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Metal Clusters in Catalysis. 12.[1] Selective Catalytic Hydrogenation of Isocyanides and Nitriles

Sir:

As part of a general investigation to establish boundary conditions for the putative analogy[1-7] between metal clusters and metal surfaces in the chemisorption and catalytic processes, we have attempted with metal cluster catalysts[1,7] hydrogenations of molecules and ions that have triple bonds, a class of generally[8] difficult catalytic reactions. Here we describe a selective catalytic hydrogenation of an isocyanide with a nickel–isocyanide-cluster catalyst precursor and also a hydrogenation of acetonitrile.

The nickel cluster, $Ni_4[CNC(CH_3)_3]_7$,[9] an effective catalyst precursor[7,10] for the selective hydrogenation of acetylenes to cis olefins, does not undergo a reaction with hydrogen at 20 °C (toluene solution) but does at 90 °C and 1–3 atm to form as volatile reaction products $(CH_3)_3CNHCH_3$, and methylcyclohexane[11] in about equimolar amounts. The recovered insoluble product, which contained nickel metal, was shown to be an active catalyst for the 90 °C hydrogenation of a toluene solution of *tert*-butyl isocyanide with the formation of the two amines and methylcyclohexane in the molar ratios similar to those produced in the cluster reaction. In a separate experiment, we demonstrated that nickel metal[12] at 90 °C can catalyze the hydrogenation of the isocyanide; a toluene solution of the isocyanide gave $(CH_3)_3CNHCH_3$, $(CH_3)_3CNH_2$, and methylcyclohexane in ~2:1:0.6 proportions, respectively.

Prevention of nickel metal formation in the hydrogenation of the nickel cluster requires a continuing source of free isocyanide. Since direct addition of excess isocyanide to the cluster leads to the formation[7] of $Ni[CNC(CH_3)_3]_4$ (vide infra), we employed a "buffered" reaction system composed of a toluene solution of $Ni_4(CNR)_7$ and $Ni(CNR)_4$, in a 1:10 molar ratio, and hydrogen. This system was homogeneous, catalytic, and ~99% selective. No solids formed in the course of a 42-h hydrogenation at 90 °C and no methylcyclohexane was produced during this reaction period.[13] Lack of methylcyclohexane formation was a key analytical observation that provided an unequivocal characterization of a homogeneous catalytic reaction (absence of nickel metal formation). The products detected[13] were $(CH_3)_3CNHCH_3$ and $(CH_3)_3CNH_2$ with the latter ~1% of the total product. Experimental checks[14] on materials balance were good for the overall reaction outlined in eq 1.

$$4Ni(CNR)_4 + 18H_2 \xrightarrow{Ni_4(CNR)_7} 9RNHCH_3 + Ni_4(CNR)_7 \quad (1)$$

The turn-over rate based on molecules of amine per molecule of cluster was low at 90 °C and 1–3 atm, ~0.1/h. At 127 °C, the turnover rate increased to ~0.7/hr, but the selectivity dropped slightly to ~97%.[15,16] These experiments represent the first demonstration of a homogeneous catalytic hydrogenation of an isocyanide. Analogous studies with *n*-butyl, isopropyl, and cyclohexyl isocyanides gave selectivities of secondary to primary amines of ~77, 73, and 36%, respectively. The dramatic effect of substituent on selectivity is not readily explicable on either steric or electronic grounds.

In the direct hydrogenation of $Ni(CNR)_4$ under comparable conditions, a red color, characteristic of the cluster, developed and the only volatile product detected was $(CH_3)_3CNHCH_3$; however, the average hydrogenation rate was only ~7% that of the $Ni_4(CNR)_7$–$Ni(CNR)_4$ system. In this system, the initial cluster concentration would be extremely small and the primary solution species should be $Ni(CNR)_4$ and $Ni(CNR)_3$ as shown in eq 2 (vide infra).

$$Ni(CNR)_4 \rightleftarrows Ni(CNR)_3 + RNC \quad (2)$$

A reaction system composed of a toluene solution of $Ni(CNR)_4$ + 2RNC and hydrogen underwent no hydrogenation at 90 °C, a result fully consistent with the shift in equilibria like **2** on addition of free isocyanide.

In an attempt to develop a practical synthesis of alkylmethylamines based on our catalytic system, the reagents were modified so as to circumvent the separate syntheses of $Ni_4(CNR)_7$ and $Ni(CNR)_4$, to comprise hydrogen, toluene (solvent), isocyanide, and bis(cyclooctadiene)nickel, $Ni(COD)_2$. Since the latter two reagents react[7,10] rapidly and irreversibly to form $Ni_4(CNR)_7$ and $Ni(CNR)_4$, as shown in eq 3

$$Ni(COD)_2 + xRNC \rightarrow 2COD + \left(\frac{4-x}{9}\right) Ni_4(CNR)_7 + \left(\frac{4x-7}{9}\right) Ni(CNR)_4 \quad (3)$$

the molar ratio of the two reagents determines the initial concentrations of $Ni_4(CNR)_7$ and $Ni(CNR)_4$. Such a reaction system based on a 1:3 molar ratio of $Ni(COD)_2$–$(CH_3)_3CNC$ gave a turnover rate of 0.5/h, at 125 °C with a selectivity to the secondary amine of 99%.

The low reaction rates flaw this general catalytic synthesis of alkylmethylamines, and these rates are even lower for isocyanides in which the substituent is nonbulky simply because the solubility of the nickel cluster is vanishingly small in these instances.[7,10] For example, we found that CH_3NC was converted to $(CH_3)_2NH$ with high selectivity but the rate was extremely low at 90 °C. Of some mechanistic significance are the results of a hydrogenation of a starting toluene solution of $Ni_4[CNC(CH_3)_3]_7$ and $Ni(CNCH_3)_4$ wherein the less soluble CH_3NC nickel cluster formed and separated out: the hydrogenation product was $(CH_3)_2NH$; no $(CH_3)_3CNHCH_3$ was detected in the reaction product. In a similar experiment with benzyl isocyanide, the system was heterogeneous because the insoluble benzyl isocyanide cluster separated out and the hydrogenation rate was low. Selectivity was not obtained; the product consisted of equal amounts of benzylamine and benzylmethylamine. As in the methyl isocyanide system, neither *tert*-butylamines nor methylcyclohexane were formed. The mixed isocyanide systems implicate the cluster as the primary catalyst or catalyst precursor.

We have tried to extend the catalytic hydrogenation to other molecules with triple bonds.[17] A hydrogenation of acetonitrile to ethylamine was achieved in a 90 °C homogeneous reaction of hydrogen and an acetonitrile solution of $Ni_4[CNC(CH_3)_3]_7$.[18] 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 one per hour at 63 °C but the system became visibly heterogeneous after 1 h.

The mechanisms of these catalytic hydrogenations of CN triple bonds are not defined. In the cluster, the unique bridging isocyanide ligands[7,9] may be more susceptible to hydrogenation than terminally bound isocyanide ligands, since the bond order of the CN bond is lower[19] for these bridging ligands.[20] Hence, the most active intermediate could be $Ni_4(CNR)_7$ or possibly $Ni_4(CNR)_6$[7] which is formed when the parent cluster is heated. Alternative mononuclear intermediates are $Ni(CNR)_4$, $Ni(CNR)_3$, and $Ni(CNR)_2$. Our results show that the first is not an active intermediate in the reaction with hydrogen. NMR studies have failed to give evidence of the two possible unsaturated nomonuclear complexes but UV data[21] implicate a species like $Ni(CNR)_3$.

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(11) This product resulted from a catalytic hydrogenation of the solvent toluene.

(12) The metal was generated in the reaction flask by the hydrogenation of Ni(1,5-cyclooctadiene)$_2$.

(13) This system and analogous systems with other isocyanides were analyzed by gas chromatography, utilizing either a 10-ft copper column of 10% Carbowax 20M and 2% KOH on Gas-Chrom Q, or a 6-ft stainless steel column of Chromosorb 103. Reference samples of the secondary amines were prepared by literature methods. The cyclohexyl isocyanide system was additionally characterized by gas chromatographic mass spectroscopy.

(14) Materials balance checks were based on (1) measurement of the hydrogen uptake, (2) measurement of the amount of amine produced, and (3) the molar ratio of $Ni_4(CNR)_7$ to $Ni(CNR)_4$ determined by NMR analysis.

(15) A very small amount of solid formed in the late stages of the reaction, but no methylcyclohexane.

(16) The rate acceleration at substantially higher pressures has not been established yet. Experimental complications due to metal surface catalyzed decomposition of the nickel clusters and other related problems have not been resolved.

(17) In attempts to effect the hydrogenation of $^{15}N_2$ with $Ni_4[CNC(CH_3)_3]_4(C_6H_5C{\equiv}CC_6H_5)_3$, very small amounts of ammonia were detected. However, we have never detected $^{15}NH_3$ in $^{15}N_2$ 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.

(18) Attempts to isolate an $Ni_4(CNR)_x(NCR)_{7-x}$ cluster have not been successful to date.

(19) Indicated from the infrared and x-ray (CN distance) data.

(20) Since there is a fast, intramolecular exchange of isocyanide ligands between terminal and bridging sites ($E_a \sim 16$ kcal/mol), it could be argued that there is a small energy difference between the bridging and terminal bonding modes. Although this view may be reasonably accurate, it is possible that the difference in ligand bond energies could be relatively large if the nickel-nickel interactions were substantially different in the ground state and the intermediate or transition states for ligand intramolecular exchange.

(21) The complexes we have isolated in this $(CH_3)_3CNC$ system are $Ni(CNR)_4$, $Ni_4(CNR)_7$, and $Ni_4(CNR)_6$. NMR studies of mixtures of Ni_4L_7 and NiL_4 show only the characteristic resonances of the two species below +60 °C (above which there is fast intermolecular ligand exchange). NMR studies of the reaction mixture from nickel(1,5-cyclooctadiene)$_2$ and RNC show, in addition to cyclooctadiene resonances, only the Ni_4L_7 and NiL_4 resonances in the reactant ratio range of RNC:Ni(COD)$_2$ of 7:4 to 4:1; at 4:1 and higher ratios only NiL_4 or the exchange singlet for $NiL_4 + L$ was observed. UV studies of $Ni(CNR)_4$ show a departure from Beer's Law behavior at very low concentrations. Analogous UV studies of $Ni(CNR)_4 + x$CNR exhibited a similar departure at $x = 5$ and a conformance to Beer's Law at $x = 100$ ($R = C(CH_3)_3$). These data may reflect the equilibrium $Ni(CNR)_4 \rightleftharpoons Ni(CNR)_3 + CNR$ since absorptions due to $Ni_4(CNR)_7$ could not be detected in the dilute $Ni(CNR)_4$ solution spectra at 20 °C. Very dilute solutions of $Ni_4[CNC(CH_3)_3]_7$ obeyed Beer's Law at 20 °C.

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Metal Promoted Alkyl Migration in a Bimetallic Complex

Sir:

It is currently thought[1] that in selected cases transition metal cluster complexes may function as soluble analogues of heterogeneous catalysts. It is hoped that these cluster complexes will mimic the range of activity and reactions of heterogeneous catalysts, yet retain the selectivity and efficiency of homogeneous catalysts.

The key feature which distinguishes classic mononuclear homogeneous catalysts from heterogeneous or cluster catalysts is that the latter possess two or more adjacent metal sites. Novel modes of substrate-cluster binding and new reaction paths involving adjacent metals should prove central to the development of this field.

Oxidative addition[2] and alkyl migration[3] have been unifying concepts in the development of organo transition metal chemistry. Although pervasive in mononuclear systems, oxidative additions and alkyl migrations involving polynuclear complexes have been little studied.[4] In the case of clusters, the preparation of the reduced complexes which are required for the addition reaction is complicated by concurrent metal-metal bond cleavage and fragmentation.[5] Herein we report (i) the rational and efficient synthesis of a binuclear transition metal cluster complex, (ii) the reduction of the neutral parent cluster to the corresponding dianion, and (iii) the reaction of the dianion with alkylating agents affording *acyl* complexes via a novel metal-promoted alkyl migration.

Inasmuch as clusters are subject to reductive fragmentation, we have chosen to employ binuclear complexes containing bridging ligands. Di-μ-(diphenylphosphido)bis[tricarbonyliron(I)], $Fe_2[P(C_6H_5)_2]_2(CO)_6$ (**1**), was first prepared by Thompson[6] by reaction of iron pentacarbonyl with tetraphenyldiphosphine at 220 °C. We have developed an alternative synthesis which entails the addition of diphenylchlorophosphine to disodium octacarbonyldiferrate(−I)[7,8] which is in turn derived from disodium tetracarbonylferrate(−II)[7,9] and iron pentacarbonyl (Scheme I). The neutral dimeric complex **1** is isolated as orange plates in overall 60% yield