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Nickel Vapor–Olefin Chemistry. 2. Binary Perfluoroethylenenickel Complexes $(C_2F_4)_nNi$ (Where $n = 1, 2$, or 3). Evidence for a Destabilizing Effect in High Stoichiometry Perfluoroolefin Complexes

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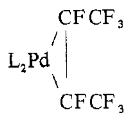
Received April 7, 1977 AIC70259F

Nickel atom–perfluoroethylene matrix cocondensation reactions are investigated for the first time. Three products are isolated from the 15 K reaction and identified by infrared and ultraviolet–visible spectroscopy. Unlike previously reported binary nickel ethylene complexes $(C_2H_4)_nNi$ (where $n = 1, 2$, or 3), the complexes of the present study are best described as perfluorometallocyclopropane–perfluoroethylene derivatives. Five-membered ring-expansion products and perfluorovinyl metal species are not observed under any of our 10–40 K reaction conditions. Interesting trends in the ultraviolet charge-transfer transitions of the Ni/C_2F_4 and Ni/C_2H_4 complexes are observed and rationalized in terms of the relative π-bonding capacities of the two ligands. In this regard, extended Hückel calculations proved to be a useful aid toward understanding the electronic properties of the perfluoroethylene complexes. The relevance of the above findings to known perfluoroolefin organometallic chemistry is discussed and an explanation for the general lack of stable binary perfluoroolefin complexes is also presented.

Introduction

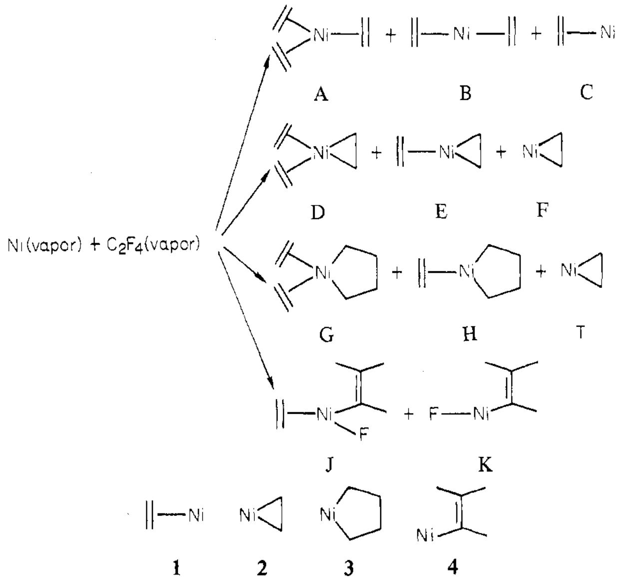
The reaction of nickel atoms with perfluoroethylene, the subject of the present study, is of considerable chemical interest in view of the recent synthesis of binary nickel ethylene complexes $(C_2H_4)_nNi$ (where $n = 1, 2$, or 3) by nickel atom–ethylene–(argon) cocondensations at 15 K and subsequent characterization by matrix infrared, Raman, and ultraviolet–visible spectroscopy.[1] Tris(ethylene)nickel, the highest stoichiometry complex in the system, was found to decompose to metallic nickel and ethylene around 0 °C.[2] An intriguing proposition would be to substitute ethylene by perfluoroethylene in these binary nickel olefin complexes, as the superior π-acceptor ability of C_2F_4 is expected to confer greater stability to the resulting complexes than that of ethylene itself.[3a,b] However, the outcome of successive perfluoroethylene incorporation in this particular situation is by no means obvious for the following reasons.

Firstly, stable complexes containing more than a single coordinated C_2F_4 ligand have not previously been reported although we note that early macroscale (−196 °C) Pd vapor-octafluoro-2-butene codepositions[3c] indicated that an unstable $Pd(C_4F_8)_3$ complex was formed and stable up to −30 °C at which temperature it clearly decomposed to Pd metal and starting olefin; however, addition of phosphine or pyridine ligands displaced two π-bonded olefins leaving a metallocyclopropyl complex of the type



Secondly, C_2F_4 is generally considered to be a weak σ donor yet a powerful π acceptor compared with C_2H_4,[3-5] so much so that coordination of C_2F_4 to a transition metal usually produces a sizeable change in hybridization of the C_2F_4 carbons.[5] In fact, it is now generally agreed that a π-alkene description is a misnomer for complexes such as $(Ph_3P)_2Pt(C_2F_4)$ and that a perfluorometallocyclopropane description for the metal–perfluoroethylene fragment is more accurate.[5,6] Thirdly, it is significant to note that studies involving low-valent nickel derivatives and unsaturated fluorinated compounds revealed an extensive fluorocarbon–nickel chemistry differing in a number of aspects from that of palladium and platinum.[6a,7] Referring mainly to the work of Green and Stone,[6a,7] one might anticipate that nickel atom–perfluoroethylene matrix cocondensations could proceed according to one or more of the pathways illustrated in Scheme I, where **1** refers to a π-perfluoroalkene ligand; **2** refers to a perfluorometallocyclopropane ligand; **3** refers to a perfluorometallocyclopentane ligand; and **4** refers to a perfluorovinyl ligand.

Scheme I



Chemically, all of the complexes (A through K) are acceptable products of this type of reaction,[6a,7,8] although we note that no F migrations of the kind indicated in J and K have been observed in contrast to the many Cl migrations from η^2-complexes; the relative bond strengths of C–F and C–Cl make F migrations unlikely until high temperatures are reached and are not expected to occur under matrix cryochemical conditions. Moreover, based on previous work in the literature, complexes A through K are distinguishable spectroscopically. The following is a detailed account of our efforts to unravel this fascinating chemical and spectroscopic puzzle.

Experimental Section

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.[9] The nickel (99.99%) was supplied by McKay, N.Y. Research grade C_2F_4 (99.9%), Ar (99.99%), and Xe (99.99%) were

Table I. Infrared Spectroscopic Data for Matrix-Isolated and Gaseous Perfluoroethylene[d]

C_2F_4 solid (15 K)	C_2F_4/Ar $\simeq 1/50$ (15 K)	C_2F_4/Xe $\simeq 1/50$ (15 K)	C_2F_4 gaseous (ref 12e)[b,c]
1952 w	1955 w	1950 w	1952
1876 w	1876 w	1872 w	1880
1724 w	1726 w	1725 w	1724
1556 vw	1552 vw	1550 vw	1550
1524 vw	1523 vw	1520 vw	1521
1350 m sh	1348 m sh	1342 m sh	1340
1324 s	1324 s	1324 s	
1288 m, w	1292 m	1289 m	
1170 s	1176 s	1168 s	1186
1156 m sh	1164 m sh		1179
	1124 w	1116 w	1125
1096 m, w	1092 vw	1092 vw	1070
	990 vw	988 vw	985
958 w	960 w	956 w	952
925 w	922 w	912 w	910
a	*a*	*a*	666
600 vw	604 vw	610 vw	620
			600
554 m	556 m	554 m	559
510 vw	510 vw	504 vw	
416 m	414 m	410 m	
274 vw	280 vw		

[a] CO_2 region. [b] We did not observe weak bands reported by Torkington and Thompson[12e] at 1607 (water region), 1459, 1157, 1035, 876, 807, 720, and 697 cm^{-1}. We suspect that this may be related to trace impurities involved in their $SbCl_5/SbF_3/CHCl_3$ synthesis. In our experiments we employed research grade C_2F_4 (99.90%). [c] Band intensities were not reported in this study. [d] Bands reported in cm^{-1}.

supplied by Matheson of Canada. The rate of Ni atom deposition was continuously monitored using a quartz crystal microbalance.[10]

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

Results

Infrared Experiments. Matrix-Isolated Perfluoroethylene. Although vibrational spectroscopic investigations and normal-coordinate calculations for ethylene and its ^2H and ^{13}C isotopically substituted molecules abound in the literature,[11] this certainly does not appear to be the case for perfluoroethylene.[12] This may be related to the unavailability of fluorine isotopes. Of the 12 fundamental modes of vibration predicted for C_2F_4, only five are permitted to appear in the infrared spectrum (in cm^{-1}): B_{3u}, CF stretching, 1186, CF_2 deformation, 558; B_{2u}, CF stretching, 1337, CF_2 rocking, 250; B_{1u}, CF_2 bending, not observed. By reference to the existing literature for gaseous, liquid, and solid C_2F_4,[12] four *infrared* fundamentals can be assigned as listed above. Besides the intense, fundamental infrared vibrational modes, Torkington and Thompson[12e] observed a fair number of weaker combination modes in their infrared study of gaseous C_2F_4. Under the conditions of a C_2F_4 matrix isolation experiment, one would expect to observe some of these weak combination modes and therefore before describing the results of our Ni/C_2F_4 cocondensation experiments, it is pertinent to establish the infrared frequencies of solid C_2F_4 and C_2F_4 isolated in inert gas matrices. Table I summarizes the results of our C_2F_4 matrix infrared experiments from which it can be seen that a number of combination modes are indeed observed in addition to the fundamentals. The agreement with the literature data for most of the observed bands is reasonable after taking into account small matrix-induced frequency shifts of the order of ±10 cm^{-1}.

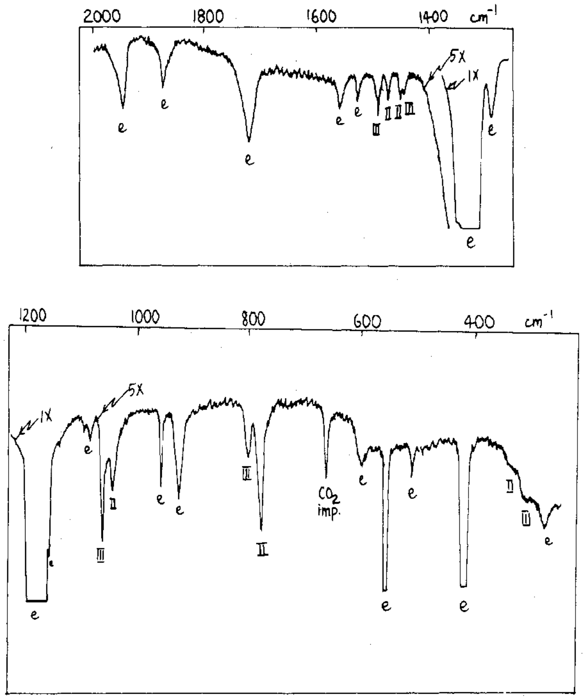


Figure 1. Matrix infrared spectrum of the products formed when Ni atoms are cocondensed with C_2F_4 at 15 K under conditions which favor the generation of mononuclear complexes ($Ni/C_2F_4 \approx 1/10^4$). In Figures 1, 2, and 3, I, II, and III denote $(C_2F_4)Ni$, $(C_2F_4)_2Ni$, and $(C_2F_4)_3Ni$, respectively, and e denotes uncomplexed C_2F_4.

With reference to the dipole-forbidden ν(C=C) stretching vibration, we note that the Raman spectrum of gaseous C_2F_4 has been observed and the in-plane modes are assigned as follows (cm^{-1}):[12d,f] A_g, C=C stretching, 1872, C—F stretching, 778, C—F deformation, 394; B_{1g}, C—F stretching, 1340; C—F deformation, 551. The high frequency of the ν(C=C) stretching mode is striking, especially when compared with the corresponding mode for ethylene at 1623 cm^{-1}. In line with these observations we note the higher C=C bond stretching force constant ($k_{C=C}^{C_2F_4} = 12$, $k_{C=C}^{C_2H_4} = 9$ mdyn/Å) and shorter C=C bond distance ($r_{C=C}^{C_2F_4} = 1.313$ Å, $r_{C=C}^{C_2H_4} = 1.337$ Å) for C_2F_4 compared with C_2H_4.[12d] Furthermore, this bond strengthening effect is reflected in the ionization potentials (IP's) of the π^* and π levels and the greater π^*–π energy separation for C_2F_4 relative to C_2H_4.[13] These properties of C_2F_4/C_2H_4 will be referred to later on in our discussions of the Ni/C_2F_4 and Ni/C_2H_4 vibrational data.

Nickel Atom–Perfluoroethylene Cocondensations; Pure C_2F_4 Matrices. When Ni atoms are cocondensed with pure C_2F_4 matrices at 15 K, under conditions that favor mononuclear complex formation[14] ($Ni/C_2F_4 \simeq 1/10^4$), besides the known absorptions of C_2F_4, one observes new absorptions in the frequency ranges 1500–1400, 1100–1000, 800–700, and 400–300 cm^{-1}. These are labeled III and II in Figure 1 and Table II. Warmup experiments in the temperature range 20–40 K indicate that the bands denoted III and II belong to different species with those of III dominating at the higher temperature extreme. Probably the most dramatic observation in these infrared spectra is the existence of four ν(CC) stretching modes in the 1500–1400-cm^{-1} region, *two* being associated with species III at 1488/1444 cm^{-1} and *two* with species II at 1472/1450 cm^{-1}. These absorptions appear under a variety of deposition and annealing conditions, indicating that they do not originate from a multiple trapping site effect.

Table II. Infrared Spectra of the Ni Atom–C_2F_4 Cocondensation Reaction[a]

C_2F_4 (15 K)	C_2F_4/Ar (1/50)	C_2F_4/Xe (1/50)	Species	Tentative vib assignment
1488	1496		III	ν(CC)
1472	1476	1464	II	ν(CC)
1450	1460	1445	II	ν(CC)
1444	1450		III	ν(CC)
	1418	1400	I	ν(CC)
1064	1073 1068 } [b]		III	ν(CF)
1046	1056	1048	II	ν(CF)
	1046	1038	I	ν(CF)
804	806 798 } [b]		III	ν(CF)
778	784 774	812 798	II	ν(CF)
	750 724 } [c]	715	I	ν(CF)
	370	366	I	$\delta(CF_2)$ or ν(NiC)
338	338	332	III	$\delta(CF_2)$ or ν(NiC)
318	314		III	$\delta(CF_2)$ or ν(NiC)

[a] Frequencies quoted in cm^{-1}. [b] "Temperature-dependent" doublet components indicating a matrix site splitting effect for these modes in solid Ar. [c] The 750-cm^{-1} band is very strong in high-temperature depositions (~50 K) and could indicate the presence of some unidentified polymeric material (see text).

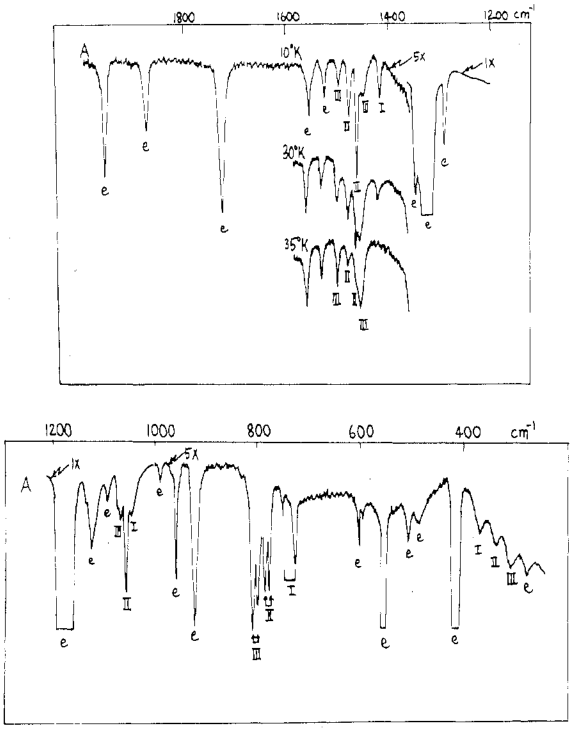


Figure 2. Same as Figure 1 but using C_2F_4/Ar ≈ 1/50 mixtures. In the ν(C=C) stretching region, 30 and 35 K warmup results are also illustrated.

We will return to this point later on.

Dilute C_2F_4/Ar Matrices. When Ni atoms are cocondensed with C_2F_4/Ar ≃ 1/50 matrices under conditions which favor mononuclear complex formation (Ni/Ar ≃ $1/10^4$), spectra of the type shown in Figure 2 and Table II were obtained. Groups of new absorptions in regions similar to those observed in C_2F_4 matrices were observed, and the correlation with those labeled III and II in Table II is quite apparent. Noteworthy under these dilute matrix conditions is the presence of *four* new absorptions at 1418, 1046, 724, and 370 cm^{-1} which we associate with a low-stoichiometry species labeled I. The results of warmup experiments in the range 20–40 K show the gradual *decay* of the *four* absorptions ascribed to species I and the *five* absorptions of species II but at different rates. Concomitant with the disappearance of I and II, one observed the *growth* of the *five* absorptions ascribed to species III. At 40 K the entire spectrum gradually decays to zero leaving only broadened absorptions of matrix-isolated C_2F_4. Summarizing up to this point, one can deduce that *three* complexes are generated in C_2F_4/Ar matrices in the temperature range 15–35 K, two of which are common with those formed in pure C_2F_4 matrices. Particularly noteworthy is the confirmation of *two* ν(CC) stretching modes for both species III and II in the 1500–1450-cm^{-1} region, having suffered small matrix-induced frequency shifts of about 4–10 cm^{-1} on passing from C_2F_4 to C_2F_4/Ar matrices. On the other hand, species I, suspected to be the lowest stoichiometry perfluoroethylene complex in the Ni/C_2F_4 system, displays only a *single* ν(CC) stretching mode at 1418 cm^{-1}.

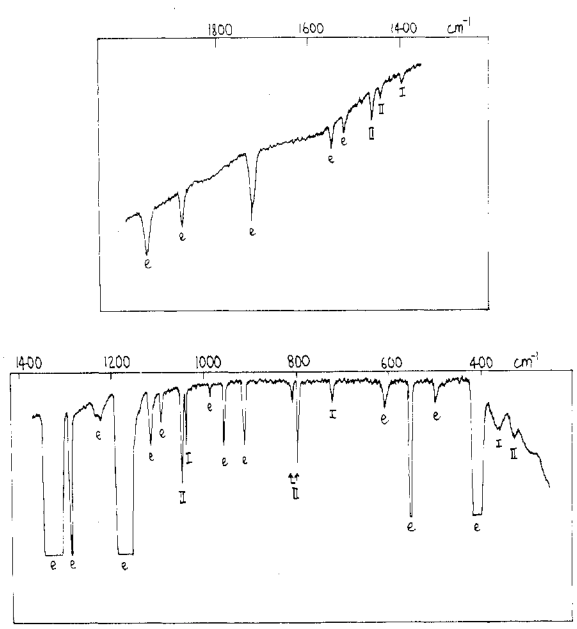


Figure 3. Same as Figure 1 but using C_2F_4/Xe ≈ 1/50 mixtures.

Dilute C_2F_4/Xe Matrices. Using dilute C_2F_4/Xe matrices (1/50–1/100) one expects higher quenching efficiencies than C_2F_4/Ar matrices under comparable conditions and hence preferential isolation of the lower stoichiometry complexes in the Ni/C_2F_4 system. Our results for C_2F_4/Xe ≃ 1/50 matrices are in Table II and Figure 3. In particular, one observes that the absorptions of species II and I have experienced matrix-induced *red* frequency shifts (typical on passing from Ar to Xe matrix supports)[15] of the order of 5–20 cm^{-1}. Furthermore, species II retains two ν(CC) stretching modes in Xe matrices at 1464/1445 cm^{-1}, in line with the observations in Ar matrices (1476/1460 cm^{-1}) and in C_2F_4 matrices (1472/1450 cm^{-1}). The observation of *two* ν(CC) stretching modes for species III and II and *one* for species I in the 1500–1400-cm^{-1} region of the infrared spectrum is central to our formulation of complexes III, II, and I presented in a later section.

Ultraviolet–Visible Experiments. Perfluoroethylene itself, either pure or diluted with the inert gases, displays no absorptions in the ultraviolet–visible spectral range 200–900 nm. However, when Ni atoms are cocondensed with C_2F_4/Ar ≃ 1/50 mixtures under comparable conditions to those described for the matrix infrared measurements, *three* strong ultraviolet absorptions are observed at 326, 280, and 242 nm (see Figure 4 and Table III). On deposition at 15 K, the low-energy band at 326 nm (labeled I) dominates the ultraviolet spectrum. However, on warming the matrix in the temperature range 15–35 K, one observes a gradual diminution in the absorbance

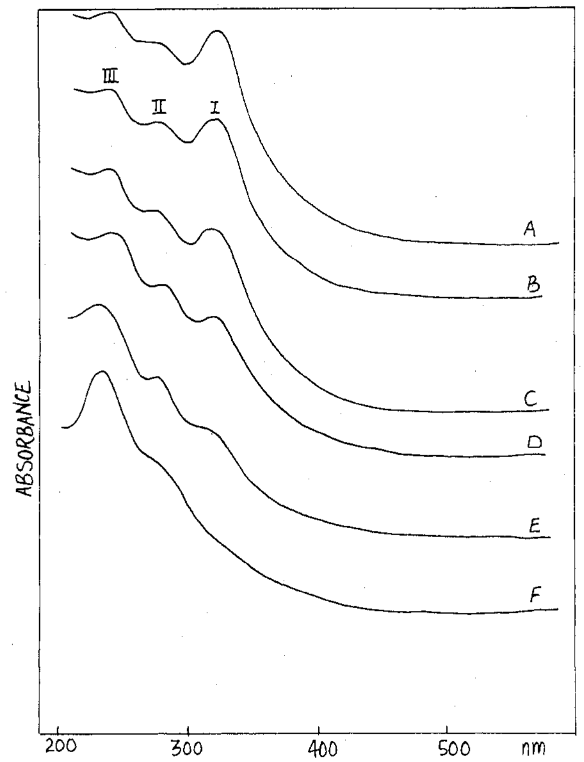


Figure 4. (A) Matrix ultraviolet–visible spectrum of the products formed when Ni atoms are cocondensed with $C_2F_4/Ar \simeq 1/50$ mixtures at 15 K under conditions which favor the generation of mononuclear complexes. B through F illustrate the effect of matrix annealing at 20, 25, 30, 35, and 37 K and recooling to 10 K for spectral recording.

Table III. Ultraviolet-Visible Spectra for the Products of the $Ni/C_2F_4/Ar$ and $Ni/C_2H_4/Ar$ Matrix Cocondensation Reactions

λ, nm			
C_2F_4/Ar $\simeq 1/50$	C_2H_4/Ar $\simeq 1/50$	Species	Δ,[a] cm^{-1}
326	280	I	5039
280	250	II	4286
242	236	III	1051

[a] $\Delta = \nu_{Ni(C_2H_4)_n} - \nu_{Ni(C_2F_4)_n}$.

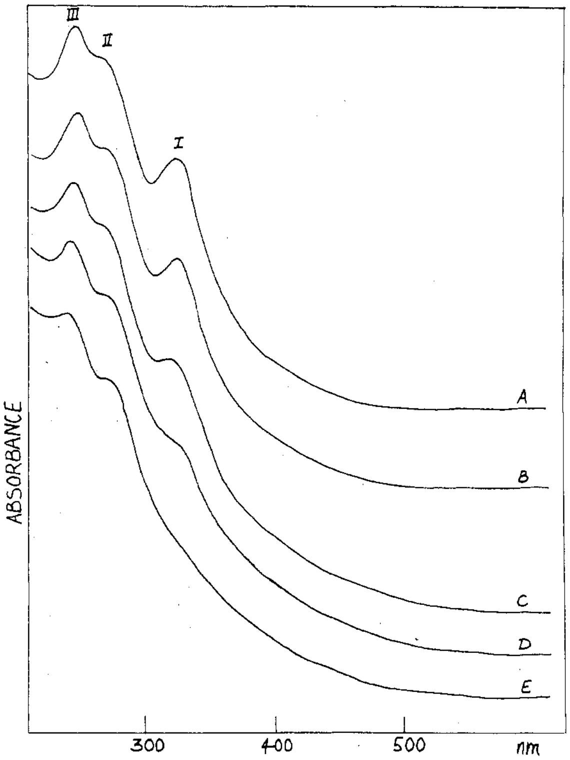


Figure 5. (A) Same as Figure 4 but using $C_2F_4/Ar \approx 1/10$ mixtures. (B through E) The effect of matrix annealing at 20, 25, 30, and 35 K and recooling to 10 K for spectral recording.

of band I with a concomitant increase in the absorbance of the high-energy band at 242 nm (labeled III). During this annealing procedure the medium-energy band (labeled II) displays an initial slight increase and then a slow decay. At 35 K, only bands III and II are detectable. Similar absorbances were observed in more concentrated $C_2F_4/Ar \simeq 1/10$ matrices at 326, 276, and 248 nm except that all three bands have comparable intensities on deposition (Figure 5). Warming these matrices in the range 15–35 K shows the gradual decay of band I with bands III and II dominating the spectrum at 35 K.

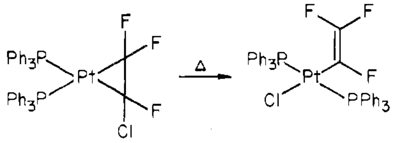
The growth and decay behavior of the spectral absorbances described above depict the presence of three reaction products in the $Ni/C_2F_4/Ar$ reaction, in accordance with the infrared experiments described earlier. Moreover, the close resemblance of the ultraviolet spectral data of species I, II, and III to those previously reported for $(C_2H_4)_nNi$ (where $n = 1$, 2, or 3) is particularly striking[1] (see Table III for this comparison). Noteworthy features in Table III are (i) the monotonic *blue* shift on passing from species I to II to III, (ii) the predominance of species III both at the high-temperature extreme and in more concentrated C_2F_4 matrices, (iii) contrariwise, the domination of I both at the low-temperature extreme and in more dilute C_2F_4 matrices, and (iv) the *blue* shift on passing from a $(C_2F_4)_nNi$ complex to the corresponding $(C_2H_4)_nNi$ complex.

Collecting together the infrared and ultraviolet–visible spectral information for the products of the Ni/C_2F_4 cocondensation reaction, it would seem that a reasonable a priori assignment of the *three* products is $(C_2F_4)_3Ni$ (III), $(C_2F_4)_2Ni$ (II), and $(C_2F_4)Ni$ (I). This situation exactly parallels that reported for $(C_2H_4)_{3,2,1}Ni$ binary complexes.[1] Whether or not one is justified in proposing an analogous bonding and electronic description for binary nickel perfluoroethylene and binary nickel ethylene complexes will form the subject of the following discussion.

Discussion

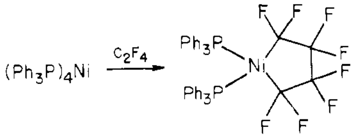
It is clear from our matrix infrared and ultraviolet–visible experiments that *three* mononuclear compounds exist in the Ni/C_2F_4 system. Those labeled III and II form preferentially in pure C_2F_4 while I through III can be generated in dilute C_2F_4/Ar matrices. The relative amounts of each depend on the chosen matrix ratio. The difficulty experienced in isolating I in the absence of II and III might relate to the prerequisite of a 15 K deposition temperature for reaction (*below 15 K, only Ni atoms are isolated*). On the other hand, excessive matrix diffusion made possible from heat generated in an exothermic reaction could also account for these observations. Whatever the case in practice, the association of III with the highest stoichiometry complex and I with the lowest stoichiometry complex in the system is quite apparent. Let us now consider the problem of assigning structure to I, II, and III.

Referring to the Ni/C_2F_4 reaction paths illustrated in Scheme I, one can immediately eliminate perfluorovinyl reaction products by reference to the work of Stone and Green.[6a] In particular, compounds of the type $(Ph_3P)_2Pt(CF_2CFX)$ are known (where X = F, Cl, Br) in which the metal–olefin interaction is metallocyclopropane in nature.[6a] This type of compound undergoes a facile transformation on warming in vacuo

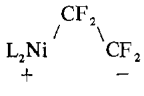


to form a perfluorovinylplatinum(II) chloride complex[6a] (we note with great interest that this is a situation analogous to the dissociative chemisorption of haloalkenes on Pt surfaces;[16] see ref 26 for an elaboration of this important general concept). We note here that a characteristic spectroscopic feature of a perfluorovinyl ligand is the presence of a strong infrared absorption in the 1700–1800-cm^{-1} range corresponding to the ν(C=C) stretching mode.[6a] As expected, this vibration is only slightly shifted from that of C_2F_4 itself[12d,f] which shows the ν(C=C) at 1872 cm^{-1}. For the $(C_2F_4)_nNi$ complexes of the present study, infrared bands were *never* observed in the 1800–1700-cm^{-1} region. On these grounds, a perfluorovinyl formulation for I, II, or III can be safely rejected. Moreover, the relatively high temperature conditions required to effect the perfluorometallocyclopropane to perfluorovinyl rearrangement makes an analogous transformation for $(C_2F_4)_nNi$ in low-temperature matrices (10–40 K) most unlikely.

In the context of the present discussion, it is significant that studies involving low-valent nickel derivatives and unsaturated fluorinated compounds have revealed an extensive fluorocarbon–nickel chemistry differing in some aspects from Pd and Pt.[7,8] For example, ring expansion reactions of the following type are quite common for nickel



These octafluoronickelacyclopentane complexes are generally very stable and it has been suggested that they are formed via "reactive" nickelacyclopropane ring compounds such as $(Ph_3P)_2Ni(C_2F_4)$.[7a] Evidently, a delicate balance between the factors concerned with five- and three-membered ring formation are important here.[24,25] The favored mechanism for ring expansion involves coordination of a *second* perfluoroethylene to the monoperfluoroethylene complex.[7a] Ring expansion is very rapid for Ni and does not occur for Pt. The currently accepted pathway[7,8] involves 1,3-dipolar intermediates



$$\overset{+}{L_2Ni}\!-\!CF_2\!-\!\overset{-}{CF_2}$$

Obviously, if the metal becomes too oxidized, no residual nucleophilicity will be left to bond an incoming olefin molecule. Thus, in $(Ph_3P)_2Pt(C_2F_4)$, which is stable to ring expansion,[6a] it is thought that the metal is closer to Pt(II) than in the nickel analogue, so coordination of a second C_2F_4 molecule followed by ring expansion does not occur.

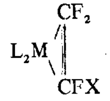
Comparative infrared spectroscopy between our complexes $(C_2F_4)_nNi$, the ring expansion complexes $(Ph_3P)_2Ni(CF_2)_4$[7] and $(OC)_4Fe(CF_2)_4$[17] (Table IV), and C_2F_4 itself (Table I) is useful here. To begin with, we note that the 1800–1350-cm^{-1} region of the perfluorometallocyclopentane moiety is *devoid* of infrared absorptions (this is especially clear in $(OC)_4Fe(CF_2)_4$[17] which does not have Ph_3P ligand vibrations in this region that tend to confuse the situation). Secondly, characteristic ν(CF) stretching modes of the saturated five-membered ring system, particularly in the region of 1260–1230 and 970–910 cm^{-1}, are *absent* in the infrared spectra of our $(C_2F_4)_nNi$ complexes (in this analysis we have not considered ν(CF) stretching modes which could be hidden by those of matrix-isolated C_2F_4—Table I). On the basis of this type of "fingerprint" analysis, we feel reasonably confident that a perfluorometallocyclopentane formulation for either I, II, or III can be rejected.

Table IV. Representative Infrared Spectra of Perfluorometallocyclopentane Complexes

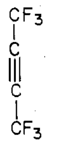
$(Ph_3P)_2Ni(CF_2)_4$ (ref 7)	$(OC)_4Fe(CF_2)_4$ (ref 7)	Tentative assignments
	2480	ν(CO)
	2160	
	2108	
	2088	
	2055	
1589		PPh_3[a]
1479		
1439		
1434		
1349		ν(CF)
1338	1332	
1311		
1268	1263	ν(CF)
1253		
1226	1228	ν(CF)
1180	1170	ν(CF)
1158		PPh_3[a]
1149		
1138		
1131		
1118		
1099	1103	ν(CF)
1089		
1084		
1078	1060	ν(CF)
1022		PPh_3[a]
1019		
991		
977		
963		
	968	ν(CF)
959		
909	910	ν(CF)

[a] Ph_3P vibrational modes, by comparison with Ph_3P, $(Ph_3P)_4Ni$, and $(Ph_3P)_2Pt(C_2F_4)$.

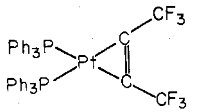
We therefore find ourselves in a situation where it remains to distinguish a series of binary perfluoroethylene nickel complexes (A, B, and C in Scheme I) from mixed perfluorometallocyclopropane–perfluoroethylene complexes (D, E, and F also shown in Scheme I). On the grounds that we observe *three* distinct complexes (I, II, and III), we will not entertain an assignment involving a mixture of A, B, C and D, E, F complexes. From the outset, however, we note that the infrared spectra of the $(C_2H_4)_nNi$ complexes display only a single ν(C=C) stretching mode for each complex in the 1500–1400-cm^{-1} region, which is to be *contrasted* with *two* each for species III and II and *one* for species I under all conditions so far investigated. This specific difference between $(C_2F_4)_nNi$ and $(C_2H_4)_nNi$ suggests one of two alternatives. Either I, II, and III are best formulated as D, E, and F or we accept that the plurality of ν(C=C) stretching modes originate from a molecular distortion of A and B from their respective D_{3h} and D_{2h}/D_{2d} symmetries. Before returning to this problem, some other points relevant to the discussion are worth noting here. In particular, Stone's inability to observe ν(C=C) stretching modes for complexes like $L_2M(CF_2{=}CFX)$ (where M = Ni, Pd and X = F, Cl) in the region of 1500 cm^{-1} is noteworthy.[7] He ascribed this to the presence of a metallocyclopropane-type bonding of the type



in which the C–C bond order is close to unity. However, because of the complexity of the ligand vibrational spectrum no assignment of the actual ν(C–C) was attempted.[7] We believe that certain useful information concerning this assignment can be drawn from comparative data, such as that shown below.

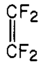


ν(C≡C) 2300 cm^{-1} [4]



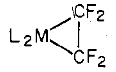
ν(C=C) 1775 cm^{-1} [4]

Although the C–C bond order in the metallocyclopropene is likely to be slightly greater than 2, it is our contention that a shift of around 500 cm^{-1} could also be experienced on passing from



ν(C=C) 1872 cm^{-1}

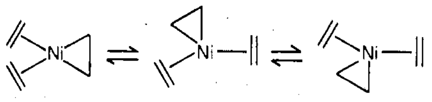
to



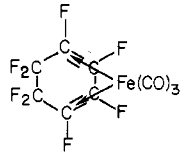
ν(C–C) estimated at 1400–1300 cm^{-1}

Taking into account the initially very high ν(C=C) (1872 cm^{-1}) of free C_2F_4, one can deduce that the observations of ν(CC) stretching modes in the 1500–1400-cm^{-1} region of $(C_2F_4)_nNi$ (where $n = 1, 2,$ or 3) is highly indicative of a CC bond order of the coordinated perfluoroethylene, "intermediate" between that of a double and single bond but closer to the side of single. This is probably a fair comment to make as frequency shifts on passing from free to complexed olefins are normally only of the order of 100–200 cm^{-1}, *not* 400–500 cm^{-1}, as experienced with $(C_2F_4)_nNi$.[4]

We would therefore propose that a straightforward binary perfluoroethylene assignment A, B, and C for complexes III, II, and I, respectively, in which the nickel is formally zero-valent is not an appropriate description for this particular system. Rather an intermediate type of bonding description in which some charge transfer has occurred from the nickel to the perfluoroethylene is probably more accurate. On a vibrational time scale one is obliged to consider the "frozen" structures D, E, and F for III, II, and I, respectively, although with a slower type of detection technique a fluxional situation such as

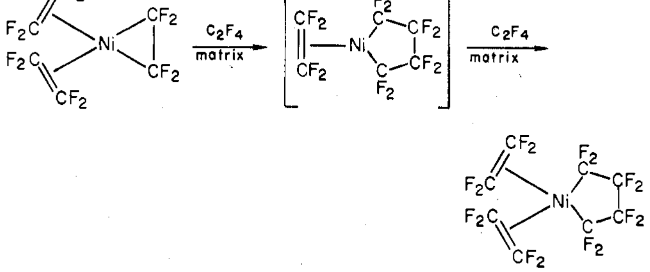


is likely to prevail. In essence we are proposing that oxidative addition of a single perfluoroethylene ligand to Ni(0), to produce an oxidation state close to Ni(II), is acceptable for $(C_2F_4)Ni$. However, successive oxidative additions of perfluoroethylene ligands to $(C_2F_4)Ni$ to yield oxidation states close to IV in $(C_2F_4)_2Ni$ and VI in $(C_2F_4)_3Ni$ are deemed unlikely. Therefore, a "π-perfluoroethylene" description for the addition of second and third perfluoroethylene ligands is favored on both chemical and spectroscopic grounds. It is interesting to note here that the residual nucleophilicity of the nickel atom after it has oxidatively added the first C_2F_4 ligand (achieving a formal oxidation state close to II) is such that it will probably only bind in a weak "π-alkene" fashion to other demanding π-acceptor ligands such as C_2F_4. This could well explain the "thermal instability" of $(C_2F_4)_nNi$ complexes (remembering $(C_2H_4)_3Ni$ decomposes at 0 °C) and in fact the general paucity of data for complexes containing more than a single perfluoroalkene ligand. In this context we note that the presence of a coordinated conjugated perfluorodiene has been shown to produce stable complexes of the type[18]



Of special interest here is the observation of a ν(C=C) stretching mode at 1550 cm^{-1}. This observation is significant in that it provides a precedent for a zero-valent iron perfluorodiolefin complex with a "π-alkene" bonding interaction rather than that of a metallocyclopropane on the grounds that the ν(C=C) stretching mode is shifted by *only 200 cm*$^{-1}$ relative to that of the free diene (1750/1712 cm^{-1}).

It is amusing to finally consider reasons for the "nonobservation" of ring expansion reactions of the type



Such reactions do not appear to proceed on 15 K deposition nor during bulk diffusion up to 35 K. Possibly the degradation of our matrices around 40 K originates from a highly exothermic polymerization process of C_2F_4 through successive C_2F_4 ring expansions. According to Stone's picture of ring expansions,[7] such a reaction would be expected to proceed under room temperature conditions and one may conclude that under our low-temperature conditions it is kinetically impeded. Support for this idea can be considered to stem from Klabunde's[19] −196 °C Ni/C_2F_4 cocondensations, which showed the presence of very unstable reaction products (as yet unidentified) as well as some polymeric material suspected to be Teflon. Further studies concerning the nature of the Ni/C_2F_4 reaction products as a function of deposition temperature *above* 40 K will be required to clarify problems of ring expansion and polymerization.

Electronic Properties and Nature of the Bonding in $(C_2F_4)_nNi$ Complexes (Where $n = 1, 2,$ or 3)

The optical spectra for $(C_2F_4)_nNi$ described in an earlier section indicate that a single ultraviolet electronic transition can be associated with each of the species I, II, and III and that these shift monotonically to higher energies with increasing perfluoroethylene stoichiometry. Furthermore, each species shows a *red* frequency shift in its associated ultraviolet band compared with the analogous $(C_2H_4)_nNi$ complex. Each of these observations is interesting and carries considerable information regarding the electronic and bonding properties of binary, transition metal–ethylene, and perfluoroethylene complexes.

To begin, let us try to rationalize the red frequency shifts of the ultraviolet optical bands on passing from a $(C_2H_4)_nNi$ complex to a corresponding $(C_2F_4)_nNi$ complex. This can be qualitatively achieved by reference to their respective molecular orbital energy level schemes shown in Figure 6. These diagrams have been calculated by extended Hückel computational procedures using methods similar to those previously

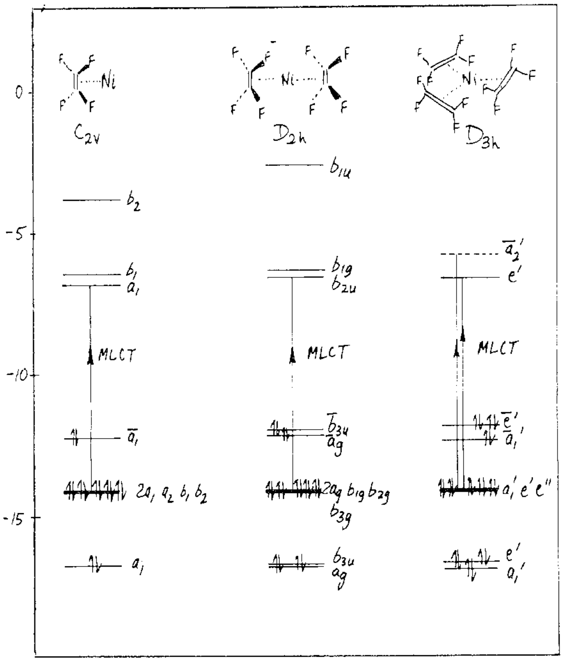


Figure 6. Partial extended Hückel molecular orbital energy scheme for $(C_2F_4)_nNi$ showing the MLCT electronic transitions assigned to the observed ultraviolet bands at 326, 280, and 242 nm (Figures 4 and 5) for $n = 1$, 2, and 3, respectively. Symmetry labels with a bar are meant to signify orbitals which are mainly ligand in character.

Table V. Parameters[a] Used in the Extended Hückel Molecular Orbital Calculations of $(C_2F_4)_nNi$ (Where $n = 1$, 2, or 3)[b]

	Orbital	Orbital exponents[c]	H_{ii},[d] eV
Ni	3d	4.176	−14.16
	4s	1.500	−8.96
	4p	0.860	−4.98
C	2s	1.625	−21.40
	2p	1.625	−11.40
F	2s	2.564	−40.12
	2p	2.550	−18.65

[a] Bond lengths and angles employed for coordinated C_2F_4 in $(C_2F_4)_nNi$ were r(C–F) = 1.313 Å, r(C–C) = 1.313 Å, r(Ni–C) = 2.10 Å, ∠FCC = 123°, and ∠FCF = 114°. [b] Cusach's approximation employed: L. C. Cusachs, *J. Chem. Phys.*, 43, 5157 (1965). [c] Reference: E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, 38, 2686 (1963). [d] Reference: H. Basch, A. Viste, and H. B. Gray, *Theor. Chim. Acta*, 3, 458 (1965).

described for $(C_2H_4)_nNi$.[1,20] The parameters, approximations, and geometries used in these calculations are listed in Table V. In view of the assignment of metal → olefin charge-transfer transitions in the 200–300-nm region of a variety of stable olefin complexes[21] as well as for $(C_2H_4)_nM$ (where M = Co,[22a] Ni,[1] Cu,[22] Pd;[23] $n = 1$, 2, 3), a similar description would also seem to be appropriate for the $(C_2F_4)_nNi$ complexes of the present study. A noticeable difference between the molecular orbitals of the uncomplexed ligand C_2F_4 compared with C_2H_4 is the destabilization of the π^* level of C_2F_4 ($\simeq$0.8 eV) and a greater π–π^* energy separation for C_2F_4 (~6.76 eV compared with ~5.95 eV).[13c] Note, however, that the observed vertical ionization potentials for the π levels of $C_2H_4(1b_{2u})$ and $C_2F_4(2b_{2u})$ are essentially the same, that is, 10.51 and 10.52 eV, respectively.[13a,b]

Considering specifically the monoolefin complexes $(C_2F_4)Ni$ and $(C_2H_4)Ni$ and assuming that the major π-bonding interaction involves the symmetry-allowed d_π orbital on Ni and the π^* orbital on the olefin,[27] one can see that a number of metal-to-ligand charge-transfer transitions are allowed, the lowest energy of which probably corresponds to our observed ultraviolet absorptions at 326 and 280 nm, respectively (Table III). Qualitatively one would expect *less* $Ni(d_\pi) + C_2F_4(\pi^*)$ orbital overlap than $Ni(d_\pi) + C_2H_4(\pi^*)$[13] and hence any Ni → C_2F_4 charge transfer would be expected to *red*-shift with respect to the corresponding Ni → C_2H_4 transition, consistent with the trend observed in practice (Table III). A similar situation can be expected to hold true for $(C_2F_4)_2Ni$ compared with $(C_2H_4)_2Ni$ as seen by inspection of Figure 6. It is significant to note that for the bis- and monoolefin complexes, these *red* shifts are substantial, namely, 5039 and 4286 cm^{-1}, respectively. This is reasonable as the electric dipole spin-allowed transitions under consideration involve upper states which are best described as antibonding $Ni(d_\pi)$–$C_2F_4(\pi^*)$/$Ni(d_\pi)$–$C_2H_4(\pi^*)$ combinations. On the other hand, the trisolefin complex has an additional A_2' olefin π^* level which is nonbonding in character (see Figure 6). Hence, $Ni(d_\pi)$ to $C_2F_4(\pi^*)$ charge transfer into this level might not be expected to undergo such a pronounced red shift with respect to the corresponding $(C_2H_4)_3Ni$ transition energy. In view of the observed 400–500% smaller *red* shift for the tris complexes compared with the bis- and monocomplexes (Table III), it would appear that the above rationale is reasonable.

The observation of a monotonic *blue* frequency shift in the MLCT energies with increasing olefin stoichiometry is probably best rationalized in terms of the concomitant changes in nickel–olefin π bonding. Let us assume that the nickel → olefin π charge transfer per ligand decreases with increasing n. Qualitatively, this effect would be expected to result in a strengthening of the olefin C=C bonding interaction, a spreading apart of the π^*–π separation, and a general stabilization of the π and π^* levels. Depending on the extent of MLCT, the nickel d orbitals could remain essentially unperturbed or stabilize slightly with increasing n. Only with hindsight are we able to deduce that any stabilization in the nickel 3d orbitals must more than offset any accompanying stabilization in the upper recipient π^* levels. In this context, our extended Hückel results, displayed in Figure 6, indicate relative insensitivity of the Ni d levels with respect to increasing n, whereas the upper π^*-type orbitals show a tendency to destabilize. This situation mirrors our observed trend of *blue* shifting MLCT with increasing olefin stoichiometry in $(C_2F_4)_nNi$.

Acknowledgment. This research was completed while G.A.O. was a Sherman-Fairchild Distinguished Scholar at California Institute of Technology. The hospitality of the Chemistry Division of Caltech is greatly appreciated. We gratefully acknowledge the financial assistance of the National Research Council of Canada, the Atkinson Foundation, the Connaught Foundation, Imperial Oil of Canada, Erindale College, and the Lash Miller Chemistry Laboratory. An NRCC scholarship for W.J.P. is also greatly appreciated.

Registry No. I, 63833-65-8; II, 63833-64-7; III, 63833-63-6; C_2F_4, 116-14-3.

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Bimetal Atom Chemistry. 1. Synthesis, Electronic Absorption Spectrum, and Extended Hückel/Self-Consistent Field-Xα-Scattered Wave Molecular Orbital Analyses of the CrMo Molecule; Relevance to Alloy and Bimetallic Cluster Catalysis

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Received March 18, 1977

AIC70213M

The simultaneous cocondensation of Cr atoms and Mo atoms with low-temperature argon matrices at 10 K provides a controlled synthetic pathway to the heteronuclear diatomic molecule CrMo. Mixed-metal concentration, UV–visible experiments enable the electronic absorptions of CrMo to be identified in the presence of the parent diatomics, Cr_2 and Mo_2. Extended Hückel and SCF-Xα-SW molecular orbital techniques are employed to probe the electronic and bonding properties of CrMo. Both methods indicate that the heteronuclear molecule has properties essentially intermediate between those of the corresponding homonuclear molecules (a similar suggestion has recently been made for the σ–σ^* transition energies of discrete, heteronuclear metal–metal bonded complexes). The relevance of this type of "few-atom data" to the more complex problem of alloy and bimetallic cluster catalysis is also briefly considered.

Introduction

Incentives for experimental and theoretical research in the field of small, well-defined metal clusters often originate with problems in the fields of chemisorption and heterogeneous catalysis.[1-6] One question of paramount importance concerns the number of metal atoms required by a cluster for it to display characteristic bulk properties. Here one is inquiring into the dependence of the electronic, molecular, and chemical properties of a collection of metal atoms as a function of cluster size and geometry. The development of reliable techniques for handling this type of problem is crucial as the outcome impinges directly on our way of thinking about electronic factors in catalysis,[2,3] structure sensitivity of catalytic reactions,[2,4] localized bonding models of the chemisorbed state,[2,5] and alloy and bimetallic catalysis,[2,6] to name but a few.

Some of the essential experimental groundwork in the field of few-atom clusters is now being laid mainly as a result of recent breakthroughs in metal atom matrix techniques.[7] The isolation and measurement of the electronic spectra of the molecules Sc_2,[8] Ti_2,[9] Cr_2,[10a] Cr_3,[10b] Mn_2,[11] Fe_2,[11a] $Fe_{3,4}$,[11b] $Co_{2,3}$,[12] Ni_2,[11a,13] Ni_3,[13b] Cu_2,[14a] Nb_2,[15] Mo_2,[15] Mo_3,[10b] Rh_2,[16] Pd_2,[17] Ag_2,[14b] $Ag_{2,3,4,5,6,7}$[14c] attests to the success of the method. With the emergence of such complete sets of experimental data, the theoretician can begin to answer fundamental questions relating to metal–metal bond orders and the extent of d vs. s vs. p orbital contributions to the bonding in transition-metal diatomic molecules.

Historically, the deliberate cryochemical synthesis and spectroscopic characterization of small, naked metal clusters began only a few years ago.[10a] During some experiments with Cr atoms it was discovered that quantitative UV-visible monitoring of the surface diffusion processes of metal atoms in low-temperature matrices provided a means of identifying the various clusters that form in the embryonic stages of metal aggregation. Using this method, Cr_2[10a] and subsequently Mo_2[15] were generated and their electronic absorptions identified. Independent confirmation of these assignments came recently from observations of gaseous Cr_2 and Mo_2 generated by flash photolysis of $Cr(CO)_6$ and $Mo(CO)_6$.[18] Although the mechanism of formation of the gaseous diatomics is not obvious, the close agreement between the flash photolysis[18] and matrix data[10a,15] is particularly gratifying.

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