for electronic compensation of ohmic potential loss were incorporated into the instrument. Large-scale, controlled-potential electrolysis was carried out on a second potentiostat, which used a Harrison Model 6824A amplifier (±50 V, 1 A) in the control circuit. Readout for cyclic voltammetric experiments was accomplished by a Hewlett-Packard Model 7035B X-Y recorder or Tektronix Model 5103N storage oscilloscope.

Chemicals. The zerovalent $Co(bpy)_2$ used in electrochemical studies was prepared as described above. The $Co(bpy)_3(ClO_4)_2$ was prepared by standard methods.[33] Tetraethylammonium perchlorate was prepared according to the method of Kolthoff and Coetzee.[34]

Electrodes and Cells. All electrochemical experiments were carried out on an all-glass vacuum line, which has been previously described.[35] Acetonitrile solvent was distilled from flask to flask until totally degassed. Finally, the solvent was distilled into the cell on the vacuum line, and the contents in the cell were freeze–pump–thawed at least twice. After the cell and its contents were brought to ambient temperature, helium, which was passed over BASF catalyst R3-11, was introduced until normal atmospheric pressure was obtained. A conventional three-electrode three-compartment cell was used on the vacuum line; in addition, a large platinum basket electrode was placed in the working electrode chamber to carry out coulometric and voltammetric experiments as desired. The working electrode for microscale experiments was a modified Beckman platinum button electrode (No. 39273) with a geometric area of 0.24 cm^2 or a glassy carbon (Tokai) electrode (area, 0.20 cm^2), which was prepared by previously reported methods.[36] Both electrodes were polished with 0.1-μm alumina prior to use. A silver wire, which was used as a quasi-reference electrode in several experiments, was also polished with alumina immediately before use. An aqueous saturated calomel electrode was used as a reference electrode; the reference electrode was isolated by means of a glass frit and a bridge containing a 0.2 M solution of tetraethylammonium perchlorate in acetonitrile. No attempt was made to position the reference electrode to minimize IR loss; however, electronic compensation as stated above was used in all voltammetric experiments. The auxiliary electrode for microscale experiments was a platinum foil, which was positioned within 1 cm of and parallel to the working electrode surface. The auxiliary electrode for coulometric studies was a large coil of platinum wire, which was isolated by a glass frit from the working-electrode compartment.

Acknowledgment. The generous support of the National Science Foundation and the University of North Dakota Faculty Research Committee is acknowledged with gratitude. We also thank Mr. Mike Edwards and Professor Keith Purcell of Kansas State University for their assistance in obtaining the magnetic susceptibility data.

Registry No. $Co(bpy)_2$, 71534-63-9; $(bpy)_2CoBr$, 78683-94-0; $(bpy)_2Co(TCNQ)_2$, 78624-84-7; (bpy)Co(TCNE), 78624-85-8; $(bpy)_3Co(ClO_4)_2$, 21349-81-5; $Co(bpy)_2(ClO_4)_2$, 78624-86-9.

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Solvated Nickel Atoms and Nickel Slurries: Nickel Atom–Toluene Microsolution and Matrix Optical Spectroscopy

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The "solvated" nickel atoms and nickel slurries initially described by Klabunde and co-workers have been probed by nickel atom–toluene microsolution and matrix optical spectroscopy in methylcyclohexane and argon, over the extended temperature range 12–290 K. In Klabunde's terminology "solvated" nickel atoms are interpreted in terms of a highly thermally unstable bis(arene)nickel complex. The stages I to IV described by Klabunde in his procedure for preparing nickel cluster catalysts from nickel atom–toluene condensates appear to be best ascribed as follows: bis(arene)nickel coexisting with Ni_2 and Ni_3, stage I; nickel clusters of colloidal dimensions or less, stage II; bulk nickel microcrystallites, stages III and IV. Stages I and II appear also to be formed on depositing nickel atoms into 150 K toluene/methylcyclohexane solutions and 210 K poly(methylphenyl)siloxane (DC510) liquid films. An appreciation of the nickel atom and cluster species existing at the various stages of a Klabunde-type preparation should greatly enhance the value of the method as a viable synthetic route to finely dispersed, narrow-size-distribution metal cluster catalysts.

Introduction

One of the most significant recent developments in the field of metal vapor synthesis is the discovery by Klabunde and co-workers of "solvated" metal atoms and their application for the production of highly reactive metal slurries and supported metal catalysts.[1] The method consists of cocondensing metal vapors with various organic solvents (toluene, tetrahydrofuran, alkanes, etc.), usually at liquid-nitrogen temperature, to create lightly stabilized or "solvated" metal atoms. These condensates are often highly colored and, when subjected to controlled meltdown, solvent evaporation, and pyrolysis procedures in either the absence or the presence of an oxide support, can lead to finely dispersed, narrow-size-distribution metal cluster compositions whose catalytic efficacy can rival that of some of the best known catalyst systems. The morphological, magnetic, and chemical properties of these materials continue to be of considerable interest[2] even though the nature of the species formed at various stages of the preparation remains uncertain. In this paper we wish to report the results of an optical spectroscopic study, using both matrix and microsolution techniques,[3] which sheds considerable light on

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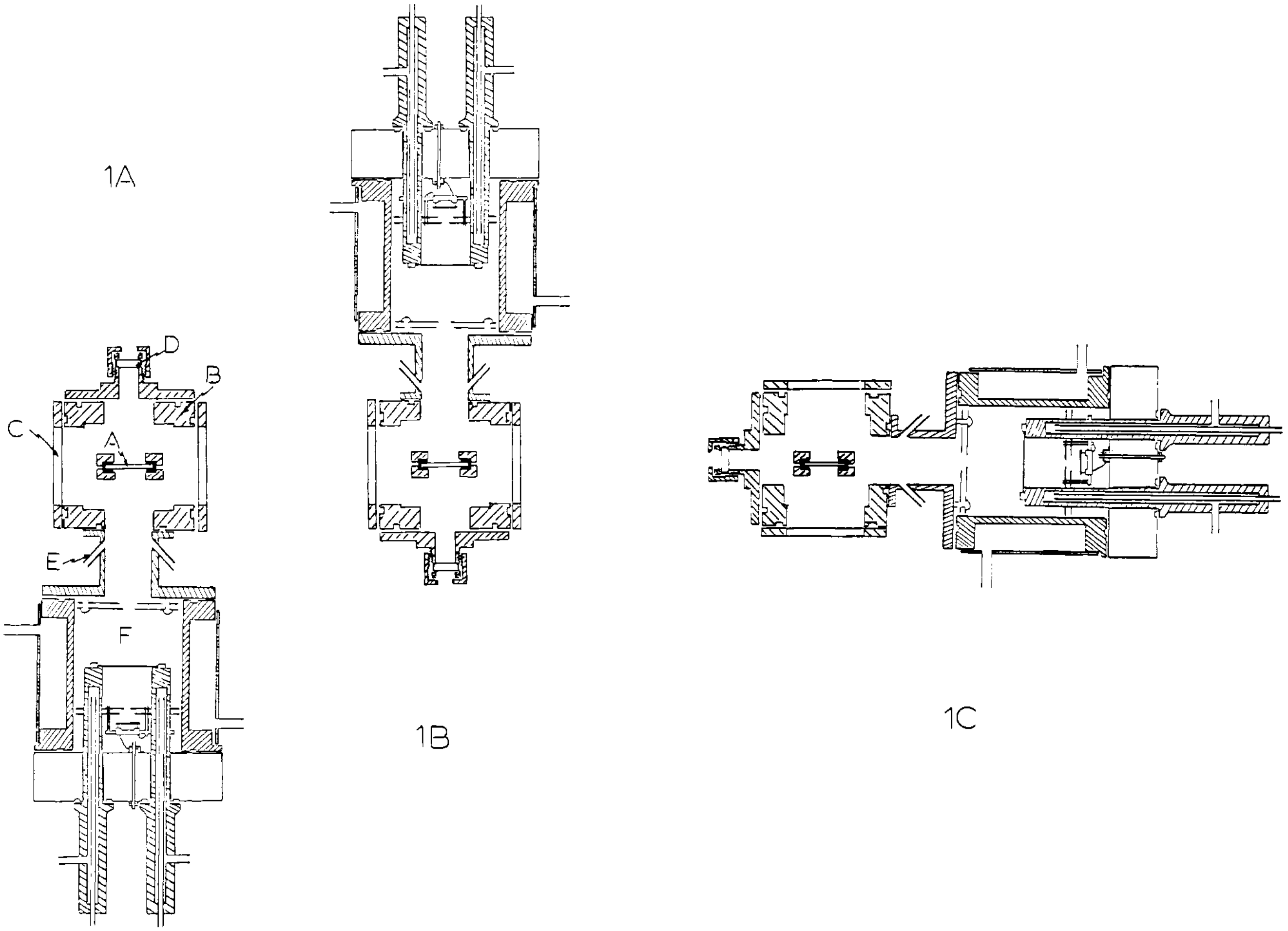

Figure 1. Schematic representation of vacuum furnace–closed-cycle helium refrigeration system used for metal vapor–microsolution optical spectroscopy, as well as conventional metal vapor–matrix isolation experiments: (A) NaCl or Surpasil optical window, horizontal configuration; (B) stainless-steel vacuum shroud; (C) NaCl or Suprasil optical viewing ports; (D) cajon-rubber septum, liquid or solution injection port; (E) gas deposition ports; (F) vacuum furance–quartz-crystal microbalance assembly.[10,11] With the optical window in a fixed horizontal configuration, liquid or solution sample injection onto the window at any desired temperature in the range 12–300 K is performed in position 1A, metal deposition is conducted in position 1B, and optical spectra are recorded in position 1C (see Experimental Section).

the interaction between nickel atoms and toluene over the extended temperature range 12–290 K. The optical data of the present study permit one to assess the various stages of nickel atom diffusion, complexation, and agglomeration that ensue in both the solid and the solution phases during co-condensation, metldown, and solvent evaporation steps, in the presence of toluene. Experiments of this kind should help with the design of metal vapor syntheses intended to optimize the yields of a particular metal cluster composition for subsequent catalyst evaluation.

Experimental Section

Monatomic nickel was generated by directly heating a nickel filament (0.15 in.; 99.999%), supplied by A. D. MaKay. Toluene (reagent grade) was dried over Na–K alloy and distilled under N_2. Spectral grade methylcyclohexane (purchased from Eastman) and poly(methylphenyl)siloxane (Dow Corning, DC510) were used (without further purification). Nickel was evaporated as previously described,[10] and metal–deposition rates were monitored by using a quartz–crystal microbalance.[11] All solid, liquid, and solution samples were deposited onto a NaCl or Suprasil window, held in a horizontal configuration for the UV-visible experiments, and were fixed at a predetermined temperature anywhere in the range 12–300 K by using an Air Products Displex closed-cycle helium refrigerator in combination with a proportional temperature controller. UV–visible spectra were recorded on a Varian Techtron 635.

As experimental details of the metal vapor–microsolution spectroscopic procedure were not presented in our original communication of the technique,[3] this aspect of the present study will now be described. The vacuum furnace–shroud assembly of a metal vapor–matrix isolation spectroscopy apparatus of the Torromis[12] type is arranged as shown in Figure 1. The vacuum furnace can be rotated into any one of the positions 1A, 1B, and 1C, to allow sample injection, metal vapor deposition, or spectral recording, respectively, simply by twisting the shroud. During all of these operations, the sample optical window remains fixed in a horizontal configuration (Figure 1). The liquid or solution sample is supported on a NaCl or Suprasil optical window, the latter being sandwiched between indium gaskets within a copper housing. This assembly is attached to the second stage of a Displex closed-cycle helium refrigerator system. The horizontal arrangement is required to maintain a liquid film of even thickness on the optical window. In the case of involatile liquid samples such as poly(methylphenyl)siloxane (DC510), approximately 0.3 μL of liquid is applied directly to the upper surface of the optical window by using a vacuum microsyringe (position 1A). This in situ liquid injection procedure is accomplished through a side flange on the vacuum shroud, to which is attached a vacuum-tight rubber septum–cajon assembly. As the

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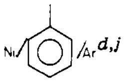
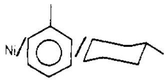
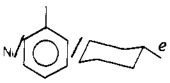
(12) Torromis, Model No. M1; Torrovap Industries, Toronto, Ontario, Canada.

Table I. Optical Data for Nickel Atom Reaction Products with Argon, Toluene/Argon, Toluene/Methylcyclohexane, and Poly(methylphenyl)siloxane

Ni/Ar	^{d,j}						^{e}	Ni/DC510			
12-30 K solid	12 K solid	12 K solid	77 K^e solid	120 K solid	150 K soln	200-290 K evapn	150 K soln	210 K^f liquid	230-300 K liquid	species assignt	Klabunde terminology^i
240^c						~220			~230	$\mathrm{Ni_{bulk}}^g$	III; IV
265^c						~260					
	~280	~290	~290							$(C_6H_5CH_3)_2Ni$	I
	~320	~320	~320								
330^b				~320^h	~320^h					$\mathrm{Ni_{colloid}}$	II
340^c							~340			Ni_n $(n > 3)$	
350^c								~350		Ni_m $(n > 3)$	
377^a										Ni_2	I′
	~370	~370	~370							$(C_6H_5CH_3)_2Ni$	I
410^a										Ni_2	I′
420^a							~420			Ni_3	
	~440		~450								
480^a										Ni_2	
	~505		~510								
530^a											

[a] Optimum yield obtained by depositing at 25-30 K in Ar.[6,7] [b] Obtained in high nickel concentration experiments on depositing at 25-30 K and on annealing concentrated Ni/Ar matrices at 35-40 K[6]. [c] Observed in nickel atom photoaggregation experiments involving concentrated argon matrices containing $Ni_{1,2,3}$.[7] [d] 1/20 mixtures. [e] 1/10 mixtures. [f] Optimum reaction temperature for product formation in thin liquid DC510 films. [g] Bulk nickel films absorb at 230 nm.[9] [h] Suspected overlap region of stages I and II; see text. [i] See ref 1 for details. [j] The corresponding optical absorptions in benzene/argon ≃1/10 mixtures occur at 280, 320, 390, 445, and 505 nm.

optical window can be fixed at any desired temperature in the range 12-300 K, this vacuum-injection technique also works for the introduction of volatile microliquid and microsolution samples such as toluene/methylcyclohexane used in the present study. Alternatively, one can use conventional gas-handling procedures for depositing the vapors of volatile liquids and solutions onto the optical window at a temperature below that of the melting point of the sample. With subsequent warming of the frozen sample, a temperature range can usually be established in which the material can be maintained under dynamic vacuum, on the optical window as a liquid (10^{-5}-10^{-6} Torr in the shroud), without appreciable loss for the duration of a typical experiment (usually 3-6 h). Approximately 0.3 μL of liquid sample is sufficient to create a film close to 1 μm in thickness, with the assumption of an exposed optical surface of 1.9 cm in diameter. A resistively heated nickel filament (28 × 5 × 0.25 mm) is used as the source of nickel atoms. The rate of metal deposition is monitored in situ by a line-of-sight quartz-crystal microbalance protected by a radiation shield. A second radiation shield interposed between the filament and the sample helps to collimate the metal vapor and effectively minimizes heating of the microliquid and solution films. An absolute value of the number of moles of metal deposited into the sample can be obtained by a calibration in which the optical window is replaced by a second mass monitor. This allows the ratio of the forward/backward metal flux to be obtained. The geometrical correction factor σ is then

$$\sigma = \frac{\text{forward metal flux}}{\text{backward metal flux}}$$

Once the vapor pressure-temperature profile of the liquid film has been established, the UV-visible spectrum of the liquid or solution sample, prior to metal atom deposition, is scanned in the range 200-900 nm with the furnace assembly in position 1C. With the furnace assembly rotated into position 1B, the nickel filament (previously outgassed) is then heated resistively and a steady nickel atom deposition rate is obtained. Depending on the desired products, metal fluxes are usually selected in the range 10-5000 ng s^{-1}. The furnace is subsequently returned to position 1C, heating of the filament is stopped, and an absorption spectrum of the product is collected. By repetition of the above procedure a quantitative metal atom-liquid or -solution phase titration can be effected and in situ formation of reactive intermediates and products can be spectroscopically monitored.

Results and Discussion

Our optical experiments were formulated to probe stages I-IV of nickel atom complexation and agglomeration, in the presence of toluene, described in Klabunde's scheme[1] (Scheme I). The diluents chosen for nickel vapor-toluene mixtures in our study comprise both argon and methylcyclohexane. In this way optical spectroscopic information for the interaction of nickel atoms, molecular clusters, and colloid or bulk microcrystallites with toluene can be evaluated.

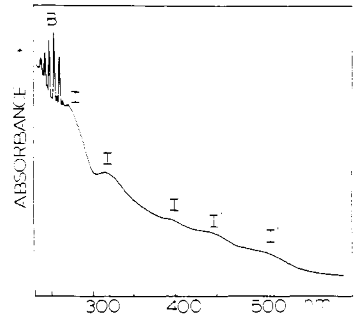


Figure 2. Optical spectrum obtained on depositing nickel atoms with $C_6H_6/Ar \simeq 1/20$ and $Ni/Ar \simeq 1/10^3$ at 12 K (see text and Table I for letter notation I and I′; B = C_6H_6).

Scheme I

$$\mathrm{Ni(g)} + \text{toluene} \xrightarrow{77\ \mathrm{K}} \underset{\mathrm{I}}{\underset{\text{(colored)}}{\text{M–solvent complex}}} \xrightarrow{\text{meltdown}}$$

$$\underset{\mathrm{II}}{\text{M–solution}} \xrightarrow[\text{warming}]{\text{further}} \underset{\mathrm{III}}{\underset{\text{(black)}}{\mathrm{M}_n\text{–solvent slurry}}} \xrightarrow[25\ ^\circ\mathrm{C}]{\text{vaporize solvent}}$$

$$\underset{\mathrm{IV}}{\underset{\text{crystallites)}}{\underset{\text{(black; small}}{\mathrm{M}_n\text{–solvent adduct}}}} \xrightarrow{\text{pyrolysis}} \underset{\mathrm{V}}{\mathrm{M}_n + \text{organics}}$$

Consider first the optical spectra observed following the cocondensation of nickel atoms with $C_6H_5CH_3/Ar \simeq 1/10$ or $C_6H_6/Ar \simeq 1/20$ mixtures ($Ni/Ar \simeq 1/10^3$) at 12 K shown in Table I and Figure 2. Aside from the vibronic structure associated with uncomplexed toluene or benzene in the matrix around 250-260 nm, weak new absorptions are observed around 280, 320, 370-390, 440-450, and 505-510 nm. By working in a more rigid matrix at 12 K such as

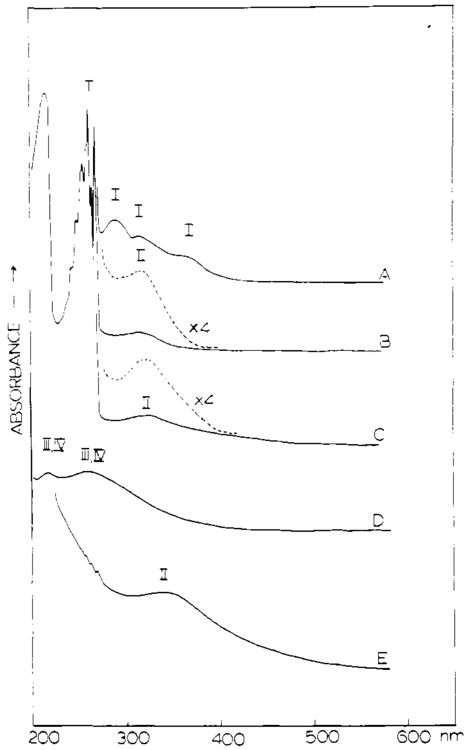


Figure 3. Optical spectra obtained on depositing nickel atoms with $C_6H_5CH_3/C_6H_{11}CH_3 \simeq 1/10$ (A) at 12 K, (B) after warming to 120 K, (C) after warming to 150 K, and (D) after warming to 200–290 K. Curve E shows the optical spectrum obtained on depositing nickel atoms with liquid poly(methylphenyl)siloxane DC510 at 210 K (see text and Table I for letter notation I–IV; T = $C_6H_5CH_3$).

methylcyclohexane/toluene, one observes absorptions around 290, 320, and 370 nm (Figure 3A), which always appear in the same proportion, with no sign of the bands to lower energy found for toluene/argon and benzene/argon matrices. However, one finds that toluene/methylcyclohexane cocondensations performed at 77 K show (in addition to the 290-, 320-, and 370-nm features) the aforementioned low-energy absorptions around 450 and 510 nm (Figure 4). When the 12 K $Ni/C_6H_5CH_3/C_6H_{11}CH_3$ condensate shown in Figute 3A is warmed to 120 K, which is still below the melting point of the matrix, the only discernible spectral feature occurs at 320 nm (Figure 3B). This absorption remains essentially unperturbed (Figure 3C) on melting the matrix at 140–150 K under dynamic vacuum conditions. By employment of these conditions, thin toluene/methylcyclohexane solution films can be retained on a horizontal optical window without noticeable change for a period of several hours. The 140–150 K stage of this meltdown experiment (Figure 3C) should be compared with the outcome of depositing nickel atoms into a thin film of $C_6H_5CH_3/C_6H_{11}CH_3 \simeq 1/10$ held at 150 K under dynamic vacuum conditions, which shows optical absorptions around 340 and 420 nm. Warming the meltdown microsolution sample, shown in Figure 3C, from 150 to 180 K (just below the evaporation temperature of the solvent mixture) causes initial broadening of the 320-nm band, which, within a short period of time, decays to zero.

Within the range 180–200 K the solvent mixture evaporates and new spectral features around 260 and 220 nm emerge and remain essentially unchanged up to room temperature (Figure 3D).

It is particularly significant that when nickel vapor is deposited into a thin liquid film of DC510 [a poly(methylphenyl)siloxane] at 210 K, a broad absorption around 350 nm is observed (Figure 3E). This band decays to zero on warming the film above 230 K, leaving a broad, weak absorption around 230 nm. Metal depositions into DC510 films at higher temperatures only produce the broad absorption at 230 nm. Recall that such metal vapor–liquid polymer experiments yield very low-nuclearity, polymer-stabilized metal clusters for M = Ti, V, Cr, or Mo,[4] yet metal slurries of undetermined metal particle size for M = Fe, Co, or Ni.[5]

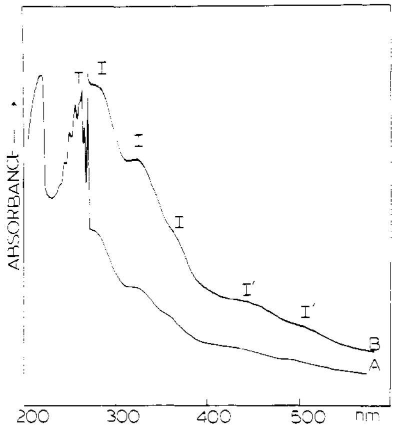
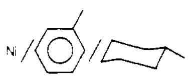
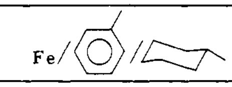


Figure 4. Optical spectra obtained on depositing nickel atoms with $C_6H_5CH_3/C_6H_{11}CH_3 \simeq 1/10$ at 77 K: (A) short deposition; (B) longer deposition (same notation as Figure 1).

Other optical spectroscopic information that is pertinent to the present study concerns the aggregation data for nickel atoms in argon matrices. Nickel–argon concentration studies, deposition temperature and thermal annealing behavior, and photoaggregation experiments[6,7] have led to the optical assignments for nickel clusters, colloid, and microcrystallites shown in Table I.

Examination of the optical data of Table I allows one to draw a number of conclusions regarding the probable state of nickel atom complexation and aggregation at various stages of the Klabunde experiment with nickel vapor–toluene cocondensations. From the toluene/argon (12 K), benzene/argon (12K), and toluene/methylcyclohexane (12–77 K) cocondensations of the present study one can readily identify bands around 290, 320, and 370 nm associated with a single species with stage I of the Klabunde preparation. Earlier IR studies of Ni/C_6H_6 (77 K) and $Ni/C_6H_6/Ar$ (12 K) condensates[8] identified two nickel–benzene metal–ring stretching modes at 445 and 346 cm^{-1}, red shifted with respect to the analogous modes of $(C_6H_6)_2Cr$ at 492 and 466 cm^{-1}. In fact a monotonic trend was observed for these modes in the M/C_6H_6 (M = Cr, Fe, Co, Ni) series[8], which we believe would tend to favor an assignment to an isostructural bis(arene)metal group of complexes, rather than a mono(arene)metal assignment for M = Fe, Co and Ni, despite the claims to the contrary. Also relevant to the present discussion are the microsolution and matrix optical data obtained for the Fe/toluene/methylcyclohexane system,[3] which show the presence of a low-temperature species (77–140 K) absorbing at 310 (w), 340 (s), and 378 (w) nm and a high-temperature species (150–250 K) absorbing at 300 (s), 355 (w), and 436 (s) nm. Without going into detail, these species have both been ascribed to bis(arene)iron complexes (with a change in coordination of the aromatic ring occurring on going from the low A to the high B (Table II) temperature form). The striking similarity between the iron/toluene and the nickel/toluene optical data (Table II), namely, the observation of three UV–optical absorptions for both complexes that blue shift on passing from iron to nickel, suggests a metal-to-ligand charge-transfer assignment for the observed UV bands[4] and an isostructural formulation. Thus stage I of the Klabunde preparation can be associated with a highly labile bis(toluene)nickel complex, and hence we have justification for Kla-

Table II. Iron and Nickel Vapor–Toluene/Methylcyclohexane Reaction Products

			
77 K solid	77 K solid	150 K soln	assignt[a]
290		300 (s)	B
	310 (w)		A
320			
	340 (s)		A
		355 (w)	B
370			
	378 (w)		A
		436 (s)	B

[a] Tentative species identification: A = bis(η^6-toluene)iron; B = (η^4-toluene)(η^6-toluene)iron (see ref 3).

bunde's terminology "solvated nickel atom" in the nickel/toluene system.[1]

Returning to the optical data collected in Table I, one observes that coexisting with the absorptions ascribed to bis(toluene)nickel in freshly deposited 12 K toluene/Ar, 12 K benzene/Ar, and 77 K toluene/methylcyclohexane matrices are two absorptions at 440–450 and 505–510 nm, which occur at energies close to the weak absorptions found for Ni_2 and Ni_3 in pure Ar matrices.[6,7] One must therefore presume that nickel dimers and trimers (possibly "solvated" or lightly stabilized with toluene[13]) may also be present in Klabunde's stage I as well as bis(arene)nickel, and these are designated I′ in Figures 2 and 4 and Table I. Both I and I′ decay to zero at 120 K, at which point the toluene/methylcyclohexane matrix is still solid.

A band around 320 nm grows in, broadens, and then remains essentially unchanged when the matrix melts at 140–150 K. It is particularly significant that this meltdown solution stage displays an absorption at energies very close to the 330-nm absorption observed for $Ni_{colloid}$ in solid argon.[6] Further warming (200–290 K) causes the toluene/methylcyclohexane solvent mixture to evaporate, together with the loss of the 320-nm absorption. In its place, new absorptions appear in the UV at 220 and 260 nm. The latter absorptions are close in energy to those reported for bulk nickel films (230 nm).[9]

An assessment of the deposition, meltdown, solvent evaporation, and warm-up data for the Ni/toluene/methylcyclohexane system implies that Klabunde stage II can be associated with nickel clusters of colloidal dimensions (giving rise to the characteristic 320–330-nm optical resonance) which may or may not be weakly stabilized (solvated) by interaction with toluene. Solvent evaporation, however, leads to Klabunde stages III and IV, which display the optical characteristics of bulk nickel microcrystallites absorbing at 220–260 nm.

Some other details which are worthy of mention concern the results of depositing nickel atoms into a 150 K toluene/methylcyclohexane solution and a 210 K thin film of DC510. The former displays two absorptions around 340 and 420 nm while the latter shows one around 350 nm. From considerations similar to those described earlier, one can tentatively assign the 150 K solution species and the 210 K polymer-stabilized species to very low-nuclearity nickel clusters of colloidal dimensions or less—see Table I. The warm-up and deposition data for Ni/DC510 at temperatures above 210 K display only a weak broad spectral feature at 230 nm, the region of nickel microcrystallite absorption.[9] One can interpret the results for nickel atom deposition into toluene/methylcyclohexane solution at 150 K and liquid DC510 at 210 K in terms of Klabunde stage II. At higher temperatures, however, both of these samples lead to Klabunde stages III and IV and probably reflect the state of nickel agglomeration previously reported for Ni/DC510 metal slurries.[5]

Conclusion

An insight into the nature of Klabunde's "solvated" nickel atoms and nickel slurries has been obtained by nickel atom–toluene microsolution and matrix optical spectroscopy, over the extended temperature range 12–290 K. The "solvated" nickel atom is associated with a highly thermally labile bis(toluene)nickel complex that exists in solid argon and methylcyclohexane in the range 12–77 K. One can associate this species with Klabunde stage I in the nickel atom–toluene experiment. Coexisting with the bis(arene)nickel species in 77 K toluene/methylcyclohexane condensates are some Ni_2 and Ni_3 (I′), and these should also be considered to be present in Klabunde stage I. Whether or not these molecular nickel clusters are stabilized to some extent by interaction with toluene cannot be ascertained from the present study. Klabunde stage II is attained on warming these matrices to 120 K or melting them at 150 K, at which point nickel clusters of colloidal dimensions appear to predominate. Further warming of these solutions to 170–180 K and solvent evaporation in the range 200–290 K take the sample to Klabunde stages III and IV, at which point cluster nuclearities are achieved that display optical characteristics resembling those of bulk nickel microcrystallites. It appears that nickel clusters in a size regime lower than that associated with nickel colloid can be stabilized in 150 K toluene/methylcyclohexane solutions and 210 K poly(methylphenyl)siloxane DC510 liquid films and can be related to Klabunde stages I and II. Data of the type presented in this paper should greatly assist with the design and fabrication of supported and unsupported nickel clusters with narrow size distributions of predetermined dimensions using the Klabunde solvated metal atom approach. By an attempt to more carefully control the composition of the metal clusters created by the metal atom–solvent method, gains in product selectivity may be realized in future research employing such catalysts.

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(13) Support for this idea stems from the recent discovery of binary (arene)$_2$M$_2$ complexes for M = V or Cr: M. Andrews and G. A. Ozin, submitted for publication in *J. Am. Chem. Soc.*