Modeling Catalytic Reactions with Transition Metal Atoms. 1. Synthesis and Characterization of Reactive Intermediates in the Nickel–Ethylene System, $(C_2H_4)_nNi$ (where $n = 1, 2,$ or 3) in Low Temperature Matrices

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Abstract: The cocondensation reaction of Ni atoms with C_2H_4/Ar and C_2H_4 matrices at 15 K is shown to provide a direct and efficient route to binary nickel–ethylene complexes of the form $(C_2H_4)_nNi$ (where $n = 1, 2,$ or 3). The complexes are identified and characterized by infrared and uv-visible spectroscopy coupled with nickel and ethylene concentration studies and warm-up experiments. The infrared active ν(C=C) stretching modes for all three complexes are assigned and discussed as are their respective Ni → C_2H_4 uv-charge transfer transitions. Experiments performed in solid C_2H_4 yielded the intriguing result that both $(C_2H_4)_3Ni$ and $(C_2H_4)_2Ni$ form on deposition at 15 K but $(C_2H_4)_2Ni$ rather than $(C_2H_4)_3Ni$ is the favored complex on warming in the range 20–60 K. This observation is rationalized in terms of the lattice restrictions of a Ni atom residing in a substitutional site of solid ethylene rather than an inherent preference for the bis(ethylene) complex. The possible uses of these complexes as matrix models for studying the catalytic role of "naked" nickel in the nickel effect, olefin oligomerization, and olefin hydrogenation are briefly considered.

Not long after the synthesis of tris(ethylene)nickel(0) from the reaction of *cis*-(1,5,9-cyclododecatriene)nickel(0) and ethylene,[1] it was demonstrated that the same compound could be directly obtained by cocondensing Ni atoms with C_2H_4 at −200 °C.[2]

The success of the metal vapor technique for producing the 16-electron $(C_2H_4)_3Ni$ complex was significant in that it implied that similar reactions performed in the lower temperature cryogenic range (4.2–20 K) might provide a direct and simple pathway to the 12- and 14-electron reactive intermediates $(C_2H_4)Ni$ and $(C_2H_4)_2Ni$, respectively.

Organometallic compounds of this type, in which only olefinic C=C double bonds coordinate to a transition metal center, are of considerable chemical and catalytic interest. Tris(ethylene)nickel itself has already proven to be of value in providing an insight into the catalytic role that the so-called "naked" nickel plays in the industrially important "nickel effect".[3] Binary nickel–ethylene complexes are also significant in that they may serve as unique models for probing the various steps in olefin oligomerization reactions such as, the technically important cyclotrimerization of 1,3-butadiene to 1,5,9-cyclododecatriene,[4] which is a major precursor of HOOC-$(CH_2)_{10}$COOH, the latter being used in the manufacture of nylon-12 and space vehicle lubricants.

In the context of metal vapor chemistry, a "naked" metal atom can be construed to be a useful model (in the localized bonding approach to chemisorption)[5a] for a "coordinatively unsaturated" metal atom in a catalytic surface and one might anticipate that at least one of the 12-, 14-, and 16-electron $(C_2H_4)_nNi$ complexes might resemble ethylene chemisorbed onto a nickel surface and consequently serve as a matrix model for probing the surface intermediates and mechanisms of catalytic hydrogenation reactions.[5b,c]

In view of the intense interest in binary nickel–ethylene complexes and the recent theoretical treatments of the interaction of ethylene with a single nickel atom[6] and a nickel dimer,[7] we decided to initiate a program of research focusing on metal atom–olefin cocondensation reactions. Most of our work so far has centered on the Cu/C_2H_4 and Ag/C_2H_4 systems, and we have been successful in synthesizing and characterizing $(C_2H_4)_nCu$ (where $n = 1, 2,$ or 3),[8] $(C_2H_4)Ag$,[9] and $(C_2H_4)Au$.[9]

In this paper we wish to report that by using Ni/C_2H_4 and Ni/C_2H_4/Ar matrix reactions, we have been able to synthesize and characterize, for the first time, the extremely labile reaction intermediates $(C_2H_4)Ni$ and $(C_2H_4)_2Ni$ as well as the known compound $(C_2H_4)_3Ni$.[2] The complexes were characterized by matrix infrared and uv-visible spectroscopy, coupled with nickel/ethylene concentration studies and warm-up experiments.

Experimental Section

Monoatomic Ni vapor was generated by directly heating a 0.010 in. ribbon filament of the metal with ac in a furnace similar to that described previously.[10] The nickel (99.99%) was supplied by McKay, N.Y. Research grade C_2H_4 (99.99%) and Ar (99.99%) were supplied by Matheson of Canada. The rate of Ni atom deposition was continuously monitored using a quartz crystal microbalance.[11]

In the infrared experiments, matrices were deposited onto a CsI optical plate cooled to 15 K by means of an Air Products Displex closed cycle helium refrigerator. Infrared spectra were recorded on a Perkin-Elmer 180 spectrophotometer. Uv-visible spectra were recorded on a standard Varian Techtron in the range 190–900 nm, the sample being deposited onto a NaCl optical plate.

Results and Discussion

Infrared Experiments. When Ni atoms are cocondensed with $C_2H_4/Ar \simeq 1/50$ at 15 K (using very low concentrations of Ni to eliminate complications due to cluster formation, $Ni/Ar \simeq 10^{-4}$),[12] aside from infrared absorptions belonging to free ethylene isolated in the Ar matrix (labeled E in Figures 1, 2, and 3), a number of new absorptions were observed in the ν(CH), ν(C=C), $\delta(CH_2)$, and $\rho_w(CH_2)$ regions (Figure 1A) which are clearly associated with ethylene coordinated to nickel. Of particular note is the fact that infrared absorptions previously assigned to $(C_2H_4)_3Ni$[2] at 1517, 1246, and 911 cm^{-1} (labeled III in Figure 1A) appear only as *weak* features under the conditions of a $C_2H_4/Ar \simeq 1/50$ experiment at 15 K. On the other hand, the group of five absorptions at 2963, 1499, 1166/1155, and 902 cm^{-1} are quite prominent (labeled I in Figure 1A). Especially noteworthy is the gradual disappearance of these absorptions during warm-up experiments in the range 25–35 K, maintaining approximately the same relative intensities at all times (Figure 1B), implying that they are associated with a single species. The remaining absorptions at 2948/2890, 1466, 1277/1220, and 906 cm^{-1} (labeled II) do not change appreciably during this annealing procedure

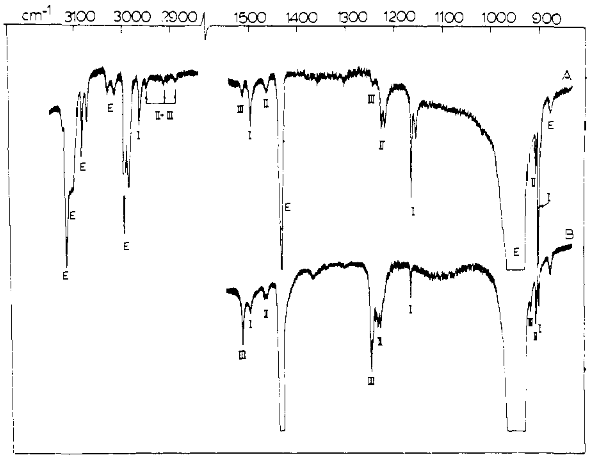

Figure 1. The matrix infrared spectrum observed (A) on depositing Ni atoms with a $C_2H_4/Ar \simeq 1/50$ mixture at 15 K and (B) after warm-up to 35 K (absorptions associated with free C_2H_4 in the matrix are labeled E) showing $(C_2H_4)_3Ni$, $(C_2H_4)_2Ni$, and $(C_2H_4)Ni$ labeled (III), (II), and (I), respectively.

although the absorptions of $(C_2H_4)_3Ni$ do grow in markedly concomitant with the decay of species I (Figure 1B).

An a priori assignment on the basis of these results is that three complexes have been generated where

$$I \equiv (C_2H_4)Ni$$

$$II \equiv (C_2H_4)_2Ni$$

$$III \equiv (C_2H_4)_3Ni$$

To verify these assignments we performed similar experiments in more concentrated $C_2H_4/Ar \simeq 1/10$ and pure C_2H_4 matrices (Figures 2 and 3 and Table I). In agreement with our proposed assignments, appreciable quantities of all three complexes form in $C_2H_4/Ar \simeq 1/10$ matrices (see for example the appearance of *three* intense ν(C=C) stretching modes at 1512, 1496, and 1465 cm^{-1} in Figure 2A). The monoethylene formulation (I) is strengthened by two observations. Firstly, its rapid decay on warming $C_2H_4/Ar \simeq 1/10$ matrices to 25–30 K (Figure 2B) and, secondly, its absence on depositing Ni atoms with pure C_2H_4 at 15 K (see later—Figure 3).

In an effort to isolate pure $(C_2H_4)_3Ni$ we cocondensed Ni atoms with pure C_2H_4 at 15 K (Figure 3). Surprisingly, however, under these conditions both $(C_2H_4)_2Ni$ and $(C_2H_4)_3Ni$ formed with roughly equal absorbances in the ν(C=C) stretching region. This observation should be sharply contrasted with the exclusive isolation of $(C_2H_4)_3Ni$ when Ni atoms are cocondensed with C_2H_4 at liquid N_2 temperatures.[2]

The absence of I in pure C_2H_4, taken in conjunction with its appearance in the dilute matrices and its rapid and complete disappearance in the warm-up experiments, provides convincing support for the assignment of I to $(C_2H_4)Ni$.

An intriguing effect was noticed on warming the *pure* C_2H_4 matrix containing $(C_2H_4)_2Ni$ and $(C_2H_4)_3Ni$. At 40 K $(C_2H_4)_2Ni$ began growing in at the expense of $(C_2H_4)_3Ni$ and dominated the infrared spectrum up to 70 K, at which point the C_2H_4 was beginning to sublime away. We believe that this surprising reversal of stability may be an artifact relating to the packing requirements of $(C_2H_4)_2Ni$ and $(C_2H_4)_3Ni$ in the crystal lattice of solid C_2H_4[13] (space group D_{2h}[12] (*Pnnm*)). Examination of the symmetry of a substitutional site in solid ethylene (C_{2h}) reveals that it is sterically unfavorable for a nickel atom to simultaneously coordinate to three ethylene molecules, appropriately oriented to form the desired D_{3h} tris(ethylene) complex. However, two C_2H_4 molecules are favorably oriented for quasi-planar D_{2h} coordination (actually C_{2h} in the substitutional site of solid C_2H_4), and hence the bis(ethylene) complex (II) may be preferentially stabilized under these conditions. (A detailed investigation of the temperature dependence of the $(C_2H_4)_3Ni/(C_2H_4)_2Ni$ product distributions in solid C_2H_4 is currently underway and will be reported later.)

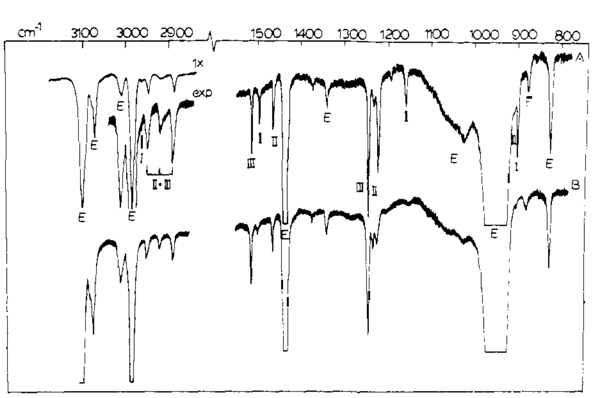

Figure 2. The same as Figure 1 except $C_2H_4/Ar \simeq 1/10$ mixture used at 15 K.

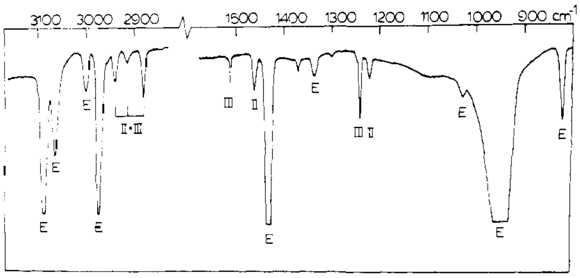

Figure 3. The same as Figure 1 except that a pure C_2H_4 matrix was used at 15 K.

Having assigned I to $(C_2H_4)Ni$ and III to $(C_2H_4)_3Ni$, it is possible to assign II to $(C_2H_4)_2Ni$ by a process of deductive elimination as well as by comparison with the recently reported bis(ethylene)copper(0) complex[8] (see Table II).

At this point it is worth mentioning the amonotonic trend in the frequencies of the ν(C=C) stretching modes observed for $(C_2H_4)_nNi$ (where n = 1, 2, or 3), that is $(C_2H_4)_3Ni > (C_2H_4)Ni > (C_2H_4)_2Ni$. This should be compared with the amonotonic order for the ν(CO) stretching modes of the binary nickel carbonyls[14] $Ni(CO)_3 > Ni(CO) > Ni(CO)_2$ but contrasted with the *monotonic* trend observed for the ν(C=C) stretching modes of the binary copper ethylene complexes[8] $(C_2H_4)_3Cu > (C_2H_4)_2Cu > (C_2H_4)Cu$.

The inversion in the order of the CO stretching modes for $Ni(CO)_2$ and Ni(CO) is not reflected in their k_{CO} bond stretching force constants. This has previously been shown to be an artifact related to the vibrational coupling between the CO stretching modes of $Ni(CO)_2$ which is not possible in Ni(CO). In Cotton-Kraihanzel terminology[16] this is equivalent to saying that $Ni(CO)_2$ has an F-matrix element of the form $k_{CO} - k_{CO\cdot CO}$ whereas that for Ni(CO) is of the form k_{CO}' (both complexes having identical G-matrix elements, namely, μ_{CO}, the reduced mass of CO). Thus for a positive $k_{CO\cdot CO}$ force constant one can anticipate a ν(CO) frequency inversion as observed in practice for $Ni(CO)_2$ and Ni(CO), even though the k_{CO} force constant trend is monotonic.[16]

In a similar way the ν(C=C) stretching modes of the coordinated ethylene groups in $(C_2H_4)_nNi$ may be crudely considered in terms of the diatomic oscillator approximation and a finite and positive $k_{CC\cdot CC}$ interaction force constant could be responsible for the observed ν(C=C) frequency inversion for $(C_2H_4)_2Ni$ and $(C_2H_4)Ni$.[23]

Table I. The Infrared Spectra of $(C_2H_4)_nNi$ (where n = 1, 2, or 3) in C_2H_4/Ar and C_2H_4 Low-Temperature Matrices[a]

$(C_2H_4)_3Ni$ (III)			$(C_2H_4)_2Ni$ (II)			$(C_2H_4)Ni$ (I)	
Pure C_2H_4	C_2H_4/Ar $\simeq$1/10	C_2H_4/Ar $\simeq$1/50	Pure C_2H_4	C_2H_4/Ar $\simeq$1/10	C_2H_4/Ar $\simeq$1/50	C_2H_4/Ar $\simeq$1/10	C_2H_4/Ar $\simeq$1/50
2915 m[c]	2918 mw[c]	2920 mw[c]	2940 ms 2880 s	2945 m 2886 m	2948 m 2890 m	~2960 m[b]	2963 s
1512 s	1512 s	1517 s	1464 s	1465 s	1466 m	1496 s	1499 s
1243 vs	1245 vs	1246 s	1225 m	1235 msh 1224 vs	1227 s 1220 s	1158 vs	1166 vs 1155 s
b	*b*	911 m	*b*	~906 m[b]	906 s	900 s	902 vs

[a] Frequencies in cm^{-1}. [b] In concentrated C_2H_4/Ar and pure C_2H_4 mixtures, these bands were partially or completely obscured by the absorptions of free C_2H_4 in the matrix. [c] The original assignment of the ν(CH) stretching mode of $(C_2H_4)_3Ni$ to a band at 3065 cm^{-1} [2] seems to be doubtful on the basis of the present study, although it may be obscured by a free C_2H_4 absorption.

Table II. The Infrared Spectra of $(C_2H_4)_nNi$ and $(C_2H_4)_nCu$ (where n = 1, 2, or 3)[a,b]

$(C_2H_4)_3M$		$(C_2H_4)_2M$		$(C_2H_4)M$		
M = Ni (this study)	Cu (ref 8)	Ni (this study)	Cu (ref 8)	Ni (this study)	Cu (ref 8)	Assignment
2918[d]	3054	2945 2886	*c*	~2960[c]	3120	ν(CH)
1512	1517	1465	1508	1496	1475	ν(C=C)
1245	1252	1235 1224	1230 1216	1158	1164 1155	$\delta(CH_2)$
c	810	~906[c]	862	900	840	$\rho_w(CH_2)$

[a] Frequencies in cm^{-1}. [b] Frequencies quoted refer to C_2H_4/Ar $\simeq$ 1/10 matrices. [c] In concentrated C_2H_4/Ar and pure C_2H_4 mixtures, these bands were partially or completely obscured by the absorptions of free C_2H_4 in the matrix. [d] The original assignment of the νCH stretching mode of $(C_2H_4)_3Ni$ to a band at 3065 cm^{-1} [2] seems to be doubtful on the basis of the present study although it may be obscured by a free C_2H_4 absorption.

In contrast, the monotonic order for the ν(C=C) stretching modes of $(C_2H_4)_nCu$ (where n = 1, 2, or 3[8]) indicates that $k_{CC\cdot CC}$ is very small, which is not unreasonable in view of the considerably lower thermal stability (weaker copper-olefin interaction) of the $(C_2H_4)_nCu$ compared to the corresponding $(C_2H_4)_nNi$ complexes. This difference in stability is best appreciated from the observation that $(C_2H_4)_3Ni$ decomposes to Ni metal and C_2H_4 at about 0 °C whereas $(C_2H_4)_3Cu$ decomposes at about 40 K[8]).

Uv-Visible Experiments

For 12-, 14-, and 16-electron systems of the type $(C_2H_4)_nNi$ (where n = 1, 2, or 3), visible absorptions are not expected if the nickel center is formally Ni(0). Both the 14-electron $(C_2H_4)_2Ni$ complex (in quasi-tetrahedral D_{2d} and quasi-planar D_{2h} conformations) and the 16-electron $(C_2H_4)_3Ni$ complex (in the all-planar D_{3h} conformation) have been examined using extended Hückel molecular orbital techniques (ref 6) and predict that electronic transitions should be observable in the uv region 200-300 nm and are best described as Ni(d) → $C_2H_4(\pi^*)$ charge transfer type transitions. The available energy level schemes predict that charge transfer should shift to higher energies on passing from $(C_2H_4)_2Ni$ to $(C_2H_4)_3Ni$.[6]

The assignment of metal → olefin charge transfer transitions in the 200-300 nm region is not in fact unexpected in view of a number of earlier studies involving platinum-olefin complexes of the type $[(olefin)PtCl_3]^-$,[18] copper halide-norbornene complexes,[19] and silver(I)-benzene and styrene complexes.[20]

Using conditions similar to those described for our C_2H_4/Ar $\simeq$ 1/50 infrared experiments (which favored $(C_2H_4)Ni$ on deposition at 15 K, Figure 1A) we recorded the corresponding matrix uv-visible spectra (Figure 4A).

Aside from the presence of the well-characterized atomic Ni resonance absorptions[21] (labeled Ni in Figure 4A) and trace amounts of Ni_2 (as seen by the vibrational progression centered around 350 nm, with an average vibrational spacing of 360 cm^{-1} and previously ascribed to Ni_2 from quantitative Ni/Ar concentration experiments[22]) a new intense absorption at about 280 nm can be associated with the Ni(d) → $C_2H_4(\pi^*)$ charge transfer transition of $(C_2H_4)Ni$ (Figure 4A). On warming this matrix to 30-35 K (remembering that the corresponding infrared experiments show the rapid growth of $(C_2H_4)_3Ni$ and concomitant decay of $(C_2H_4)Ni$) one observes the rapid growth of *two* new absorptions centered at about 236 and 250 nm (Figure 4B and 4C).[24] At 35-40 K the absorption attributed to $(C_2H_4)Ni$ at 280 nm has essentially disappeared (Figure 4C), as has the atomic Ni which was isolated in the Ar matrix during the original deposition process. The two absorptions at 250 and 236 nm can be assigned to Ni(d) → $C_2H_4(\pi^*)$ charge transfer transitions of $(C_2H_4)_2Ni$ and $(C_2H_4)_3Ni$, respectively, on the grounds that (a) further warming of the C_2H_4/Ar $\simeq$ 1/50 matrix to 40 K enhances the 236-nm absorption at the expense of the 250-nm shoulder (Figure 4D) and (b) only the 236- and 250-nm absorptions appear when Ni atoms are cocondensed with pure C_2H_4 at 15 K. Incidentally this assignment is in accordance with the predicted[6] charge transfer energy order $(C_2H_4)_3Ni$ > $(C_2H_4)_2Ni$.[25]

We may conclude by stating that nickel atom-ethylene cocondensation reactions at 15 K provide a direct and convenient route to $(C_2H_4)_nNi$ (where n = 1, 2, or 3) complexes

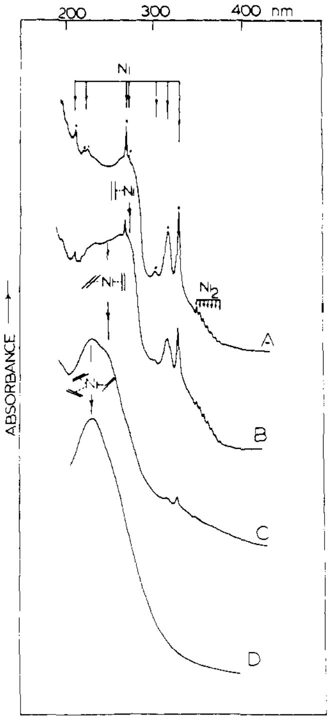

Figure 4. The matrix uv-visible spectrum observed (A) on depositing Ni atoms with a $C_2H_4/Ar \simeq 1/50$ mixture at 15 K (showing the absorptions of atomic Ni, trace amounts of Ni_2 as well as the Ni(d) → $C_2H_4(\pi^*)$ charge transfer transition of $(C_2H_4)Ni$) and (B)-(D) after warm up to 30, 35, and 40 K (showing the decay of the $(C_2H_4)Ni$ charge transfer transition and the concomitant growth of the corresponding Ni(d) → $C_2H_4(\pi^*)$ charge transfer transitions of $(C_2H_4)_2Ni$ and $(C_2H_4)_3Ni$).

which may be identified and characterized from their infrared and uv spectra.

The synthesis of these compounds is important other than for their novelty, in that they will undoubtedly serve as valuable matrix models for studying the catalytic role of "naked" nickel in the "nickel effect" as well as olefin oligomerization and hydrogenation reactions.

Further matrix studies of this system as well as ethylene interactions with other group 8 metal atoms and small metal clusters, using infrared, uv-visible, Raman, and, where applicable, ESR spectroscopy will form the subject of subsequent publications.

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References and Notes

(1) K. Fischer, K. Jonas, and G. Wilke, *Angew. Chem.*, **85**, 620 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 565 (1973).

(2) (a) E. P. Kündig and G. A. Ozin in "Cryochemistry", M. Moskovits and G. A. Ozin, Ed., Wiley, New York, N.Y., 1976, first communicated at the Merck Symposium "Metal Atoms in Chemical Synthesis", Darmstadt (Germany), May 1974; (b) P. L. Timms, communicated in a paper given at C.I.C. Meeting "Chemistry under Extreme Conditions", Toronto, June 1975; (c) R. M. Atkins, R. McKenzie, P. L. Timms, and T. W. Turney, *J. Chem. Soc., Chem. Commun.*, 764 (1975).

(3) K. Fischer, K. Jonas, P. Misbach, R. Stabba, and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **12**, 943 (1973) (and references therein).

(4) K. Jonas, P. Heimbach, and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **7**, 949 (1968).

(5) (a) R. Ugo, *Catal Rev.*, **11**, 225 (1975); (b) J. Kwiatek in "Transition Metals in Catalysis", G. N. Schrauzer, Ed., Marcel Dekker, New York, N.Y., 1971. (c) F. Basolo and R. L. Burwell Jr., Ed., "Catalysis", NATO Scientific Affairs Division, Plenum, London and New York, 1973.

(6) N. Rösch and R. Hoffmann, *Inorg. Chem.*, **13**, 2656 (1974).

(7) N. Rösch and T. N. Rhodin, *Discuss. Faraday Soc.*, **58**, 28 (1974).

(8) H. Huber, D. McIntosh, and G. A. Ozin, *J. Organometallic Chem.*, **C50**, 112 (1976).

(9) H. Huber, D. McIntosh, and G. A. Ozin, *J. Organometallic Chem.*, in press.

(10) E. P. Kündig, M. Moskovits, and G. A. Ozin, *J. Mol. Struct.*, **14**, 137 (1972).

(11) M. Moskovits and G. A. Ozin, *J. Appl. Spectrosc.*, **26**, 487 (1972).

(12) E. P. Kündig, M. Moskovits, and G. A. Ozin, *Angew. Chem., Int. Ed. Engl.*, **14**, 292 (1975).

(13) C. W. Bunn, *Trans. Faraday Soc.*, **40**, 24 (1944), and R. W. G. Wykoff, "Crystal Structures", Vol. 5, Interscience, New York, N.Y., 1966, p 258.

(14) R. DeKock, *Inorg. Chem.*, **10**, 1205 (1971).

(15) E. P. Kündig, D. McIntosh, M. Moskovits, and G. A. Ozin, *J. Am. Chem. Soc.*, **95**, 7234 (1973).

(16) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

(17) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953), and M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C71 (1951).

(18) R. G. Denning, F. R. Hartley, and L. M. Venanzi, *J. Chem. Soc. A*, 1322 (1967).

(19) D. J. Trecker, J. P. Henry, and J. E. McKeon, *J. Am. Chem. Soc.*, **87**, 3261 (1965).

(20) T. N. Murrel and S. Carter, *J. Chem. Soc.*, 6185 (1964).

(21) D. M. Mann and H. P. Broida, *J. Chem. Phys.*, **55**, 84 (1971), and W. Klotzbücher and G. A. Ozin, *Inorg. Chem.*, **15**, 292 (1976).

(22) W. Klotzbücher and G. A. Ozin, to be submitted for publication.

(23) In this context, the ν(C=C) stretching frequencies for $(C_2H_4)_3M$ (where M = Cu or Ni) are predicted and observed to have the highest values in the $(C_2H_4)_nM$ series (Table II) in view of (a) the Dewar-Chatt-Duncanson-description[17] of the bonding of olefins to a transition metal center (extended to account for the changing ethylene coordination number, that is, decreasing C_2H_4 → Ni and Ni → C_2H_4 σ and π charge transfers per coordinated C_2H_4 with increasing n) and (b) its F-matrix term being of the form $k_{CC} - k_{CC\text{-}CC}$. Matrix Raman data will be required to establish whether or not the actual k_{CC} bond stretching force constants increase monotonically with increasing n in the series $(C_2H_4)_nNi$.

(24) A Ni concentration study established that the uv absorptions observed under these experimental conditions can only be ascribed to mononuclear $(C_2H_4)_nNi$ complexes.

(25) Intuitively, one would expect that, as the nickel-ethylene interaction decreases with increasing ethylene stoichiometry, the corresponding Ni(d)/$C_2H_4(\pi^*)$ energy separation should increase.