

METAL CLUSTERS IN CATALYSIS XVI¹. THE SELECTIVE HYDROGENATION OF TRIPLE BONDS WITH ORGANOMETALLIC TRANSITION METAL COMPOUNDS

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Abstract - A thesis is developed that solution phase catalysis of triple bond hydrogenation, e.g. in carbon monoxide, nitrogen, isocyanides and nitriles, can be more readily achieved with a polynuclear complex, a metal cluster, than with a mononuclear complex. Experimental support of the thesis was obtained from an exploratory study of the catalytic properties of the highly reactive metal cluster, $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$. This cluster selectively catalyzed the hydrogenation of acetylenes to cis-olefins at 20°. At 90°, the cluster proved to be a selective catalyst for the hydrogenation of t-butyl isocyanide, using $\text{Ni}[\text{CNC}(\text{CH}_3)_3]_4$ as the isocyanide source, to give t-butylmethylamine. Using the derivative cluster, $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_4^- [\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5]_3$, a hydrogenation of acetonitrile to ethylamine was achieved. The nickel cluster systems proved incapable of catalyzing the hydrogenation of either CO or N_2 . However, $\text{Ir}_4(\text{CO})_{12}$ dissolved in a molten mixture of sodium chloride and aluminum chloride proved to be a very active Fischer-Tropsch catalyst at 150-180° and 3 atmospheres: under flow conditions, carbon monoxide was converted to a mixture of hydrocarbons of which isobutane was the major component.

INTRODUCTION

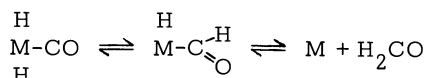
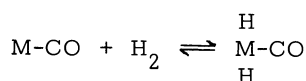
Coordination catalysis with mononuclear coordination and organometallic complexes has become an important and very broad area of catalysis science.²⁻⁸ The scope of coordination catalysis is impressively broad; it ranges from the water gas shift reaction to hydrogenations of multiply bonded functionalities in organic molecules and of aromatic hydrocarbons to carbonylation to oligomerizations and polymerizations to the extraordinary methathesis reaction. It falls short of matching the scope established for solid state catalysts in two technologically important areas: carbon skeletal rearrangements and dehydrocyclizations in saturated hydrocarbons and the hydrogenation of triple bonds in molecules like carbon monoxide and nitrogen. Our recent research has addressed these issues for coordination catalysis with soluble complexes and we describe here our studies of the catalytic hydrogenation of triple bonds.

POSSIBLE MODELS FOR THE HYDROGENATION OF TRIPLE BONDS BY COORDINATION CATALYSIS

Until recently, there was no example of coordination catalysis of the hydrogenation of triple bonds with the exception of acetylenic triple bonds⁹. Unknown had been the hydrogenation of carbon monoxide, nitrogen, organic isocyanides and nitriles with soluble coordination catalysts¹⁰. In contrast, metallic, solid state catalysts easily effect the hydrogenation of nitrogen to ammonia and of carbon monoxide to methane (methanation reaction), to methanol, and to hydrocarbon and alcohol mixtures (Fischer-Tropsch Synthesis reaction).¹⁰ Although the adjective "easily" is appropriately employed, it should be noted that the temperature range for practical rates in these hydrogenations is 200-350° a range that largely lies outside the stability range for most coordination, organometallic, and cluster complexes. An obvious, critical question here is what mechanistic features of these metal or metal oxide-catalyzed

reactions distinguish these solid state catalysts from the conventional coordination or organometallic complex.

Triple bonds between first row elements possess very high bond energies and carbon monoxide, followed closely by nitrogen, has the largest known bond energy. Clearly, activation of such molecules for a reduction or hydrogenation step would be facilitated by an initial mode of interaction between the molecule and the metal center in which the bond order of the molecule is substantially reduced. Of the metallic catalysts effective in the hydrogenation of CO and of N₂, many metals, e.g. iron, chemisorb these molecules in a dissociative fashion, i.e., with complete scission of the triple bond. This ultimate form of activation is unlikely to have any analog in conventional coordination or organometallic compounds. There are, however, alternative activation schemes realistically applicable to coordination complexes. One mechanistic tack has a complete analogy to the hydroformylation reaction, a reaction readily catalyzed by a myriad of coordination catalysts. However the product in this analogy would be formaldehyde which is a thermodynamically unfavored product in the hydrogenation of carbon monoxide:



The analog of a carboxylation reaction is the conversion of CO to HCCOOH, a reaction that is readily catalyzed by hydroxide ion¹⁰. The difficult step is the conversion of CO beyond the formic acid or formate state to give methanol or methane with the latter step comprising C-O bond scission, a step unprecedented in coordination catalysis without the intervention of a reducing agent that has Al-R, Al-H or B-H bonds.¹⁰

A conventional σ - π interaction of a molecule like CO or N₂ with a metal atom can reduce the CO bond order into the range of ~ 2.5 to 2.0 but probably not lower¹¹. Furthermore, it appears that the bond order for carbon monoxide in a bridging position in a dinuclear metal complex or an edge or face (three metal atoms) bridging position in metal carbonyl clusters is lower but not greatly lower than the 2.5 to 2.0 range commonly found for terminally bonded carbon monoxide.¹² The C-O distances in bridging carbonyls do in some case rise to values of ~ 1.20 Å, a value that is greater than the range observed for C-O double bonds. A similar bond order reduction is observed for N₂, RNC and RCN where there is bonding of one N, C or N atom of the ligand, respectively, with one or two metal atoms.¹⁰

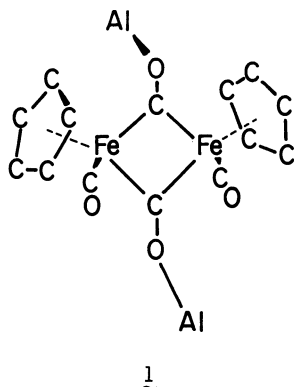
If both of the triply bonded atoms interact with metal atoms, there appears to be a more substantial reduction of bond order at least as judged by the increase in the bond distance (bond order and bond length do not necessarily display a linear relationship)¹⁰. For example, the N-N distance in simple mononuclear metal nitrogen complexes is about 1.11 to 1.12 Å whereas the distances are usually, but not invariably, longer in M-NN-M complexes as illustrated below:

TABLE 1. Structural data for nitrogen complexes

| COMPLEX | BRIDGING NN DISTANCE, Å | Reference |
|---|----------------------------|-----------|
| (H ₃ N) ₅ RuNNRu(NH ₃) ₅ ⁴⁺ | 1.124 | 13 |
| [(CH ₃) ₅ C ₅] ₂ TiNNTi[C ₅ (CH ₃) ₅] ₂ | 1.16 | 14 |
| [(CH ₃) ₅ C ₅] ₂ (N ₂)ZrNNZr(N ₂)[C ₅ (CH ₃) ₅] ₂ | 1.18 | 15 |
| C1[(CH ₃) ₂ PC ₆ H ₅] ₄ ReNNMoC1 ₄ (OCH ₃) | 1.21 | 16 |

This type of interaction with two transition metals is unknown for carbon monoxide. However, data are available for M-CO-Al bonding interactions. The crystal structure of cis

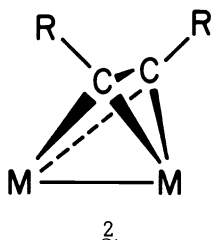
$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2 \cdot 2\text{Al}(\text{C}_2\text{H}_5)_3$ has the basic geometry shown below, 1.



In this complex, the terminal Fe-CO and the bridging COAl carbonyls have indistinguishable bond distances, 1.19 (2) and 1.20 (2) Å, respectively¹⁷ and these distances are not significantly different from those in the parent cis and trans dimers, $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$.^{18,19}

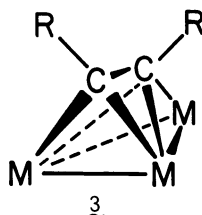
These crystallographic data point to a weak donor-acceptor interaction¹⁷ between the bridging carbonyl oxygen atom and the aluminum alkyl. Perhaps a stronger Lewis acid could have a more dramatic effect upon the C-O bond order. However, it should be noted that the bridging C-O bond distance in the iron complexes is relatively large even in the parent dimers.

There is an alternative mode of binding between a molecule or ion with a triple bond and transition metal atoms in which the bond order of the initial triple bond can be reduced, unequivocally, below 2.0.¹⁰ In this alternative binding mode, there is a rehybridization at the atoms of the triple bond with the formation of σ bonds with two or more metal atoms. This optimal complexation for activation of triple bonds for reduction or hydrogenation is accurately documented only for acetylenes. In dinuclear metal-acetylene complexes, the acetylene C_2 axis lies over and perpendicular to the M-M bond so that the M_2C_2 skeleton describes a tetrahedron, 2.

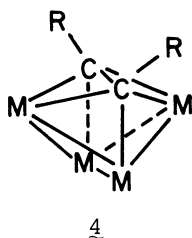


This type of bonding is crystallographically established for about eleven dinuclear metal acetylene complexes²⁰, e.g. $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{HC}\equiv\text{CH})$ ²¹ and $(\text{OC})_6\text{Fe}_2[(\text{CH}_3)_3\text{C}\equiv\text{C}(\text{CH}_3)_3]$ ²².

In metal clusters, there may be metal-carbon interactions in addition to those shown in 2. In trinuclear cluster acetylene complexes and in the interaction of an acetylene with a triangular face of a larger cluster, the basic geometric features are illustrated in 3. A model reference complex is $\text{Fe}_3(\text{CO})_9(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ ²³. There is one example of a four metal atom

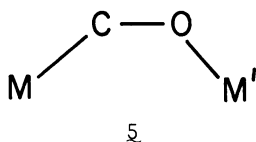


interaction with an acetylene, $(OC)_{10}Co_4(C_6H_5C\equiv CC_6H_5)$ which is shown in skeleton outline in 4; the four cobalt atoms and the two acetylenic carbon atoms describe an octahedron²⁴.

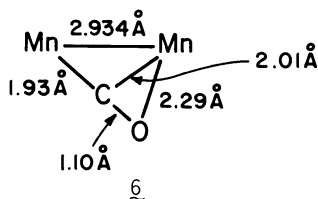


In these dinuclear and polynuclear metal acetylene complexes, there is a dramatic reduction in bond order as judged by the increase in the acetylenic C-C bond distance. In the dinuclear complexes, the C-C distances are in the range of 1.31 to 1.39 Å (1.35 Å average) and are 1.41 and 1.44 Å, respectively, for the trinuclear iron complex²³, 3, and the tetranuclear cobalt complex²⁴, 4. These values are to be compared with distances of ~1.20, 1.34 and 1.54 Å for C-C triple, double and single bonds, respectively. Binding of the N₂ molecule, in a fashion analogous to 2 is established for two similar and quite complex nickel compounds^{25,26} and a binding of t-butyl isocyanide in a form similar to 3 is established²⁷ in the nickel cluster, Ni₄[CNC(CH₃)₃]₃⁷.

There is no example of a binding of carbon monoxide by metal atoms that is analogous to 2, 3, or 4 and such a binding of this molecule is relatively unlikely, except in a short-lived intermediate or in a transition state, because of the intrinsic polarization within this molecule. Alternatively, there may be interactions of form 5 although these are presently



unknown in transition metal chemistry. There is a curious, close analog of 5 but the long M-O distance and unperturbed CO distance suggest that the M-O interaction is very weak. This example is found in the framework of Mn₂(CO)₅[(C₆H₅)₂PCH₂CH₂P(C₆H₅)₂]₂²⁸ which is summarily outlined in 6. Note the short C-O bond distance of 1.10 Å; this suggests little



activation of the CO bond. The other example of 5 with M' a nontransition metal is established for the previously cited iron complex, 1.

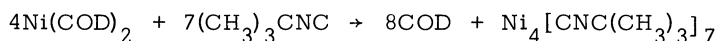
The facility with which a triple bond undergoes a hydrogenation should to a first approximation correlate with the bond order of the triple bond in the complexation mode with one or more metal atoms. Hence, we anticipate that in complexes like 2, 3 and 4 hydrogenation of the triple bonds will be more facile than in simple σ - π complexes with a single transition metal. Other factors are, of course, essential to a hydrogenation process, e.g. electron density on the metal atom to facilitate the hydrogen oxidative addition and coordination unsaturation (or a minimally activated process that generates a coordinately unsaturated intermediate) so that hydrogen addition may proceed easily. In the specific case of carbon monoxide, complexes like 1 or 5¹⁷ seem to be the only viable and available alternatives to 2,

3 or 4 with respect to C-bonded terminal complexes although edge and face bridged carbonyls in clusters would appear to be more susceptible to hydrogenation than the terminal type of carbonyl.

Described below is a successful experimental prosecution of the foregoing thesis with respect to the hydrogenation — and a relatively selective hydrogenation — of acetylenes, organic isocyanides and nitriles and of carbon monoxide. The results support but do not validate the thesis. Furthermore, neither the thesis nor the results imply nor are intended to imply that catalytic activation of molecules like carbon monoxide or nitrogen for a hydrogenation process is not feasible with a single isolated metal center. I submit only that such catalytic activation generally will be more facile with two or more adjacent metal centers than with an isolated metal center.

CLUSTER CATALYZED ACETYLENE HYDROGENATIONS

Reaction of bis(1,5-cyclooctadiene)nickel with a deficiency of *t*-butylisocyanide yields dark red crystals of the tetranuclear nickel cluster,



$\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$. This cluster is extremely reactive toward oxygen and strong field ligands like CO, RNC and phosphites with resultant conversion of the cluster to mononuclear nickel complexes.

The solid state structure²⁷ of the nickel cluster is outlined in Fig. 1. There is a rather compressed tetrahedron of nickel atoms with isocyanide groups bridging the unique basal edges

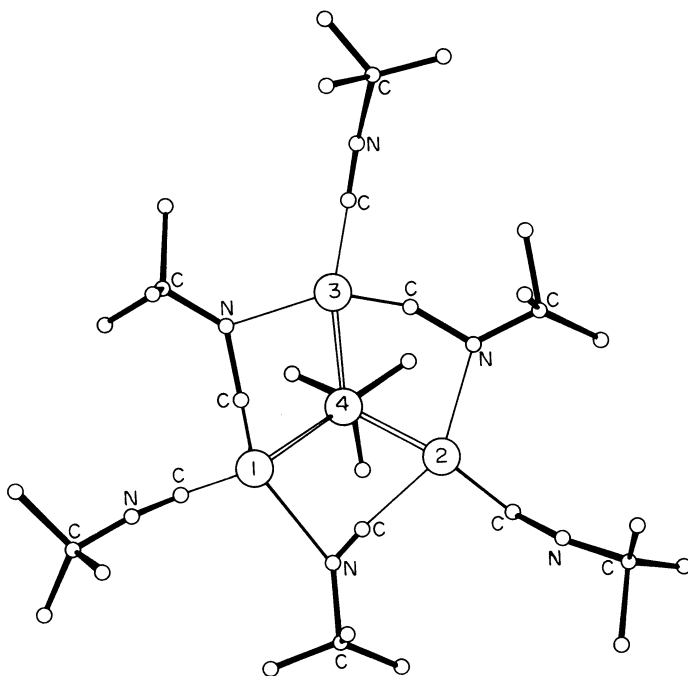


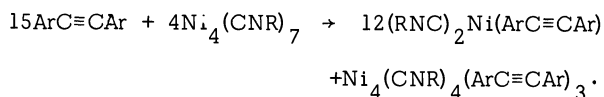
Fig. 1. A representation of the $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ structure along the three fold axis of the compressed tetrahedron of nickel atoms²⁷. The apical (4) to basal (1,2,3) nickel-nickel distance is 2.34 Å. Hydrogen atom positions are not shown.

(the position of these bridging ligands was not precisely fixed because of thermal disorder in the crystal). The cluster shows no evidence of dissociation in inert solvents (Beers Law is obeyed down to concentrations of 10^{-6} molar) and the proton nmr spectrum of the cluster in solution is fully consistent with the solid state structure. The cluster is stereochemically nonrigid and undergoes a fast intramolecular exchange of isocyanide ligands at 0–50° and

then an apparent intermolecular ligand exchange at 90–110°. Decomposition of the cluster occurs above ~ 130°.

$\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ is a catalyst for the hydrogenation of acetylenes but not for olefins.^{29,30}

In the acetylene hydrogenations, there is selectivity: the *cis*-olefin is produced in >95% yield. The cluster undergoes no detectable reaction with hydrogen alone at 20° but acetylenes alone interact to give tetranuclear nickel-acetylene clusters which are then intermediates in the hydrogenation reaction. Diarylacetylenes react irreversibly with $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ to form $(\text{RNC})_2\text{Ni}(\text{ArC}\equiv\text{CAr})$ and $\text{Ni}_4(\text{CNR})_4(\text{ArC}\equiv\text{CAr})_3$ ³¹:



Although $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_4(\text{ArC}\equiv\text{CAr})_3$ does not detectably dissociate (Beers Law is obeyed at concentrations as low as 10^{-6} moles), the acetylene ligands in the tetranuclear nickel acetylene cluster are subject to exchange reactions. Acetylene exchange between $\text{Ni}_4(\text{CNR})_4$ ⁴⁻ ($\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$)₃ and (*p*- $\text{CH}_3\text{C}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{CH}_3$ -*p*)₃ is slow at 20°; nmr studies showed that the exchange was about 10% complete in five days. Interaction of dialkylacetylenes (2-butyne and 3-butyne) and of methylphenylacetylene with $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ gave an equilibrium mixture of $(\text{RNC})_2\text{Ni}(\text{RC}\equiv\text{CR})$ and $\text{Ni}_4(\text{CNR})_{7-x}(\text{RC}\equiv\text{CR})_x$ ($x = 1, 2$ and 3). Unlike the diarylacetylene reactions, an excess of dialkylacetylene added to $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ generates increasing amounts of $(\text{RNC})_2\text{Ni}(\text{RC}\equiv\text{CR})$ and some unidentified nickel species (see Note a) and these systems are catalytic for hexaalkylbenzene formation by acetylene trimerization (acetylene trimerization was not observed in the diarylacetylene systems). The dialkylacetylene and alkylarylacetylene reactions with $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ are fully reversible: the acetylene and the $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ cluster were recovered and separated simply by removal of the acetylene under high vacuum.

The mononuclear $(\text{RNC})_2\text{Ni}(\text{ArC}\equiv\text{CAr})$ complexes undergo no reaction with hydrogen and are catalytically inactive for acetylene hydrogenation reactions up to about 80°. Above 80°, a slow reaction with hydrogen was observed but only after the development of the red coloration common to the tetranuclear nickel clusters. $\text{Ni}_4(\text{CNR})_6$ and $\text{Ni}_4(\text{CNR})_6(\text{ArC}\equiv\text{CAr})$ clusters were apparently present in these reaction mixtures.

In contrast to the mononuclear nickel acetylene complex, $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_4(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)_3$ ³¹ reacts with hydrogen at 20° to form nickel, free isocyanide and *cis*-stilbene and catalyzes at 20° the hydrogenation of acetylenes. The structure of this cluster²⁹, shown in Fig. 2, has the acetylene ligands bound as in model structure 3; the acetylenes lie over three of the four faces of the tetrahedron and the acetylenic bond distance is increased to 1.341 Å. This type of cluster is clearly an intermediate in the acetylene hydrogenation reaction. Attempts to detect the next intermediate, a nickel hydride-acetylene complex, by nuclear magnetic resonance studies were unsuccessful. Hydrogen addition to these clusters is the rate determining step and the subsequent hydrogen atom migration to the bound acetylenes is fast relative to the hydrogen addition step. In the $\text{Ni}_4(\text{CNR})_4(\text{ArC}\equiv\text{CAr})_3$ cluster, hydrogen addition is thought to occur initially across the relatively weak Ni-Ni basal bonds (2.69 Å) rather than the strong Ni-Ni basal-apical bonds (2.37 Å) since a similar addition takes place in

Note a. This species is believed to be $\text{Ni}(\text{RC}\equiv\text{CR})_2$ which could be the intermediate for the catalytic trimerization of dialkylacetylenes to hexaalkylbenzenes.

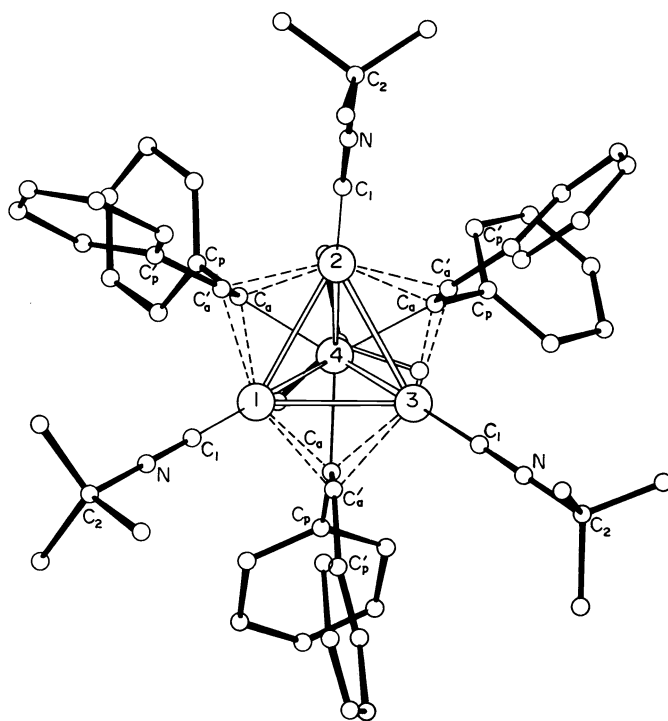


Fig. 2. The tetrahedral $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_4[\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5]_3$ structure.

The nickel atoms lie nearly at the vertices of a regular tetrahedron, and each has a terminally bound isonitrile ligand. In this view, the unique nickel atom, labeled 4, is in the center and lies on a threefold axis. Each of the unique basal edges of the Ni_4 tetrahedron are symmetrically bridged by diphenylacetylene molecules. In these acetylene ligands, the acetylenic carbon atoms, C_a and C_a' , are bonded to basal and apical nickel atoms. The C_a carbon atom, nearer the reader, is bound to two basal nickel atoms, and the C_a' carbon atom, farther away, is bound to two basal nickel atoms and to the apical nickel atom. Here, the acetylene formally is a four-electron donor ligand. The acetylenic carbon-carbon distance is 1.344 Å. Hydrogen atoms associated with the ligands are not shown.²⁹

$(1,5\text{-cyclooctadiene-Ni})_2(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ which has a very weak Ni-Ni interaction (2.62 Å)³² and which is shown in Fig. 3.

These results show that this acetylene cluster complex with the acetylenic C-C bond order substantially decreased through three strong Ni-C interactions is a catalyst for acetylene hydrogenations at 20° whereas the conventional mononuclear acetylene complex is inactive even at elevated temperatures.

CLUSTER CATALYZED HYDROGENATIONS OF ISOCYANIDES AND NITRILES

Although hydrogen and $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ do not detectably react at 20°, they do react at 90° with the formation of nickel, *t*-butylmethylamine, *t*-butylamine and methylcyclohexane³³. The methylcyclohexane was derived from a nickel metal catalyzed hydrogenation of the solvent, toluene. Formation of nickel metal obscured the homogeneous hydrogenation

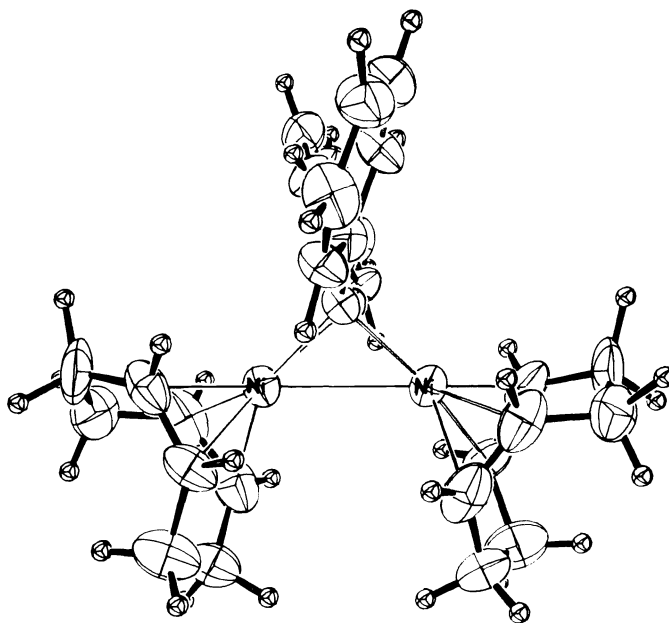
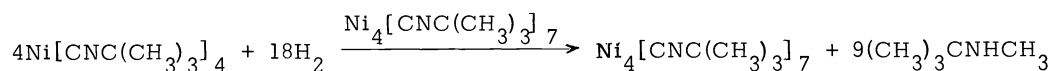


Fig. 3. Perspective (adapted from an ORTEP drawing) of the $(1,5\text{-cyclooctadiene-Ni})_2(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ structure.³² The nickel-nickel separation of 2.62 \AA is analogous to the basal nickel-nickel distances in $\text{Ni}_4(\text{CNR})_4(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)_3$ shown in Fig. 2.

reaction; separate experiments with nickel metal, hydrogen and a toluene solution of $(\text{CH}_3)_3\text{CNC}$ showed the same products to be formed. Demonstration of a catalytic hydrogenation of an isocyanide with the nickel cluster presented minor tactical problems because the cluster itself reacts with free isocyanide to form the nearly nonreactive, mononuclear $\text{Ni}[\text{CNC}(\text{CH}_3)_3]_4$. This problem was resolved by using $\text{Ni}[\text{CNC}(\text{CH}_3)_3]_4$ itself as the isocyanide reservoir. Thus, reaction at 90° of hydrogen with a toluene solution of $\text{Ni}[\text{CNC}(\text{CH}_3)_3]_4$ and $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ gave 99% *t*-butylmethylamine, 1% *t*-butylamine, and no methylcyclohexane. This is the first demonstration of a homogeneous catalytic hydrogenation of an isocyanide and it is a selective hydrogenation reaction.³³ Materials balance studies based on hydrogen consumption, gas chromatographic analyses and spectral studies were excellent for the catalytic reaction:



This catalytic reaction was also successfully extended to cyclohexyl-, isopropyl-, *n*-butyl-, and benzylisocyanides although the selectivity to alkylmethylamine formation was generally lower than with *t*-butylisocyanide.

A simple modification of the $\text{NiL}_4\text{-Ni}_4\text{L}_7$ reaction system was devised for this catalytic reaction and consists of a toluene solution of $\text{Ni}(\text{COD})_2$ and the isocyanide in a 1 to 3 molar ratio.³³

All attempts to isolate nickel clusters with nitrile ligands especially with the nitrile bound analogously to the acetylene in **3** and in $\text{Ni}_4(\text{CNR})_4(\text{ArC}\equiv\text{CAr})_3$ were unsuccessful.³³ However, the reaction of an acetonitrile solution of $\text{Ni}_4(\text{CNR})_4(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)_3$ with hydrogen at 90° yielded ethylamine (in addition to *cis*-stilbene).³³ A similar reaction with an acetonitrile

solution of $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ also yielded ethylamine with small amounts of *t*-butylmethylamine. These hydrogenation reactions infer the existence of an $\text{Ni}_4[\text{CNR}]_4[\text{RCN}]_x$ complex but only dark oils of somewhat variable composition were obtained from the hydrogenation reactions and from the reaction of equimolar quantities of $\text{Ni}(\text{COD})_2$ and $(\text{CH}_3)_3\text{CNC}$ and excess acetonitrile.³³

No evidence was obtained for nickel cluster-nitrogen complexes of the form $\text{Ni}_4[\text{CNR}]_{7-x}(\text{N}_2)_x$. Hydrogenation at 90° of $\text{Ni}_4(\text{CNR})_7$ or $\text{Ni}_4(\text{CNR})_4(\text{ArC}\equiv\text{CAr})_3$ in the presence of nitrogen occasionally gave traces of ammonia but never was $^{15}\text{ND}_3$ detected in the products from $^{15}\text{N}_2 + \text{H}_2$ reactions. It is concluded that these nickel clusters do not effect the hydrogenation of nitrogen.³³ Also, attempts to effect the hydrogenation of carbon monoxide with mixtures of $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ and $\text{Ni}(\text{CO})_4$ were unsuccessful; formation of nickel metal confounded studies at the anticipated requisite temperatures of $> 130^\circ$.³³

HYDROGENATION OF CARBON MONOXIDE

The tetranuclear nickel clusters are not really appropriate for activation of either nitrogen or carbon monoxide for a hydrogenation reaction since these hydrogenations with metallic or metal oxide catalysts require quite high temperatures. Obviously, metal clusters that have high thermal stability would be much more appropriate complexes for such catalytic studies. Thus, in our research directed to soluble, carbon monoxide hydrogenation catalysts, we have largely focused our research on tetrairidium dodecacarbonyl, $\text{Ir}_4(\text{CO})_{12}$, one of the more stable metal carbonyl clusters.

Hydrogen slowly reacts at $150\text{--}180^\circ$ with $\text{Ir}_4(\text{CO})_{12}$, dissolved in toluene, to form methane and another dark, quite insoluble cluster. Under similar conditions, hydrogen and carbon monoxide are converted to methane but at an inordinately low rate — too low even for a meaningful kinetic or mechanistic study.³⁴ A substantial activation of this reaction system was realized with the substitution of a molten mixture of $\text{NaCl}\cdot 2\text{AlCl}_3$ for the toluene solvent³⁵. Since a molten $\text{NaCl}\cdot\text{AlCl}_4$ mixture (NaAlCl_4) was not very effective, the activation or promoter effect is ascribed to the Lewis acid properties of AlCl_3 — possibly through Ir-C-O-Al interactions similar to 1 and 5. In any case, the reaction of H_2 and CO with a solution of $\text{Ir}_4(\text{CO})_{12}$ in molten $\text{NaCl}\cdot 2\text{AlCl}_3$ at $\sim 180^\circ$ and 2–3 atmospheres yields hydrocarbons at a turnover rate (molecule of CO per molecule of $\text{Ir}_4(\text{CO})_{12}$ of about one per 12 minutes.³⁵ In a flow system at atmospheric pressure, the hydrocarbon products were methane, ethane, propane, *n*-butane and *i*-butane. The major hydrocarbon product was *i*-butane; *n*-butane was a trace to minor product. In batch reaction systems, the major hydrocarbon products were methane and ethane due to an AlCl_3 catalyzed hydrogenolysis of propane and butanes³⁵.

It is believed that this novel catalytic hydrogenation of carbon monoxide is a homogeneous (solution phase) reaction. No solids were visually evident in the reaction mixture at reaction temperature and after cooling to 20° provided that the CO was not completely consumed. The observed rates were greater than those that could be expected by extrapolation from Vannice's data³⁶ for iridium metal catalyzed CO hydrogenation even with the assumption that every iridium atom initially charged as $\text{Ir}_4(\text{CO})_{12}$ were actually active as a metal atom. In addition, a high surface area iridium dust proved to be relatively inactive in the $\text{NaCl}\cdot 2\text{AlCl}_3$ reaction system. Exploratory studies with other metal carbonyls and metal halides were largely unsuccessful; only ruthenium and rhodium carbonyl clusters were active and in these two cases there was a substantial question about the homogeneity of the reaction system.³⁵

The mechanism of this novel hydrogenation system is unknown. Spectroscopic and kinetic studies are in progress to establish whether, in fact, M-C-O-M' type interactions may be responsible for the relatively low activation required for reasonable rates of hydrogenation in

this $\text{Ir}_4(\text{CO})_{12}-\text{AlCl}_3$ reaction system.

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