tert*-butyl isocyanide and ~5 mL of toluene were vacuum transferred onto the ferromagnetic residues remaining in the vessel. The vessel was charged with 3 atm of hydrogen and heated at 90 °C for 24 h. The volatiles were collected and analyzed by gas chromatography.

Volatile products were analyzed with the aid of a Perkin-Elmer 990 gas chromatograph equipped with an FID detector. Chromatographic separations were obtained with a 10 ft × $^1/_8$ in. copper column of 10% Carbowax 20-M, 2% KOH on Gas Chrom Q, or a 6 ft × $^1/_8$ in. copper column of Chromosorb 103. Methyl-*tert*-butylamine, methylcyclohexylamine, and methylisopropylamine were synthesized from the corresponding primary amines by classical methods. All other standards were commercially obtained. Peak identifications were accomplished by the standard additions method. The cyclohexyl isocyanide system was additionally characterized by gas chromatographic mass spectroscopy. Peak areas were converted into mole quantities by comparison with standard solutions. The linearity of response of the detector throughout the concentration region

---

(10) Schunn, R. A. *Inorg. Synth.* **1974**, *15*, 5.

(11) Casanova, J., Jr., Werner, N. D.; Schuster, R. E. *J. Org. Chem.* **1966**, *31*, 3473.

(12) Harris, T. V. Ph.D. Thesis, Cornell University, 1978.

(13) Harris, T. V.; Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 6966.

of interest was verified with an appropriate set of standard solutions.

Preparation of $Ni_4(C_6H_{11}NC)_7$. Cyclohexyl isocyanide, $C_6H_{11}NC$, was degassed and vacuum transferred prior to use. A solution of 191 mg (1.75 mmol) of $C_6H_{11}NC$ in 3 mL of pentane was added to a slurry of 275 mg (1 mmol) of $Ni(COD)_2$ in 15 mL of pentane. A dark red-brown solution formed within 60 s, and this solution was allowed to stand 24 h. The crystalline product formed on standing was filtered and washed four times with 3-mL portions of pentane. The yield was 185 mg (74%). Anal. Calcd: C, 58.93; H, 7.72; N, 9.82; Ni, 23.53. Found: C, 58.65; H, 7.92; N, 9.71; Ni, 23.05. IR spectrum (Nujol mull): 2075 (vs), 1700 (s), 1600 (s) cm^{-1}. ^1H NMR (benzene-d_6, internal Me_4Si reference): $-CH_2-$, broad resonance centered at δ 1.55 with shoulders at δ 1.20 and 2.10; $-CH-$, broad and centered at δ 3.28.

$Ni_4[CNC(CH_3)_3]_4(C_6H_5C_2C_6H_5)_3$. A mixture of $Ni(1,5\text{-}C_8H_{12})_2$ (275 mg, 1 mmol), $(CH_3)_3CNC$ (83 mg, 1 mmol), and diphenylacetylene (143 mg, 0.75 mmol) in 50 mL of pentane at 20 °C yielded a dark solution. After 6 h, crystals separated. The brown-red crystals were collected by filtration and washed with pentane (five 5-mL portions). The yield was 990 mg (90%). Anal. Calcd for $C_{62}H_{66}N_4Ni$: C, 66.74; H, 5.84; N, 4.78. Found: C, 67,59; H, 5.99; N, 5.08. IR (hexachlorobutadiene mull): 2150 (sh), 2100 (s), 2060 (sh) cm^{-1}. ^1H NMR ($C_6D_6-Si(CH_3)_4$ internal reference): 0.60 (s, 9), 0.79 (s, 27), 7.05 (m, 12), 7.44 (d, 9), 7.98 (d, 9) ppm.

Preparation of $Ni_4[CNC_6H_{11}]_4(C_6H_5C_2C_6H_5)_3$. Diphenylacetylene (0.267 g, 3.00 mmol) and cyclohexyl isocyanide (0.218 g, 4.00 mmol) were added to a slurry of bis(cyclooctadiene)nickel(0) 0.552 g, 2 mmol) in 25 mL of pentane; the mixture was stirred at 20 °C for 5 h. Filtration yielded a dark red-brown solid which was thoroughly washed with pentane; mp 170 °C dec. Anal. Calcd for $Ni_4C_{70}H_{74}N_4$: Ni, 19.43; C, 69.51; H, 6.43; N, 4.63. Found: Ni, 19.55; C, 69.10; H, 6.23; N, 4.62. IR (Nujol mull): ν_{CN} 2100 (sh), 2070 (s) cm^{-1}. ^1H NMR (benzene-d_6, Me_4Si internal standard): δ 0.5–1.7 (CH, cyclohexyl, m, 40), 2.65 (CH(apical), br, 3), 2.85 (CH(basal), br, 3), 6.7–8.0 (phenyl, m, 30).

Preparation of $Ni_4[CNC(CH_3)_3]_4(p\text{-}CH_3C_6H_4C{\equiv}CC_6H_5CH_3\text{-}p)_3$. The synthetic procedure described for $Ni_4[CNC(CH_3)_3]_4(C_6H_5C{\equiv}CC_6H_5)_3$ was followed and the compound was purified by recrystallization from a pentane–toluene mixture (yield ~10%). Anal. Calcd for $Ni_4C_{68}N_4H_{78}$: Ni, 23.81; C, 62.53; N, 5.68; H, 7.97. Found: Ni, 23.59; C, 62.19; N, 4.95; H, 8.31. ^1H NMR (benzene-d_6, internal $(CH_3)_4Si$ reference): 0.61 (CH_3, s, 9), 0.82 (CH_3, s, 27), 2.12 (CH_3, br, 18), 7.00 (aromatic, br, 12), 7.17 (aromatic, d, 6), 7.93 (aromatic, d, 6) ppm.

Preparation of $Ni_4[CNC(CH_3)_3]_6(CNCH_3)$. To a solution of *tert*-butyl isocyanide (1.25 mg, 1.5 mmol) in 25 mL of pentane was added $Ni(COD)_2$ (275 mg, 1 mmol). The resultant dark brown solution was filtered. Then a 5-mL solution of 11 mg (0.25 mmol) of CH_3NC in pentane was added dropwise to the above filtrate. A dark brown precipitate formed immediately which was collected by filtration, washed with pentane, and vacuum dried. Because of the solution state instability of this complex, analytically pure samples were not obtained. ^1H NMR (benzene-d_6, internal Me_4Si reference): δ 0.98 (CH_3, br s, 9), 1.31 (CH_3, br s, 9), 2.21 (CH_3 of CH_3NC, br s, 3).

Preparation of $Ni_4[CNC(CH_3)_3]_6P(OCH_3)_3$. $Ni(COD)_2$ (275 mg, 1 mmol) was added to 25 mL of pentane containing 125 mg (1.5 mmol) of $CNC(CH_3)_3$ and 31 mg of $P(OCH_3)_3$. A dark reddish solution formed immediately which was allowed to stand 6 h and then filtered. The filtrate was rotary evaporated to dryness. The residue was dissolved in a minimum of toluene and eluted on SX-2 Bio-Beads. One very elongated dark band was seen, the tail portion of which exhibited a stronger reddish hue which was collected. This fraction was immediately evaporated to a dark powder since prolonged storage of solutions gave monomeric nickel isocyanide–phosphite complexes and intractable solids. ^1H NMR (toluene-d_8 internal Me_4Si reference): δ 1.32 (CH_3, s, 3), 1.94 (CH_3, s, 3), 3.51 (OCH_3, d, J_{PH} = 12 Hz, 1).

Preparation of $Ni_4[CNC(CH_3)_3]_6$. $Ni(COD)_2$ (2.75 mg, 1 mmol) was added to a solution of 125 mg (1.5 mmol) of $CNC(CH_3)_3$ in 25 mL of pentane. A brown solution formed within 2 min. The solution was allowed to stand 24 h during which time dark crystals were sometimes observed to form which later redissolved. The dark solution was then filtered, removing a trace of dark insoluble material, and then the filtrate was rotary evaporated to dryness, giving an almost black, shiny powder. The powder was dissolved in a minimum of toluene and eluted with toluene down an SX-2 Bio-Bead column. Only one broad dark band was observed, and the center portion of this band was collected. The fraction collected was rotary evaporated to dryness and the resulting powder extracted on a fritted funnel with three 4-mL portions of pentane. The pentane extract was evaporated to a dark shiny solid. IR (Nujol mull): (RNC terminal) 2050, 2095 (s) cm^{-1}; (RNC bridging) 1715–1750 (m) cm^{-1}. ^1H NMR (benzene-d_6, internal Me_4Si reference): one dominant singlet, δ 1.33. Other seemingly identical preparations gave ^1H NMR spectra showing a complex myriad of signals from δ 1.0 to δ 2.3. Analytical data for this complex were not consistent even though spectral properties were reproducible.

Hydrogenation Experiments with Nickel Metal. Tetrahydrofuran and toluene were purified by extended refluxing over sodium and benzophenone under an argon atmosphere. Hexane was purified by refluxing over calcium hydride under an argon atmosphere. All manipulations were performed on a high-vacuum manifold or in a Vacuum Atmospheres Dri-Lab equipped with a Model HE493 Dri-Train under an argon atmosphere. The 2-butyne was obtained from Chem Samples and ascertained to be 99+% pure by gas chromatographic analysis.

Bis(1,5-cyclooctadiene)nickel(0) (110 mg) in 5 mL of toluene was placed in a reaction vessel under argon. The vessel was evacuated, refilled with 1 atm of hydrogen, and allowed to stand for 24 h. A nickel mirror and black solids resulted, along with a clear liquid phase. The nickel mirror and black solids were scraped out of the vessel, collected by filtration, washed thoroughly with tetrahydrofuran, toluene, and hexane, and vacuum dried. The yield was 20 mg (85%).

A 13-g sample of nickel(II) nitrate hexahydrate (13 g) was placed in five small porcelain boats which were placed in a quartz tube fitted with a 24/40 outer joint at one end and a 10/30 outer joint at the other end. The tube was carefully placed in a horizontal tube furnace and purged with a slow nitrogen flow at 220 °C for 3 h. At the end of this time, evolution of water and nitrogen dioxide had ceased. The furnace temperature was increased to 680 °C, and the tube was purged with hydrogen at a flow rate of 10 mL/min for 5 h. After this time the temperature was decreased to 300 °C and a vacuum applied to the tube for 12 h. The resulting nickel metal, lustrous and chunky in appearance, was collected and stored under an argon atmosphere. The yield was 2.6 g (100%).

A 20-mg sample of nickel metal generated from bis(1,5-cyclooctadiene)nickel(0) was placed in the reaction vessel to be used for the catalytic hydrogenation and exposed to the ambient vapor pressure of methyl isocyanide on a vacuum manifold for a period of 3 h. The vessel was then reevacuated for 5 min prior to the admission of 2-butyne and hydrogen.

For the catalytic hydrogenation of 2-butyne, approximately 2 g of 2-butyne and 0.1 g of methylcyclopentane were carefully weighed out, dried over 4A molecular sieves, and then vacuum transferred into a 1-L vessel containing a weighed portion of nickel metal and several small glass rods (used as a mechanical aid in agitating the gases prior to sample removal). The reaction vessel was equipped with a Kontes Teflon high-vacuum stopcock connected to a ball joint, a small septum covered stopcock for sample removal, and a glass finger for condensing volatiles after the 2-butyne and methylcyclopentane were condensed into the glass finger at −196 °C, and 1 atm of hydrogen was admitted. The vessel was placed in a large oil bath which was heated to the desired temperature. The progress of the hydrogenation was monitored by periodically sampling the gas phase with a 100-μL syringe through the small septum covered stopcock. Results are presented in Table III.

For the competitive hydrogenation of 2-butyne and *cis*-2-pentene, 1.11 g of 2-butyne (0.0206 mol) and 1.44 g of *cis*-2-pentene (0.0206 mol) were dried over 4A molecular sieves and then condensed at −196 °C into the glass finger of the reaction vessel which contained 20 mg of nickel metal. One atmosphere of hydrogen was admitted, and the hydrogenation was allowed to proceed at 55 °C and monitored by periodic sampling of the gas phase with a 100-μL syringe through the small septum covered stopcock.

For analysis, the gas samples withdrawn from the reaction vessel were analyzed with a Perkin-Elmer 990 gas chromatograph equipped with a flame ionization detector and a chart bed recorder. With the exception of the competitive hydrogenation experiment, separations were effected with a 10 ft × $^1/_8$ in. stainless-steel column of octane/Porasil C (mesh = 100/120) and a helium carrier flow of 20 mL/min. The oven temperature was maintained at room temperature for the elution of butane and the butenes and then increased to 70

Table III. Nickel Metal Catalyzed Hydrogenation of 2-Butyne

metal[a]	*t*, °C	% hydrogenation	product ratios[b,c] I	II	III	IV
A	20	9.7	16	46	31	1.5
A	20	12.6	12	65	37	1.8
A	20	14.8	13	45	29	1.6
A	20	32.8	11	53	26	2.1
A	20	33.6	9	49	28	1.6
B	20	4.2	13	63	42	1.9
B	20	25.0	15	65	42	1.6
C	20	1.25	18	37	18	2.0
C	20	1.47	21	32	20	1.6
C	80	2.2	27	30	28	1.0
C	80	5.5	30	18	27	1.1

[a] Metal source: A, nickel from $Ni(COD)_2$; B, nickel from $Ni(COD)_2$ pretreated with CH_3NC; C, nickel from $Ni(NO_3)_2 \cdot 6H_2O$. [b] Uncertainties were estimated to be about 10% for these ratios. [c] Molar ratios of I, *cis*-2-butene to butane; II *cis*-2-butene to *trans*-2-butene; III, *cis*-2-butene to 1-butene; and IV, 1-butene to *trans*-2-butene.

°C for elution of the methylcyclopentane. The column was purged of 2-butyne at 100 °C.

Chromatographic separations of the gases from the competitive hydrogenation of 2-butyne and *cis*-2-pentene were effected with a 12 ft × 1/8 in. stainless-steel column of 5% dimethyl sulfolane on Chromosorb P connected in series to a 10 ft × 1/8 in. column of octane/Porasil C operating at 50 °C with a helium flow of 20 mL/min.

Peak areas were measured by the cut-and-weigh method and converted into mole percentage conversions by using the methylcyclopentane as an internal standard and establishing relative response factors for butane, *cis*-2-butene, and methylcyclopentane. The response factors of 1-butene and *trans*-2-butene were assumed to be the same as the response factor of *cis*-2-butene. Results were corrected for residual contaminants in the 2-butyne and methylcyclopentane. The results were very similar to those obtained for 2-butyne above; only small to trace amounts of pentane were detected.

Acknowledgment. Support of this research by the National Science Foundation and by the Foundation and the Academy of Sciences of the USSR in the Joint U.S.–U.S.S.R. Program in Chemical Catalysis (A.K.) is gratefully acknowledged.

Registry No. $Ni_4[C_6H_{11}NC]_7$, 73377-51-2; $Ni_4[CNC(CH_3)_3]_4(C_6H_5C_2C_6H_5)_3$, 60818-82-8; $Ni_4[CNC_6H_{11}]_4(C_6H_5C_2C_6H_5)_3$, 73296-55-6; $Ni_4[CNC(CH_3)_3]_4$(*p*-$CH_3C_6H_4C{\equiv}CC_6H_4CH_3$-*p*)$_3$, 73296-56-7; $Ni_4[CNC(CH_3)_3]_6(CNCH_3)$, 73377-49-8; $Ni_4[CNC(CH_3)_3]_6P(OCH_3)_3$, 73377-50-1; $Ni_4[CNC(CH_3)_3]_6$, 73377-48-7; $Ni(COD)_2$, 1295-35-8; $Ni_4[CNC(CH_3)_3]_7$, 60748-55-2; $Ni[CNC(CH_3)_3]_4$, 19068-11-2; 2-butyne, 503-17-3; 3-hexyne, 928-49-4; 1,3-hexadiene, 592-48-3; 2,4-hexadiene, 592-46-1; Ni, 7440-02-0.

Contribution from the Department of Chemistry,
The University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6

Organometallic Nitrosyl Chemistry. 12.[1] New Cyclopentadienylnitrosyl Complexes of Tungsten

PETER LEGZDINS,* DAVID T. MARTIN, and CHARLES R. NURSE

Received August 13, 1979

Treatment of $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$ with an equimolar amount of iodine in CH_2Cl_2 affords $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$ in virtually quantitative yields. The dimer reacts with various Lewis bases, L (L = $P(OPh)_3$, PPh_3, $SbPh_3$, or CO), to give monomeric $(\eta^5\text{-}C_5H_5)W(NO)(I)_2L$ complexes; but the species with L = CO slowly decarbonylates in solution under ambient conditions and reverts to the original reactants. The L-containing compounds are also obtainable by the stoichiometric reaction of $(\eta^5\text{-}C_5H_5)W(CO)(NO)L$ with I_2. Reactions of $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$ in THF with $Tl(C_5H_5)$ or $Na(C_5H_5)$ in appropriate stoichiometries produce the novel complexes $(C_5H_5)_2W(NO)I$ and $(C_5H_5)_3W(NO)$, both of which are stereochemically nonrigid in solution at room temperature. Nitric oxide converts the dimer to the well-known $(\eta^5\text{-}C_5H_5)W(NO)_2I$ as the only nitrosyl product. The physical properties of all new complexes prepared are presented.

Introduction

We recently described the preparation and characteristic chemistry of $(\eta^5\text{-}C_5H_5)W(NO)_2H$.[2] Unlike related hydridocarbonyls which are Lowry–Brønsted acids in polar solvents, the hydridotungsten complex functions as a source of H^- in these solvents. This hydridic character is somewhat surprising since it is generally believed that the presence of electron-withdrawing ligands on the metal center enhances the acidic character of M–H bonds. In order to evaluate more fully the function of the NO groups, we decided to prepare other hydridonitrosyl complexes of tungsten and to investigate their physical and chemical properties. Unfortunately, very few convenient synthetic precursors of such complexes have been reported. However, considerably more work has been done with molybdenum systems; and, in particular, it has been shown that $(\eta^5\text{-}C_5H_5)Mo(CO)_2(NO)$ can be converted to a variety of other cyclopentadienylmolybdenum nitrosyl derivatives.[3] Since an efficient preparation of the tungsten congener, $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$, has now been developed,[4] it seemed likely that we could utilize it as a general starting material in an analogous manner. In this paper we report conversions of $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$ to new cyclopentadienylnitrosyl complexes of tungsten, some of which are logical precursors of the ultimately desired hydridonitrosyl species.

Experimental Section

All chemicals used were of reagent grade or comparable purity. All reagents were either purchased from commercial suppliers or prepared according to published procedures, and their purity was confirmed by elemental analyses and/or melting point determinations. Melting points were taken in capillaries and are uncorrected. All solvents were dried by standard procedures, distilled, and deaerated just prior to use. All manipulations were performed in an atmosphere of prepurified nitrogen.

Infrared (IR) spectra were recorded on a Perkin-Elmer 457 spectrophotometer and were calibrated with the 1601-cm^{-1} band of polystyrene film. Proton magnetic resonance spectra were obtained on a Varian Associates T60 spectrometer or, with the assistance of Dr. S. O. Chan and Mrs. M. M. Tracey, on a Bruker WP-80 spec-

---

(1) Part 11: Greenhough, T. J.; Kolthammer, B. W. S.; Legzdins, P.; Trotter, J. *Acta Crystallogr., Sect. B*, in press.

(2) Legzdins, P.; Martin, D. T. *Inorg. Chem.* **1979**, *18*, 1250–4.

(3) King, R. B. "Transition-Metal Organometallic Chemistry"; Academic Press: New York, 1969; pp 81–3.

(4) Hoyano, J. K.; Legzdins, P.; Malito, J. T. *Inorg. Synth.* **1978**, *18*, 126–31.