

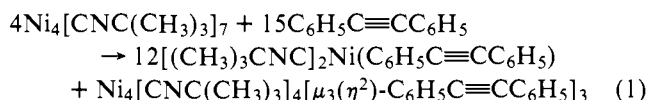
Communications to the Editor

Metal Clusters in Catalysis. 5.¹ Four-Electron η^2 -Ligand Bonding in Clusters and Catalytic Intermediates

Sir:

We describe the synthesis, structure, and chemistry of a new metal cluster, $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_4[\mu_3(\eta^2)\text{-C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5]_3$ (**1**), which presages a large class² of $\text{M}_4\text{L}_4(\mu_x(\eta^2)\text{-L}')_3$ clusters and provides mechanistic information concerning a type of cluster catalysis chemistry. The essential structural and concomitant chemical reactivity feature of the cluster class is the set of three ligands that bridge edges or equivalent faces of a Ni_4 tetrahedron and are *formally*³ four-electron ligands as shown here for the $\mu_3(\eta^2)$ -diphenylacetylene moiety in **1** and as established⁴ for RNC, but in a different bonding mode, in the parent cluster, $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$ (**2**). Cluster **2** has extensive catalytic properties of which the newest⁵ and most important is the selective hydrogenation of acetylenes to cis olefins. We present below the thesis that the key element of this catalytic reaction is in the binding of the four-electron donating ligands and we place this in general perspective for the metal cluster-metal surface analogy.⁶

Reaction of **2** with most acetylenes at 25° yielded weak 1:1 complexes⁷ which did not detectably⁸ fragment to smaller units. However, diphenylacetylene reacted irreversibly with **2** (eq 1).



The chemistry of the mononuclear and cluster acetylene complexes is compared below. A high yield synthesis of the acetylene cluster⁹ was realized in the pentane mediated reaction of a 1:1:1 molar mixture of $\text{Ni}(1,5\text{-cyclooctadiene})_2$, $(\text{CH}_3)_3\text{CNC}$, and $\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$. A qualitative structural definition of the cluster as tetrahedral $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_4[\mu_3(\eta^2)\text{-C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5]_3$ was realized from the ¹H NMR spectrum which was composed of two types of terminal isocyanide resonances (relative intensities of 3 and 1) and two types of aromatic multiplets (relative intensities of 1 and 1). Unlike the parent cluster,⁴ this "mixed" cluster is stereochemically rigid (NMR time scale) to 120° which reflects the more congested inner features of the new cluster and the preference of the acetylene for μ_3 -binding (relative to a monometal interaction).

The high yield synthetic procedure is general to $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_4[\mu_3(\eta^2)\text{-acetylene}]_3$ clusters; other well-characterized members of this new subclass include the structurally analogous 2-butyne and 3-hexyne derivatives. Phenylacetylene yielded largely, or only, a single stereoisomer; ¹H NMR data indicated that the aryl groups are in identical environments (identification of the aryl groups as distal or proximal to the unique apical nickel atom will be provided by a crystallographic analysis).

Single crystals of the benzene solvate of **1**, $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_4[\mu_3(\eta^2)\text{-C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5]_3 \cdot \text{C}_6\text{H}_6$, are monoclinic, space group $P_{2_1/c}$ (an alternate setting of $P_{2_1/c} - C_{2h}^5$) with $a = 15.794$ (1) Å, $b = 25.180$ (3) Å, $c = 16.011$ (2) Å, $\beta = 102.77$ (1)°, and $Z = 4$ ($d_{\text{calcd}} = 1.262$, $d_{\text{measd}} = 1.256$ g cm⁻³). Three-dimensional diffraction data were collected on a computer-controlled four-circle Syntex PI autodiffractometer

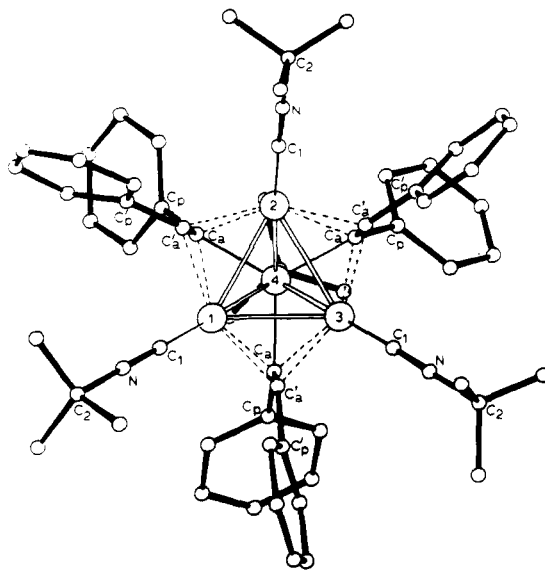


Figure 1. Perspective drawing (adapted from an ORTEP plot) of the $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_4[\mu_3(\eta^2)\text{-C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5]_3$ molecule viewed normal to the triangular base along the idealized threefold axis. Nickel atoms are represented by large 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. The tetrahedron possesses no rigorous crystallographic symmetry. There is no significant interaction between the complex and the benzene solvate molecules.

using graphite-monochromated Cu $K\alpha$ radiation and full (1° wide) ω scans. The structural parameters have been refined to convergence ($R = 0.089$ for 7056 independent reflections having $2\theta_{\text{Cu}K\alpha} < 115^\circ$ and $I > 3\sigma(I)$) in cycles of unit-weighted full-matrix least-squares refinement which employed anisotropic thermal parameters for the four nickel atoms and isotropic thermal parameters for all remaining non-hydrogen atoms.¹⁰

In addition to benzene solvate molecules, the crystal is composed of discrete, electron-precise tetrahedral $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_4[\mu_3(\eta^2)\text{-C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5]_3$ cluster molecules (Figure 1). The nickel tetrahedron, with a slight ~ 0.34 Å trigonal compression, conforms approximately to C_{3v} symmetry with the nickel atom ($\text{Ni}_a \equiv \text{Ni } 4$) displaced by 1.798 Å from the basal nickel ($\text{Ni}_b \equiv \text{Ni } 1,2,3$) plane. There is a terminal isocyanide ligand bonded to each nickel atom and the diphenylacetylene ligand is bonded to one of the three $\text{Ni}_b\text{-Ni}_a\text{-Ni}_b$ triangular faces in a manner similar to that observed for this ligand in the isostructural $\text{Ni}_4(\text{CO})_4(\text{CF}_3\text{C}_2\text{CF}_3)_3$ ² and in $\text{Fe}_3(\text{CO})_9(\text{RC}\equiv\text{CR})$.¹¹

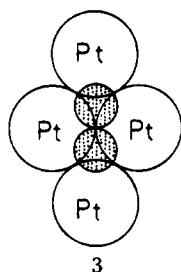
Important bond distances are: $\text{Ni}_a\text{-Ni}_b$, 2.374 (2, 5, 8) Å;¹² $\text{Ni}_b\text{-Ni}_b$, 2.686 (2, 2, 3) Å; $\text{Ni}_a\text{-C}_a$, 1.972 (8, 3, 5) Å; $\text{Ni}_b\text{-C}_a'$ (six values), 1.977 (8, 6, 10) Å; $\text{Ni}_b\text{-C}_a$ (six values), 2.203 (8, 32, 57) Å; $\text{Ni}_a\cdots\text{C}_a'$, 2.849 (8, 1, 1) Å; and $\text{C}_a\text{-C}_a'$, 1.344 (10, 7, 11) Å. All structural parameters are consistent with a bonding model in which each diphenylacetylene ligand is coordinated through C_a to the apical nickel atom by a formal σ -type bond and to the two adjacent basal nickel atoms by three-center μ -type bonds.

Structural, fluxional, and chemical differences between **1** and **2** are presumably the result of differences in the mode(s) of bonding for the three bridging ligands. The trigonal compression of the four-atom cluster in **2** is much larger than in **1**

with 0.98 Å longer Ni_b-Ni_b and 0.036 Å longer Ni_a-Ni_b separations. Whereas the shape of the Ni₄[CNC(CH₃)₃]₄[μ₃(η²)-C₆H₅C≡CC₆H₅]₃ molecule is reasonably equidimensional, the Ni₄[CNC(CH₃)₃]₇ molecule is much more disk shaped with the trigonally expanded Ni_bNi_bNi_b basal face much more exposed. The isocyanide ligands in **2** appear to be able to span the elongated Ni_b-Ni_b edges quite effectively by simply changing the hybridization of their Ni_b-bonded nitrogens from sp to sp² and directing C₁ toward the other basal nickel atom to give bent, "edge-bridging" isocyanide ligands but similar "edge-bridging" acetylenes would probably produce unfavorable steric interactions.

Hydrogen reacted with **1** in a toluene solution at 25° to yield *cis*-(C₆H₅)CH=CH(C₆H₅), isocyanide, and nickel metal. A fully analogous reaction with the 3-hexyne cluster was observed; *cis*-3-hexene and isocyanide were the only organic products detected. Addition of excess acetylene to these reaction systems fully suppressed nickel metal formation, and a catalytic reduction of the acetylene to the *cis* olefin¹³ was observed. In sharp contrast, the mononuclear complex [(CH₃)₃CNC]₂Ni(C₆H₅C≡CC₆H₅) did not react with hydrogen at 25° within a period of 2 days. These data would seem to provide a qualitative argument in support of cluster catalysis at least for acetylene reduction as differentiated from an alternative mechanistic mode which comprises cluster fragmentation to mononuclear intermediates.^{13,14} Characterization of presumed hydride intermediates is now being attempted.

A dihapto binding of CO was earlier proposed¹ by us as a possible feature in the hydrogen reduction of carbon monoxide with metal cluster catalysts. With the demonstration of this feature in acetylene reductions, we now suggest that this concept can be extended to other important catalytic reactions in which triple bonds are hydrogenated, e.g., the hydrogen reduction of dinitrogen, since the bond order of the triple bond is substantially reduced in this type of cluster bonding. By our analogy,⁶ μ_x(η²)-bonding modes for molecules with triple bonds could be important in reaction intermediates for catalytic reactions on metal surfaces. Somorjai and co-workers¹⁵ present evidence that acetylene on a platinum(111) surface is largely as shown in **3** with about a 1.34 Å C-C separation.



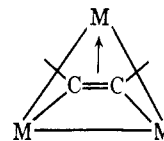
This type of interaction has a formal resemblance to the acetylene interaction in the nickel cluster.¹⁶

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References and Notes

- (1) Paper 4, M. G. Thomas, B. F. Beier, and E. L. Muetterties, *J. Am. Chem. Soc.*, **98**, 1296 (1976).
- (2) A fully analogous and the first reported example of this acetylene subclass is Ni₄(CO)₄[μ₃(η²)-CF₃C≡CCF₃]₃, a relatively unstable cluster molecule. J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, *J. Am. Chem. Soc.*, **97**, 7492 (1975).
- (3) (a) A full characterization of this type of ligand interaction as "4-electron" requires a substantial reduction of the bond order (acetylene or isocyanide bond). Actually, the observed C-C and C-N bond distances for the bridging ligands in these clusters^{2,4} are close to a double or aromatic bond value.

We purposely employ this terminology to emphasize the potential of such interaction modes in the ground or excited states in the reduction of the bridging bonds. (b) The μ₃(η²) notation is incomplete and would not discriminate between the interaction of acetylene in this cluster and an alternative arrangement of the type



A discrimination could be achieved by the notations μ₃(η²_⊥) and μ₃(η²_∥) for the two respective cases but we hesitate to introduce new connectivity notations until this problem has been more carefully considered. (The μ_x notation is taken here to simply represent the number (x) of metal atoms bridged by the ligand.)

- (4) V. W. Day, R. O. Day, J. S. Kristoff, F. J. Hlrsekorn, and E. L. Muetterties, *J. Am. Chem. Soc.*, **97**, 2571 (1975).
- (5) M. G. Thomas, B. F. Beier, and E. L. Muetterties, manuscript in preparation.
- (6) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **84**, 959 (1975).
- (7) The cluster is insoluble in pentane but dissolves in this medium if 1 mol of an acetylene, such as 2-butyne or phenylacetylene, per mole of cluster is added.
- (8) Spectroscopic studies showed no evidence of cluster fragmentation. NMR studies established that the cluster is intact although the ligand resonances are significantly shifted from those for the ligands of the cluster (dissolved in benzene). A more complete discussion of these complexes will be given elsewhere.⁵
- (9) Elemental analysis, all elements, were in full agreement with the calculated percentages for the complex which was crystallized from pentane. The crystal used in the x-ray study was selected from a set obtained by recrystallization from a benzene-pentane mixture and retained benzene of solvation.
- (10) The four crystallographically independent nickel atoms were located through direct methods and the remaining non-hydrogen atoms of the totally general position asymmetric unit were located by standard difference Fourier techniques. Further refinement is underway.
- (11) J. F. Blount, L. F. Dahl, C. Hoogzand, and W. Hubel, *J. Am. Chem. Soc.*, **88**, 292 (1966).
- (12) The first number in parentheses is the root mean square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the average value, respectively. Full structural data will be published shortly.
- (13) The critical test of catalyst selectivity in the acetylene reduction will be the hydrogenation of C₆H₅C≡CD. We also plan to explore similar catalytic reactions of other μ_x(η²)-acetylene dinuclear, trinuclear, and tetranuclear metal complexes to establish the general importance of μ_x(η²)-acetylene bonds in catalysis.
- (14) A solely cluster based catalytic cycle can never be definitively proven; it can only be definitively disproven.
- (15) Personal communication from Professor Somorjai. L. L. Kesmodel, P. C. Stair, and G. A. Somorjai, to be published in *Phys. Rev. Lett.*
- (16) This is more nearly analogous to the μ₄ binding of C₆H₅C≡CC₆H₅ in Co₄(CO)₁₀(C₆H₅C≡CC₆H₅) although the C-C bond distance is much longer (1.44 Å) in the cluster (L. F. Dahl and D. L. Smith, *J. Am. Chem. Soc.*, **84**, 2450 (1965)). In the μ₂(η²)-binding of acetylenes in Co₂(CO)₈(RC≡CR) complexes, the C-C separation is 1.32-1.37 Å (R. S. Dickson and P. J. Fraser, *J. Organomet. Chem.*, **12**, 323 (1974)) and is 1.35 Å in (C₆H₅)₂Ni₂(RC≡CR), (O. S. Mills and B. W. Shaw, *J. Organomet. Chem.*, **11**, 595 (1968)). In the μ₃-η² binding of diphenylacetylene in Fe₃(CO)₉(RC≡CR), the C-C separation is 1.41 Å,¹⁰ and in Fe₂(CO)₈[(CH₃)₃CC≡CC(CH₃)₃] the C-C separation is 1.32 Å (F. A. Cotton, J. D. Jamerson, and B. R. Stults, *J. Organomet. Chem.*, **94**, C53 (1975)).
- (17) Camille and Henry Dreyfus Teacher-Scholar.

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Feasible Route to 1,2-Epoxyalkyllithium Reagents via the Lithiation of Epoxyethylsilanes¹

Sir:

The availability of an α-metalated epoxide synthon (**1**) would be most useful in organic synthesis, for such a unit