

References and Notes

- (1) Part 6: A. Efraty, D. Liebman, M. H. A. Huang, and C. A. Weston, submitted to *Inorg. Chim. Acta*.
- (2) M. I. Bruce, *Adv. Organomet. Chem.*, **6**, 273 (1967); M. Cais and M. S. Lupin, *ibid.*, **8**, 211 (1970).
- (3) G. A. Junk and H. J. Svec, "Recent Topics in Mass Spectrometry", R. I. Reed, Ed., Gordon and Breach, New York, N.Y., 1971, pp 85-126, and pertinent references therein.
- (4) A. Efraty, M. H. A. Huang, and C. A. Weston, *Inorg. Chem.*, **16**, 79 (1977).
- (5) A. Efraty, R. Arneri, and M. H. A. Huang, *J. Am. Chem. Soc.*, **98**, 639 (1976).
- (6) J. W. Dunker, J. S. Finer, J. Clardy, and R. J. Angelici, *J. Organomet. Chem.*, **114**, C49 (1976).
- (7) (a) M. H. Quick and R. J. Angelici, to be submitted for publication; (b) T. A. Wnuk and R. J. Angelici, *Inorg. Chem.*, **16**, 1173 (1977).
- (8) R. E. Honig, *J. Chem. Phys.*, **16**, 105 (1948).
- (9) F. P. Lossing, A. W. Tickner, and W. A. Bryce, *J. Chem. Phys.*, **19**, 1254 (1951).
- (10) J. Roboz, "Introduction to Mass Spectrometry, Instrumentation and Techniques", Interscience, New York, N.Y., 1968, Appendix II, p 515.
- (11) A. Efraty, M. H. A. Huang, and C. A. Weston, *Inorg. Chem.*, **14**, 2796 (1975).
- (12) L. Friedman, A. P. Irsa, and G. Wilkinson, *J. Am. Chem. Soc.*, **77**, 3689 (1955); J. Müller and L. D'Or, *J. Organomet. Chem.*, **10**, 313 (1967).

Contribution from the Lash Miller Chemical Laboratories and Erindale College, University of Toronto, Toronto, Ontario, Canada

Nickel Atom-Olefin Chemistry. Investigation of the Optical Spectra of Binary Nickel-Olefin Complexes

GEOFFREY A. OZIN* and WILLIAM J. POWER

Received February 9, 1978

Cocondensation of nickel atoms with simple alkyl, fluoro, or chloro olefins, in the temperature range 10–77 K, has resulted in a large series of binary π complexes of the type $\text{Ni}(\text{ol})_n$ (where $n = 1-3$). A characteristic feature of these complexes is an intense absorption in the ultraviolet. This transition is only slightly sensitive to the substituent(s) on the coordinated olefin but highly sensitive to the number of coordinated olefins. Observed trends in the optical spectra are interpreted in terms of electronic transitions mainly localized on the nickel atom, and a correlation is observed between the transition energies of the mono(olefin)nickel complexes and the π^* orbital energy of the free olefin. Similar results have been obtained with a variety of palladium-olefin cocondensations. The complexes show a fair degree of thermal stability in the matrices studied. This, coupled with the absence of any evidence of oxidative addition, implies the metal-atom technique may be a general tool for the synthesis of such transition-metal π complexes.

Introduction

The study of transition-metal olefin complexes, with an eye toward understanding the effect on the metal-olefin bond of substituents on the olefin, has utilized a wide variety of techniques. These include measuring IR frequencies (and force constants),^{1,2} NMR chemical shifts and coupling constants,³ thermodynamic stability constants from olefin-displacement/competition reactions,⁴⁻⁶ and crystallographic bond lengths and angle data for coordinated olefins,⁷ among others.

Ittel² recently examined the effect of olefin substituents by measuring the changes in $\nu(\text{C}\equiv\text{N})$ stretching frequencies in compounds of the type $\text{Ni}(t\text{-BuNC})_2(\text{ol})$. He determined that substituent effects were cumulative and that the electron-withdrawal properties of the olefins were relatively inductive in nature, while the overall bond strengths were more closely related to resonance effects. Tolman³ showed that the upfield chemical shifts of ¹³C NMR resonances of coordinated olefins were an indication of the degree of π -electron density back-bonded from the metal to the olefin, with more highly activated olefins or electron-rich metals causing greater upfield shifts. Tolman⁴ has also investigated the reactions of olefins with $\text{Ni}[\text{P}(\text{O}-o\text{-tol})_3]_3$ to form $\text{Ni}[\text{P}(\text{O}-o\text{-tol})_3]_2(\text{ol})$ complexes, determining the equilibrium constants spectrophotometrically. It was found that electron-withdrawing substituents on acyclic olefins gave more stable olefin complexes, with resonance effects more important than inductive effects. In a similar study,^{5,6} nickel-olefin complexes of the types $\text{Ni}(\text{bpy})(\text{ol})$ and $\text{R}_2\text{Ni}(\text{bpy})(\text{ol})$ were investigated and from their stability constants, it was determined that the π -acceptor capacity rather than σ -donor ability of the olefin was the more important factor in the formation of stable nickel-olefin bonds.

While all of these studies have provided interesting insights into the metal-olefin bond, it must be recognized that in all cases discussed to date, other ligands besides the olefin under consideration were by necessity bonded to the central metal atom. Hence extraneous ligand electronic and geometric effects on the metal-olefin bond under study were sometimes

difficult to evaluate. Up until now, there has been a distinct absence of data⁸ of a systematic nature concerning simple binary metal-olefin complexes, consideration of which would obviate concern about these effects. In fact, in the case of nickel there is still a great deal of work to be done with binary mono(olefin) complexes, as very few have actually been synthesized.⁹ For this reason and in view of our previous success with the cryochemical synthesis of such complexes as $\text{Ni}(\text{ol})_{1,2,3}$ where ol is C_2H_4 ¹⁰ and C_2F_4 ,¹¹ we have set out to synthesize a wide variety of new nickel-olefin complexes.

A characteristic spectral feature of the binary nickel-olefin complexes turned out to be an intense absorption in the ultraviolet, one band being associated with each compound. This transition, particularly in the case of the mono(olefin) complexes, shows a *small but distinct sensitivity* to the substituents on the coordinated olefin. By reference to molecular orbital calculations of the extended-Hückel¹² and SCF- $X\alpha$ -SW¹³ types, as well as to optical data for discrete metal-olefin complexes,⁸ these intense UV absorptions have been previously assigned as metal-to-ligand charge-transfer (MLCT) transitions between closely spaced levels of the nickel(0) d-orbital manifold and empty orbitals centered mainly on the olefins involving contributions from the olefin π^* antibonding and symmetry-related $\text{Ni}(d_\pi)$ levels. The current study suggests that this is not an exact description.

Thus, by concentrating on a wide variety of binary nickel-olefin complexes, albeit on a matrix scale, we are able to overcome the difficulties associated with unwanted ligand effects, either electronic or steric, on the properties under study, and by concentrating on their UV spectra we can in principle gain a unique insight into the electronic and bonding properties of the metal-olefin bond.

Experimental Section

Monoatomic Ni and Pd vapors were generated by directly heating a 0.015-in. ribbon filament of the metal with ac in a furnace similar to that described previously.¹⁴ The nickel (99.99%) and palladium (99.99%) were supplied by McKay, N.Y., Gaseous olefins were

Table I. Optical Spectroscopic Data for Ni(ol)_n (Where n = 1, 2, 3)

	olefin	n	λ_{\max} , cm ⁻¹	T _{decomp} , ^b K	-E π^* , eV
A	C ₂ H ₄ (ethylene)	1	31 350	35	2.91
		2	35 714	28	
		3	42 373	80	
B	C ₃ H ₆ (propene)	1	30 864	40	2.58
		2	34 843	35	
		3	41 152	67	
C	C ₄ H ₆ (but-1-ene)	1	30 675	49	2.48
		2	34 722	39	
		3	40 160	77	
D	C ₄ H ₈ (isobutene)	1	30 488	48	2.51
		2	35 088	36	
		3	39 370	80	
E	C ₄ H ₈ (cis-but-2-ene)	1	30 303	105	2.01
		2	34 483	36 ^a	
		3	41 152	105	
F	C ₄ H ₈ (trans-but-2-ene)	1	30 675	51	2.16
		2	34 722	25 ^a	
		3	39 682	80	
G	C ₆ H ₁₂ (hex-1-ene)	1	30 650	38	2.29
		2	34 602	28	
		3	39 682	38	
H	CH ₂ CHCl (vinyl chloride)	1	31 153	65	3.43
		2	35 714	25	
		3	41 841	225	
I	CH ₂ CHF (vinyl fluoride)	1	31 056	37	3.08
		2	35 336	31	
		3	41 666	65	
J	CClFCF ₂ (chlorotrifluoroethylene)	1	31 056	25	2.44
		2	34 602	60	
		3	40 000	60	
K	CH ₂ CHCH ₂ Cl (allyl chloride)	1	30 864	100	
		2	35 461	100	
		3	43 290	100	
L	C ₂ F ₄ (perfluoroethylene)	1	30 675	35	1.68
		2	35 714	37	
		3	41 322	37	

^a Estimated value due to band overlap difficulties in these spectra. ^b See text.

supplied as research grade (99.5% or better) by Matheson of Canada. Liquid olefins were supplied as research grade (99.5% or better) or Gold Label grade (99.9%) by Aldrich, St. Louis, Mo. The research grade olefins were distilled prior to use and all liquid olefins were degassed using a standard multicycle freeze-pump-thaw technique. The rate of Ni and Pd atom deposition was continuously monitored using a quartz crystal microbalance.¹⁵

UV-visible spectra were recorded on a standard Varian Techtron in the range 190–900 nm, the sample being deposited onto a NaCl optical window cooled to deposition temperature by means of an Air Products Displex closed-cycle helium refrigerator.

Results and Discussion

In this paper we wish to demonstrate that nickel atom-olefin cocondensation reactions in the temperature range 12–77 K can be arranged to yield mono-, bis-, and tris(olefin)nickel complexes in relative amounts which are a function of (1) deposition temperature, (2) olefin-matrix distribution, (3) the olefin, and (4) the annealing history of the matrix. The nickel flux in all experiments described herein is such that the Ni/matrix ratio ($\approx 1/10^4$) is sufficiently low to preclude the formation of all but mononuclear nickel species.¹⁶ While our normal experimental procedures involve utilizing both IR and UV-visible spectroscopies to characterize complexes formed under cryogenic conditions, in this study we have relied more extensively on the latter.

As previously mentioned, we have thoroughly characterized the Ni/C₂H₄¹⁰ and Ni/C₂F₄¹¹ systems using both spectroscopies. Having fully convinced ourselves that we were in-

vestigating normal π -type complexes, by observing IR absorptions attributable to the $\nu(\text{C}=\text{C})$ stretching mode of the coordinated olefin in the appropriate spectral region (1550–1400 cm⁻¹), we made the observation that there was one intense UV absorption associated with each complex in each system. Subsequently, upon cocondensing Ni with the other olefins in this study, it was evident that this was a characteristic property of these complexes. Under no circumstances was more than one band associated with any complex; at no time were any bands observed in the visible which might be attributed to Ni(II) species, the result of an oxidative addition of the olefin to the nickel atom (for such reactions with Pd atoms, see ref 17). Thus we are confident that for all systems reported here we have simple π -olefin complexes of Ni(0). We have checked the IR spectra of some of these complexes, both with Ni and Cu¹⁸ and in all cases have seen $\nu(\text{C}=\text{C})$ stretching modes attributable to π -coordinated olefins.

(A) **Ethylene Complexes.** As reported previously, mono-, bis-, and tris(ethylene)nickel have been synthesized via the metal-atom route.¹⁰ We reported that for these complexes the MLCT transitions were found at 280, 250, and 236 nm, respectively. While these assignments seemed reasonable at the time, during the course of the present study it became evident that, when considering the range of olefins studied, the mono and bis complexes seemed somewhat out of line. As seen in Table I, all other mono(olefin)nickel absorptions are in the range 320–335 nm, while those of the bis(olefin)

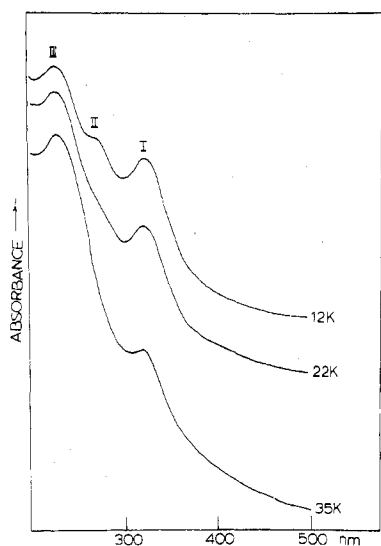


Figure 1. Matrix UV-visible spectra observed on depositing Ni atoms with $C_2H_4/Ar \approx 1/50$ at 15 K with annealing at 22 and 35 K.

complexes are found around 270–280 nm. We could think of no obvious reason that the ethylene complexes should be anomalous. For this reason we made a thorough reinvestigation of the nickel–ethylene UV spectra, and it is hereby shown that at dilutions of $C_2H_4/Ar \approx 1/50$, three absorptions are seen at 320, 270, and 235 nm. The spectra are shown in Figure 1. From the warm-up behavior, as well as ligand-dilution experiments, we feel secure in now reassigning these bands to mono-, bis-, and tris(ethylene) complexes, respectively, compatible with the other olefin complexes. It is evident that in the previous report,¹⁰ the lowest energy band (320 nm) was hidden by the presence of unreacted nickel atoms (also absorbing around 320–330 nm). That the band at 250 nm, assigned previously to bis(ethylene)nickel, is more appropriately assigned to a dinuclear nickel–olefin species, $Ni_2(C_2H_4)$, has been shown in a separate study.¹⁹ It is evident from the presence of some Ni_2 absorptions in the spectra previously published¹⁰ that this is a reasonable assignment. The infrared spectra and assignments for $Ni(C_2H_4)_{1,2,3}$ are listed in Table II for comparison purposes.

(B) Vinyl Chloride Complexes. The vinyl chloride–nickel system proved interesting in view of the thermal stability of the complexes formed on deposition. A discussion of the experimental identification of the optical transitions of the complexes formed is a good general illustration of the methodology used in this study.

Upon cocondensation of nickel atoms with vinyl chloride/ $Ar \approx 1/100$ mixtures at 15 K, three UV bands are observed at 323, ~280, and 239 nm, with the first being the most intense. Upon annealing the matrix to 30 and 37 K, it is evident that each of these bands is associated with a single species. At 30 K, the low-energy band has lost intensity, the 280-nm band has essentially disappeared, and the 239-nm band has increased in intensity. At 37 K, the 323-nm band is just a shoulder on the high-energy absorption. These effects are shown in Figure 2. Upon increasing the ligand concentration in the range 1/20 to 1/50, at 15 K the band at 323 nm becomes less pronounced while the band at 239 nm becomes the dominant feature (a typical trace is shown in Figure 3). On the basis of the dilution and annealing studies, we can assign the bands at 323, 280, and 239 nm to the species $(CH_2CHCl)Ni$, $(CH_2CHCl)_2Ni$, and $(CH_2CHCl)_3Ni$, respectively. The corresponding series of infrared experiments were performed and nicely confirmed the existence of three independent π -vinyl chloride complexes with their anticipated $\nu(C=C)$ and $\delta(CH_2)$ modes in the regions 1470–1440 and 1250–1175 cm^{-1} , respectively.

Table II. Infrared Spectroscopic Data (cm^{-1}) for Selected $Ni(\pi-ol)_n$ Complexes (Where $n = 1, 2, 3$)

$Ni(C_2H_4)_n^{a,b}$	$Ni(C_2F_4)_n^{a,b}$	$Ni(C_2H_3Cl)_n^{a,b}$
2960 I		2978 I, II, III
2945 II } $\nu(CH_2)$		2886 I, II, III } $\nu(CH_2)^c$
2930 III		2876 I, II, III
2886 II		
1512 III	1496 III	1470 III
1496 I } $\nu(C=C)^d$	1476 II	1464 I } $\nu(C=C)^d$
1465 II	1460 II } $\nu(C=C)$	1438 II } $\nu(C=C)^d$
	1450 III	
	1418 I	
1245 III		1249 I, II ^c
1235 II } $\delta(CH_2)^d$		1214 III } $\delta(CH_2)^d$
1224 II		1175 I, II ^c
1158 I		
	1073 III	
	1068 III	
	1056 II } $\nu(CF)$	
	1046 I	
911 III		864 I
906 II } $\rho(CH_2)$		846 III } $\rho(CH_2)$
900 I		840 II
	806 III	
	798 III	
	784 II	
	774 II } $\nu(CF)$	
	750 I	
	724 I	
376 I $\nu(NiC)$	370 I	482 III
	388 II } $\delta(CF_2)$	444 I
	314 III } $\nu(NiC)$	370 I, II, III ^c
		350 I, II, III ^c } $\nu(CCl)$
		330 I, II, III ^c } or $\nu(NiC)$
		300 I, II, III ^c

^a I = $Ni(ol)$; II = $Ni(ol)_2$; III = $Ni(ol)_3$. ^b Species assignments based on pure olefin and olefin/ $Ar = 1/10, 1/50, 1/100$ concentration experiments at $Ni/Ar \approx 1/10^4$. ^c Band overlap complications precluded a definitive assignment of these bands to I, II or III. ^d These modes are expected to be highly coupled.

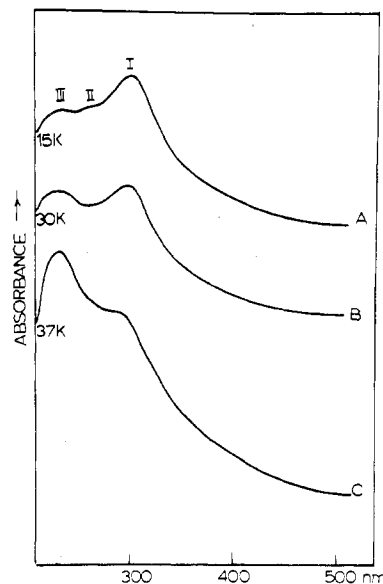


Figure 2. Same as Figure 1 except using $C_2H_3Cl/Ar \approx 1/100$ with annealing at 30 and 37 K.

The species identification and mode assignments are presented in Table II for comparison purposes.

Deposition into matrices of pure C_2H_3Cl at various temperatures gives an interesting indication of the stabilities of the complexes formed. On deposition at 10, 30, or 60 K, the major feature is an intense band associated with $(CH_2CHCl)_3Ni$. Also present under all of these deposition conditions

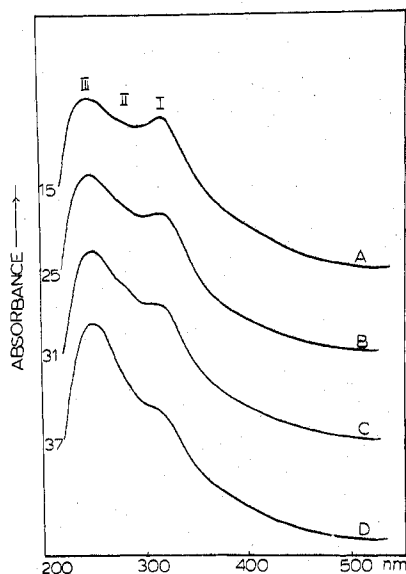


Figure 3. Same as Figure 1 except using $C_2H_3Cl/Ar \approx 1/50$ with annealing at 25, 31, and 37 K.

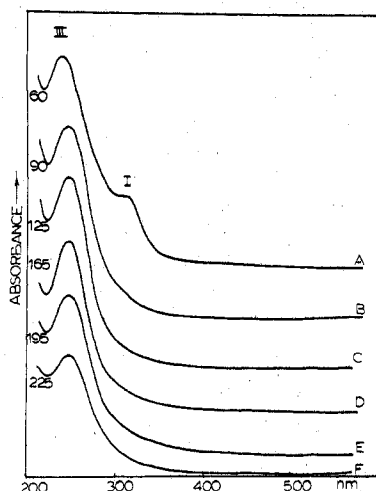


Figure 4. Matrix UV-visible spectra observed on depositing Ni atoms with pure C_2H_3Cl at 60 K with subsequent annealing at 90, 125, 165, 195, and 225 K.

is a trace of $(CH_2CHCl)Ni$ as seen by the shoulder at ~ 320 nm. Subsequent warm-up behavior shows that the mono(olefin) complex probably reacts with free vinyl chloride to form the tris(olefin) complex slightly above 60 K. Figure 4, showing a deposition into pure vinyl chloride at 60 K, illustrates the exceptional thermal stability of $(CH_2CHCl)_3Ni$; it is still present in the matrix up to 225 K, above which temperature the optical transmission properties of the matrix deteriorate rather dramatically. The corresponding infrared experiments supported these observations.

This exceptional thermal stability suggests that the synthesis of (vinyl chloride)nickel complexes on a macroscale would be quite feasible. It should also be noted at this point that at no time was there any evidence for Ni atom insertion into the C-Cl bond of the olefin to form a vinylnickel chloride complex, $(CH_2=CH)NiCl$. The spectra were, in fact, not different in any particular respect from those of any of the other olefins, either alkyl substituted or heteroatom substituted. As mentioned earlier, this was interpreted as evidence in favor of normal π -olefin complex formation.

(C) **Allyl Chloride Complexes.** Three allyl chloride (AC) complexes of nickel were formed in our cocondensation reactions at cryogenic temperatures, paralleling the behavior

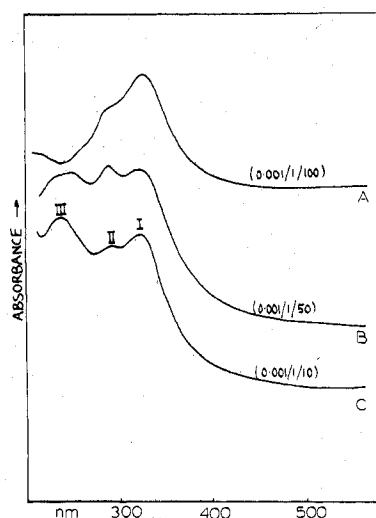


Figure 5. Typical propylene-argon concentration study under 1/10, 1/50, and 1/100 conditions deposited at 15 K, with $Ni/Ar \approx 1/10^4$.

discussed above for vinyl chloride. Characterization was achieved by the same methods as well. The best indication of the presence of three π -allyl chloride-nickel compounds was the deposition of nickel atoms into a matrix of $AC/Ar = 1/20$ at 15 K. Upon deposition, three bands are seen, at 322, 282, and 232 nm. On warming the matrix to ~ 38 K, the high-energy band increases in intensity, eventually being the only feature present; the other two bands decrease in intensity though at different rates, implying they belong to two different species. Ligand-dilution experiments support the assignment: 322 nm, $(AC)Ni$; 282 nm, $(AC)_2Ni$; 232 nm, $(AC)_3Ni$.

This result was somewhat unexpected in view of previous experiences with metal atom-allyl chloride cocondensations at 77 K. For instance, Piper and Timms²⁰ reported that $(\pi$ -allyl)nickel halides were efficiently produced (ca. 60% yield) on reacting nickel atoms with allyl chloride or bromide. The mechanism of this reaction presumably involves initial oxidative addition of the allyl halide to nickel, with subsequent rearrangement of the σ -allyl to a π -allyl system and dimerization via halogen bridges. Interestingly, platinum atoms²¹ also react with allyl chloride but form $[Pt(C_3H_5)Cl]_4$, involving both σ and π coordination of the C_3H_5 moiety. Such reactions forced us to view our results in a different light.

It seems evident that our lower temperature reactions have resulted in isolation of the *first stage of the reaction*, that is, π -complex formation. Presumably our failure to observe Timms' product on warm-up is simply the result of a lack of thermal energy in the system to permit a ready conversion to the allylnickel chloride. To satisfy our curiosity on this point, we reacted nickel with allyl chloride at 77 K. Under these conditions also, we failed to observe any feature other than those already attributed to the π -AC complexes. Nor did warm-ups to 120 K cause oxidative addition of the ligand. It is evident that a *higher temperature workup* or Ni_n clusters are responsible for the conversion to the bridged dimer species.

(D) **Other Olefin Complexes.** The spectral features of the complexes formed with all of the olefins investigated in this study are listed in Table I. For all olefins under consideration, we have observed *three* complexes, each associated with a characteristic ultraviolet transition. A typical olefin concentration study for propylene is depicted in Figure 5 and a representative warm-up study for but-1-ene is illustrated in Figure 6. Of the systems studied, none presented any particularly startling properties; hence we will not discuss any one olefin in detail, having already illustrated the general method of characterization for ethylene and the above-mentioned chloro olefins.

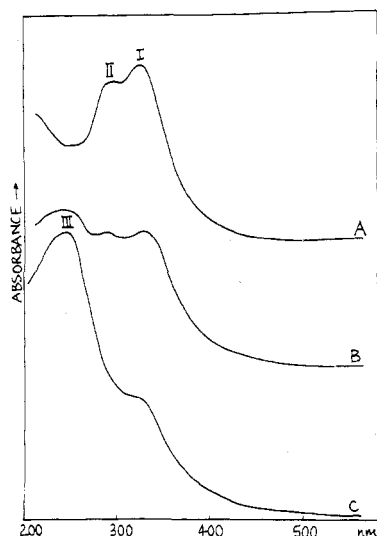


Figure 6. Same as Figure 1 except using but-1-ene/argon \approx 1/50 mixtures.

There are a number of points of interest in these binary nickel-olefin complexes, not the least of which is the thermal stability of some of them, notably the tris(olefin) complexes. In Table I we have listed the highest temperature at which each of the complexes was observed (from the disappearance of the characteristic absorption band). It should be noted that these temperatures simply represent a *lower limit* to their stability for a number of reasons. For instance, different matrices have different optical properties which affect the upper range of warm-up studies. A pure olefin matrix will usually turn opaque on warm-up, but the temperature at which this occurs varies among the different olefins. When this happens, the UV part of the spectrum usually becomes totally obscured. In addition, the matrices sublime from the optical window at different temperatures, and it is possible that some or all of the complexes (most probably the highest stoichiometry species) sublime away with the olefin. However, UV-signal annihilation (T K) does not necessarily imply that the species is unstable in the gas phase at temperature T K. This is apparent with $(C_2H_4)_3Ni$, which is known to be stable to 273 K²² but which shows no optical spectrum above 80 K,¹⁰ at which temperature ethylene sublimates from the optical window. This is unfortunate, because we cannot make any definitive statements regarding the stability of binary nickel-olefin complexes as a function of substituent. However, the data do imply that a macroscale synthesis is feasible in many cases.

Another point of interest in these systems is that it seems to be a general property of nickel-olefin reactions at cryogenic temperatures to form complexes which have a *maximum coordination of three* olefins per nickel atom. Recent theoretical calculations²³ show that even with the simplest mono(olefin), ethylene, there is no geometry which can escape steric crowding when four ethylenes surround a nickel atom. In fact, there are no known complexes in which four *simple* olefin ligands are coordinated to nickel. The only cases known where four double bonds are complexed to nickel involve such ligands as cyclooctadiene or tetraene and duroquinone or norbornadiene, in which the ligands' two double bonds are held parallel and the destabilizing steric interactions between the two olefin subunits in this arrangement are absorbed in the ligand geometry. It is evident that a steric effect is operative in our systems, preventing the coordination of a fourth olefin. However, this effect is not sufficiently dominant to preclude tris(olefin) complex formation even with bulky substituents on the olefin, as seen, for example, by the metal-vapor synthesis

of tris(styrene)nickel by Blackborow and co-workers.²⁴

It is, however, the interpretation of the optical spectral data for these systems and the rationalization of the observed trends with respect to both substituent effect and stoichiometry that are the most intriguing aspects of this study. Before we proceed with a detailed analysis, we must again refer to our reinvestigation of the nickel-ethylene system and, in the light of the new data, modify our explanation of the optical spectra of the analogous Ni/C_2F_4 complexes. From Table I it is evident that the shifts from $Ni(C_2H_4)_n$ to $Ni(C_2F_4)_n$ are not nearly as large as originally believed¹¹ and, in view of the data for the other olefins, we may have been premature in rationalizing the trends *entirely* in terms of MLCT, with the energy of the olefin π^* orbitals being chiefly responsible for the observed shifts. As will be shown, it is entirely possible that the transitions are in actuality mainly localized on the Ni atom, that is, $Ni(3d) \rightarrow (4p)$, which would not be expected to be quite as sensitive to olefin substitution as would be a $Ni(3d) \rightarrow \text{olefin}(\pi^*)$ MLCT transition.

In this context, GVB-CI molecular orbital calculations¹⁹ have recently been carried out in an attempt to understand the electronic, geometric, and bonding properties of $Ni(C_2H_4)$ and $Ni_2(C_2H_4)$ fragments. Whereas earlier SCF- $X\alpha$ -SW calculations¹³ indicated major σ/π contributions to the nickel-olefin bond (in line with Dewar-Chart bonding ideas²⁵), the GVB-CI calculations¹⁹ revealed a *major* olefin-to-nickel σ contribution but with only a *minor* nickel-to-olefin π -back-bonding effect. In view of the highly contracted, tightly bound nature of the $Ni(3d)$ valence orbital set relative to the olefin π^* orbitals, the GVB-CI description of the nickel-olefin bond seems entirely reasonable. From a GVB-CI transition-state analysis¹⁹ of the various allowed transitions for such species (noting that the UV band for both $Ni(C_2H_4)$ and $Ni_2(C_2H_4)$ is quite intense), it was suggested that the observed UV bands were most likely $Ni(3d) \rightarrow \text{olefin}(\pi^*)$ or $Ni(3d) \rightarrow Ni(4p_y)$, though the point was raised that a transition classified as $Ni(3d) \rightarrow Ni(4p_y)$ will possess some degree of orbital mixing of $Ni(4p_y)$ with $\text{olefin}(\pi^*)$. Convincing support for this proposal stems from the correlation of the observed UV transitions of $Ni(ol)$ with the π^* orbital energies of the corresponding olefin (Table I). In essence one has to rationalize the *small* change in the UV transition energies for $Ni(ol)_n$ as the olefin substituent is varied. We will restrict our discussion of this point to the mono(olefin)nickel complexes since the UV bands were best resolved for these species, but we presume that similar arguments would apply to each series of $Ni(ol)_{2,3}$ complexes. For these mono(olefin) complexes, the UV bands range from 31 250 cm^{-1} for C_2H_4 to 30 488 cm^{-1} for $i-C_4H_8$, which is a fairly narrow spread²⁶ when compared to the other physical properties measured as a function of olefin substituent.²⁻⁶ The results imply some dependence of the transition energy on substituent, but certainly *not* an overwhelming one. There are some general trends evident, however. For alkyl substituents, there is a tendency to lower energy with increasing chain length in n -alkenes, though the effect is most pronounced on passing from ethylene to propylene. In addition, disubstituted olefin complexes absorb at lower energy than monosubstituted or nonsubstituted ones. For fluoro or chloro olefins, the same tendency holds, though it is less pronounced. In Figure 7 we have plotted the band energies of the mono(olefin)nickel complexes as a function of π^* -orbital energy²⁷ for the gaseous olefin. The data are tabulated in Table I. Two reasonably linear correlations are observed, one for the alkyl substituents and one for the fluoro and chloro substituents. It is interesting to note that the mono(tetrafluoroethylene) complex does not seem to be badly out of line in view of the proposed metallocyclopropane nature of this species.¹¹ This behavior (anomalous in some cases) has

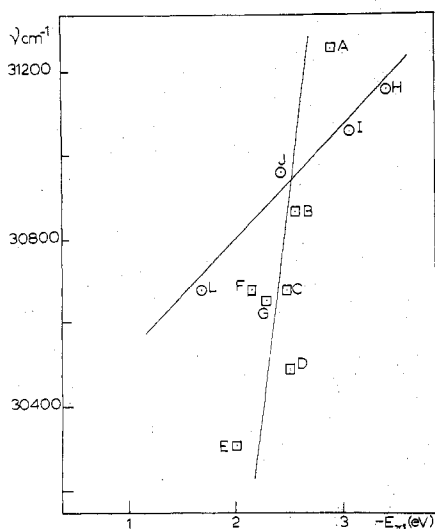


Figure 7. Graphical representation of the correlation between $\bar{\nu}$ (cm^{-1}) for $\text{Ni}(\text{ol})$ and the energy (E_{π^*}) of the π^* orbital of the free olefin. The olefins are lettered as in Table I. Squares are hydrocarbon olefins, while circles represent fluoro or chloro olefins.

been seen before with fluoro olefins, most notably for the increased stability²⁸ of tetrafluoroethylene complexes relative to those of ethylene (matrix studies of binary $\text{Ni}(\text{C}_2\text{H}_4)_n/\text{Ni}(\text{C}_2\text{F}_4)_n$ being the exception rather than the rule). It is possible that the origin of the two separate correlations in Figure 7 is similar to that found in Tolman's study⁴ of $(\text{ol})(\text{P})_2\text{Ni}$ complexes. That is, substituent effects for alkyl groups are merely the result of inductive interaction, while those for fluoro (and chloro) substituents have their origin in resonance interactions.²⁹

This *small* but obvious correlation between the UV transition energy and the olefin π^* energy can be interpreted as evidence in favor of a nickel-localized $\text{Ni}(3d) \rightarrow \text{Ni}(4p)$ assignment rather than a $\text{Ni}(3d) \rightarrow \text{olefin}(\pi^*)$ MLCT assignment, although, as mentioned earlier, the $4p$ orbital would mix somewhat with the π^* orbital. If the transition were entirely $\text{Ni}(3d) \rightarrow \text{olefin}(\pi^*)$ MLCT, then a much wider range in UV transition energies would be expected based on the spread in olefin π^* energies.

These ideas can now be extended to rationalize the *monotonic blue* shift of the UV transitions of $\text{Ni}(\text{ol})_n$ with increasing olefin stoichiometry ($n = 1-3$). If, as would seem to be the case, the UV transition is best described as a mainly localized $\text{Ni}(3d) \rightarrow \text{Ni}(4p)$ one, then the trend can be explained in terms of the following line of reasoning. Let us first consider a nickel-olefin bonding scheme which is mainly σ in character (GVB-CI description¹⁹). Under these circumstances, charge accumulation on the central nickel atom with increasing olefin stoichiometry would be anticipated, the outcome being destabilizing and level compressing with respect to the $\text{Ni}(3d)/\text{Ni}(4p)$ orbitals in question. This effect *alone* would be expected to produce UV shifts in an opposite sense (*red*) to those observed in practice. On the other hand, the $\text{Ni}(4p)$ levels in the complexes $\text{Ni}(\text{ol})_n$ (which are at roughly -6.3 eV in the free Ni atom) should smoothly converge on the olefin π^* levels (all in the range -1.68 to -3.43 eV, Table I) with increasing olefin stoichiometry and the degree of $\text{Ni}(4p)$ -olefin(π^*) mixing should correspondingly grow in importance. The $\text{Ni}(3d) \rightarrow \text{Ni}(4p)$ localized transition in, say, $\text{Ni}(\text{ol})$ would therefore be expected to gain some $\text{Ni}(3d) \rightarrow \text{olefin}(\pi^*)$ MLCT character and the $\text{Ni}(\text{ol})_{2,3}$ complexes would display *blue-shifting* UV transitions with increasing olefin stoichiometry. (GVB-CI calculations could clarify this interesting proposal.) In a sense, this is tantamount to saying that, although small, the extent of π back-donation of charge from

Table III. Optical Spectroscopic Data for $\text{Pd}(\text{ol})_n$ (where $n = 1, 2, 3$)

	olefin	n	λ_{max} , nm
A	C_2H_4	1	240
		2	221
		3	204
B	C_3H_6	1	240
		2	221
		3	204
C	$\text{C}_2\text{H}_3\text{Cl}$	1	239
		2	221
		3	204
D	$\text{CH}_2\text{CHCH}_2\text{Cl}$	1	238
		2	221
		3	203

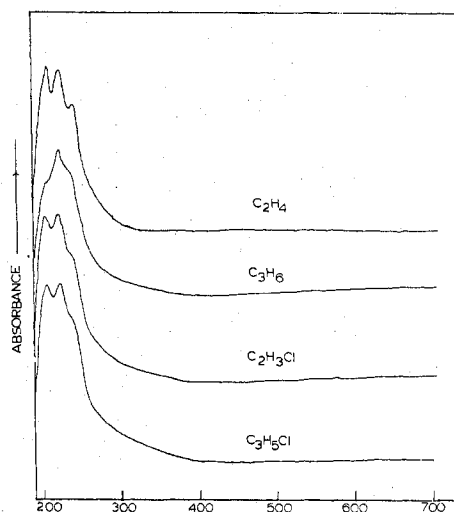


Figure 8. Matrix UV-visible spectra on depositing Pd atoms with olefin/ $\text{Ar} \approx 1/50$ mixtures at 15 K, where olefin = ethylene, propene, vinyl chloride, and allyl chloride.

the nickel to the olefin ligands increases with olefin stoichiometry, presumably to offset the increasing σ forward-donation. This could lead to an effective charge (Z^*) on the central nickel atom such that $Z_3^* > Z_2^* > Z_1^*$ which would be expected to lead to stabilization of the $\text{Ni}(3d)$ and $\text{Ni}(4p)$ orbitals with increasing olefin stoichiometry but with the $3d$ orbital *more so* than the $4p$ orbital. Hence a $\text{Ni}(3d) \rightarrow \text{Ni}(4p)$ localized transition would tend to *blue-shift* with increasing olefin stoichiometry, as observed in practice. We note, however, that our earlier rationalization of the UV spectral trends in terms of $\text{Ni}(3d) \rightarrow \text{olefin}(\pi^*)$ MLCT transitions¹⁰⁻¹² still holds true for a scheme in which $\text{Ni}(4p)$ -olefin(π^*) orbital mixing makes a substantial contribution to the nickel-olefin bond.

Our results so far with the palladium-olefin system, for ethylene, propylene, vinyl chloride, and allyl chloride (illustrated in Figure 8 and listed in Table III), in which $\text{Pd}(\pi\text{-ol})_{1,2,3}$ complexes are also generated, display a *similar small substituent effect* in the corresponding UV transitions, supporting the idea of a mainly localized palladium $d \rightarrow p$ electronic excitation.

Conclusion

In this study we have demonstrated that nickel atom-olefin cocondensations at 10-77 K result in the formation of a series of $\text{Ni}(\text{ol})_{1,2,3}$ complexes whose most striking spectroscopic characteristic is an intense band in the ultraviolet. The relative insensitivity of the energy of this band to olefin substituents is interpreted as being more consistent with a localized $\text{Ni}(3d) \rightarrow \text{Ni}(4p)$ assignment (in agreement with GVB-CI calculations

on Ni(C₂H₄)¹⁹ rather than a Ni(3d_π) → olefin(π*) MLCT assignment.

Acknowledgment. We gratefully acknowledge the financial assistance of the National Research Council of Canada's Operating, New Ideas and Strategic Energy Programmes, the Atkinson Foundation, the Connaught Fund, Imperial Oil of Canada, Erindale College, and the Lash Miller Chemistry Laboratories for support of this research. W.J.P. also expresses his appreciation for an NRCC postgraduate scholarship.

Registry No. Ni(ethylene), 61160-51-8; Ni(ethylene)₂, 52392-74-2; Ni(ethylene)₃, 50696-82-7; Ni(propene), 67316-83-0; Ni(propene)₂, 67316-84-1; Ni(propene)₃, 67316-85-2; Ni(but-1-ene), 67316-86-3; Ni(but-1-ene)₂, 67316-87-4; Ni(but-1-ene)₃, 67316-88-5; Ni(isobutene), 67316-89-6; Ni(isobutene)₂, 67316-90-9; Ni(isobutene)₃, 67316-91-0; Ni(*cis*-but-2-ene), 67316-92-1; Ni(*cis*-but-2-ene)₂, 67316-93-2; Ni(*cis*-but-2-ene)₃, 67316-94-3; Ni(*trans*-but-2-ene), 67337-41-1; Ni(*trans*-but-2-ene)₂, 67337-42-2; Ni(*trans*-but-2-ene)₃, 67337-43-3; Ni(hex-1-ene), 67316-95-4; Ni(hex-1-ene)₂, 67316-96-5; Ni(hex-1-ene)₃, 67316-97-6; Ni(vinyl chloride), 67316-98-7; Ni(vinyl chloride)₂, 67316-99-8; Ni(vinyl chloride)₃, 67317-00-4; Ni(vinyl fluoride), 67317-01-5; Ni(vinyl fluoride)₂, 67317-02-6; Ni(vinyl fluoride)₃, 67317-03-7; Ni(chlorotrifluoroethylene), 67317-04-8; Ni(chlorotrifluoroethylene)₂, 67317-05-9; Ni(chlorotrifluoroethylene)₃, 67328-93-2; Ni(allyl chloride), 67317-06-0; Ni(allyl chloride)₂, 67317-07-1; Ni(allyl chloride)₃, 67317-08-2; Ni(perfluoroethylene), 63833-65-8; Ni(perfluoroethylene)₂, 63833-64-7; Ni(perfluoroethylene)₃, 63833-63-6.

References and Notes

- (1) M. Bigorgne, *J. Organomet. Chem.*, **127**, 55 (1977).
- (2) S. D. Ittel, *Inorg. Chem.*, **16**, 2589 (1977).
- (3) C. A. Tolman, A. D. English, and L. E. Manzer, *Inorg. Chem.*, **14**, 2353 (1975).
- (4) C. A. Tolman, *J. Am. Chem. Soc.*, **96**, 2780 (1974).
- (5) T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Am. Chem. Soc.*, **93**, 3350 (1971).
- (6) T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Am. Chem. Soc.*, **93**, 3360 (1971).
- (7) S. D. Ittel and J. A. Ibers, *Adv. Organomet. Chem.*, **14**, 33 (1976).
- (8) See, for example, M. Herberhold, "Metal π Complexes", Vol. II, Part II, Elsevier, Amsterdam, 1974, and references therein.
- (9) See, for example, P. W. Jolly and G. Wilke, "The Organic Chemistry of Nickel", Vol. I, Academic Press, New York, N.Y., 1974, and references cited therein.
- (10) G. A. Ozin, H. Huber, and W. J. Power, *J. Am. Chem. Soc.*, **98**, 6508 (1976).
- (11) G. A. Ozin and W. J. Power, *Inorg. Chem.*, **16**, 2864 (1977).
- (12) G. A. Ozin, H. Huber, and W. J. Power, *Inorg. Chem.*, **16**, 979 (1977).
- (13) N. Rösch and T. N. Rhodin, *Discuss. Faraday Soc.*, **58**, 28 (1974).
- (14) E. P. Kündig, M. Moskovits, and G. A. Ozin, *J. Mol. Struct.*, **14**, 137 (1972).
- (15) M. Moskovits and G. A. Ozin, *J. Appl. Spectrosc.*, **26**, 487 (1972).
- (16) M. Moskovits and J. Hulse, *J. Chem. Phys.*, **66**, 3988 (1977).
- (17) See, for example, K. J. Klabunde, *Angew. Chem., Int. Ed. Engl.*, **14**, 287 (1975).
- (18) H. Huber, G. A. Ozin, and W. J. Power, unpublished data.
- (19) T. Upton, W. A. Goddard III, G. A. Ozin, and W. J. Power, *J. Am. Chem. Soc.*, **100**, 4750 (1978).
- (20) M. Piper and P. L. Timms, *J. Chem. Soc., Chem. Commun.*, 52 (1972).
- (21) P. S. Skell and J. J. Havel, *J. Am. Chem. Soc.*, **93**, 6687 (1971).
- (22) K. Fisher, K. Jonas, and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **12**, 565 (1973).
- (23) N. Rösch and R. Hoffmann, *Inorg. Chem.*, **13**, 2656 (1975).
- (24) J. R. Blackborow, C. R. Eady, E. A. K. von Gustorf, and A. Scriverini, *J. Organomet. Chem.*, **108**, C32 (1975).
- (25) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953); M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C71 (1951).
- (26) It should be noted that in Tolman's study,⁴ the charge-transfer bands for the same olefins range from 339 to 354 nm, with the C₂H₄ complex absorbing at 350 nm.
- (27) The energy of the π* orbital for each olefin is calculated as the difference between the IP of the π molecular orbital and the π → π* separation for each olefin.⁴
- (28) R. Cramer, *J. Am. Chem. Soc.*, **89**, 4621 (1967); *J. Chem. Soc., Chem. Commun.*, 450 (1975).
- (29) Note that no obvious correlation exists between our data and a wide variety of linear free energy constants (σ) as described in the paper of Swan and Lupton.³⁰
- (30) C. G. Swan and E. C. Lupton, Jr., *J. Am. Chem. Soc.*, **90**, 4328 (1968).

Contribution from the Department of Inorganic Chemistry,
University of Melbourne, Parkville 3052, Australia

Chemical and Electrochemical Studies of Tricarbonyl Derivatives of Manganese and Rhenium

A. M. BOND,* R. COLTON, and M. E. McDONALD

Received March 23, 1978

The interaction of manganese and rhenium pentacarbonyl halides with monodentate arylphosphines and related ligands has been reinvestigated. Tetracarbonyl and tricarbonyl derivatives were obtained, and in those cases where the tricarbonyl species obtained by direct interaction was facial, thermal, electrochemical, or chemical oxidation-reduction techniques were used to obtain the corresponding meridional isomers. Electrochemical and chemical oxidations of the tricarbonyl complexes clearly demonstrate the existence of metal(II) complexes. Relative to metal(I) they are kinetically very labile, powerful oxidants, light sensitive and unstable with respect to loss of carbon monoxide. Additionally, *fac* M(II) isomerizes to *mer* M(II) at a far greater rate than the corresponding isomerization in oxidation state I.

Introduction

In a recent study¹ it was shown that chemical and electrochemical oxidation of *fac*-Mn(CO)₃dpmX (dpm = Ph₂PCH₂PPh₂; X = Cl, Br) at room temperature gave *mer*-[Mn(CO)₃dpmX]⁺ which could be readily reduced to otherwise inaccessible *mer*-Mn(CO)₃dpmX. With a related series of complexes containing other bidentate ligands² it was demonstrated that in the 17-electron configuration (manganese-(II)) the complexes were kinetically very labile, as well as light sensitive, and that many reactions of interest occurred. However, to date, similar studies on isoelectronic 17-electron rhenium complexes or complexes containing monodentate ligands have not been described, so that the generality of the above observations in group 7 transition-metal carbonyl halides is unknown. This paper reports the extension of electro-

chemical and chemical studies on the isomerization and redox behavior of complexes of the type [M(CO)₃L₂X]⁰⁺ (M = Mn, Re) containing monodentate ligands L, where L is an arylphosphine, -arsine, or -stibine or an aryl phosphite.

Some details of the properties of the 18-electron M(CO)₃L₂X complexes (L as above) are known. Wilkinson and co-workers^{3,4} claimed that interaction of Re(CO)₅X and Mn(CO)₅X with ligands such as triphenylphosphine gave in each case *fac*-M(CO)₃L₂X. However, later investigators^{5,6} have shown that in fact the product is usually *mer*-Mn(CO)₃L₂X in the case of manganese, but rhenium does produce the facial isomers. Thus, the existence of different isomers is already documented. Furthermore, in a relevant series of kinetic studies, Basolo and co-workers⁷⁻⁹ showed that ligand exchange with *fac*-Mn(CO)₃[P(OPh)₃]₂X or substitution of