

cm^{-1} . This has caused some confusion about the meaning of the frequency near 1500 cm^{-1} .

The $\sim 1500\text{-cm}^{-1}$ band is not a pure C–C stretch in any of these compounds; there is significant coupling between the C–C stretch and the symmetric scissoring vibration even in ethylene.³⁸ In the local C_{2v} symmetry of an M–ethylene complex there will be five normal modes of A_1 symmetry ($\nu_1, \nu_2, \nu_3, \nu_4, \nu_5$) which are mixtures of symmetric C–H stretch, C–C stretch, CH_2 scissors, CH_2 wag, and M–C stretch. The column labeled $\nu_{\text{C=C}}$ in Table IV should really be labeled ν_2 . As the extent of metal π back donation increases, ν_2 falls in frequency from 1623 in free C_2H_4 to 1487 cm^{-1} in $\text{C}_2\text{H}_4\text{O}$ and goes from a mixture containing mostly C–C stretch to one with mostly CH_2 scissoring. Its infrared frequency is still useful in assessing the nature of the metal olefin bond. Examination of our Raman spectrum^{7a} of $(\text{C}_2\text{H}_4)\text{Ni}[\text{P}(\text{O}-o\text{-tolyl})_3]_2$ shows a strong line at 1245 cm^{-1} , which may correspond to Hiraishi's 1243-cm^{-1} line in Zeise's salt. The similarity of these frequencies suggests that ν_3 may be insensitive to the nature of the metal–olefin bond and therefore less useful than ν_2 .

Based on the ethylene complexes alone, one might conclude that an olefin epoxide is a fair model for (olefin) NiL_2 complexes. Other data suggest that this "metallocyclopropane" model is misleading in several respects. Table IV shows that the frequency ν_{CN} in olefin-bonded acrylonitrile complexes is lower than in free ACN and decreases as back donation from the metal increases.³⁹ Glycidonitrile, the epoxide model of an acrylonitrile complex, has a C–N stretching frequency higher than that of free ACN. While the

(38) H. W. Thompson and J. W. Linnett, *J. Chem. Soc.*, 1376 (1937).
 (39) Cenini, *et al.*,¹⁹ have also suggested that reduction of ν_{CN} or ν_{CO} of olefins with conjugated cyanide or carbonyl groups provides a measure of metal–olefin π bonding.

mean τ of the complex (8.7) is closer to that of the epoxide (6.8) than to the free olefin (5.05), the values of J_{HH} in $(\text{ACN})\text{Ni}[\text{P}(\text{O}-o\text{-tolyl})_3]_2$ are much more similar to those of free ACN than to those of glycidonitrile. Small changes in J_{HH} on coordination have also been found for iron tetracarbonyl complexes of acrylic acid, methyl acrylate, and acrylamide.⁴⁰ The frequencies of the olefin ν_{CO} bands in these complexes are uniformly lower than in the free olefins ($\Delta\nu = 15\text{--}30\text{ cm}^{-1}$). Frequencies of carbonyl groups adjacent to epoxide rings are higher than in the alkenes or even the saturated alkanes.⁴¹

Another difficulty with the metallocyclopropane model is the ambiguity of oxidation states arising from the convention of regarding σ -bonded alkyl groups as carbanions in assigning formal oxidation states. By this convention, $(\text{C}_2\text{H}_4)\text{Ni}[\text{P}(\text{O}-o\text{-tolyl})_3]_2$ should be regarded as a Ni(II) complex. The ESCA results²¹ show that the electron density on nickel in $(\text{C}_2\text{H}_4)\text{-NiL}_2$ is similar to that in NiL_3 so that the nickel should be regarded as Ni(0) if an oxidation state is to be assigned. The bonds are sufficiently covalent in character that little net transfer of electron density from metal to ethylene occurs. In the Dewar–Chatt–Duncanson description, electron withdrawal into the olefin π^* orbital is partially compensated by electron donation by the olefin π orbital, with the result that ethylene has an electronegativity in the complex comparable to that of an aryl phosphite.

Replacing the hydrogens of ethylene by substituents which lower the energy of the π^* orbital greatly enhances the stability of the olefin complexes, as we shall see in the following paper.⁸

(40) E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv. Chim. Acta*, **46**, 288 (1963).

(41) L. A. Yanovskaya, B. I. Kozyrkin, G. A. Kogan, and V. F. Kucherov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **11**, 2319 (1967).

Olefin Complexes of Nickel(0). III. Formation Constants of (Olefin)bis(tri-*o*-tolyl phosphite)nickel Complexes

Chadwick A. Tolman

Contribution No. 2098 from the Central Research Department,
 E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898.
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Abstract: The reactions of 38 olefins with $\text{Ni}[\text{P}(\text{O}-o\text{-tolyl})_3]_3$ have been investigated and equilibrium constants determined spectrophotometrically in benzene. Values of K_1 at 25° vary from $\sim 10^{-4}$ to 4×10^8 , depending on olefin structure (eq 1). Electron-withdrawing substituents on acyclic olefins give more stable olefin complexes, with resonance effects more important than inductive effects. Fluorine, alkoxy, and acetoxy substituents destabilize the complexes. $\log K_1$ correlates well with σ_p^+ with $\rho = +5.5$. For cyclic olefins K_1 is enhanced by ring strain and to a much greater extent than in Ag^+ complexes. Temperature studies in a few cases show that K_1 is determined by ΔH_1 , with $\Delta S_1 \sim 0$. Assuming a nickel–phosphorus bond strength of 30 kcal/mol, nickel–olefin bond strengths can be estimated to lie in the range of about 25 kcal/mol for *trans*-di(*tert*-butyl)ethylene to 42 kcal/mol for maleic anhydride. The results are discussed in terms of energy level separations of highest occupied and lowest unoccupied molecular orbitals of $\text{Ni}[\text{P}(\text{O}-o\text{-tolyl})_3]_3$ and the free olefins and compared with data on other metals.

Nickel occupies an important position among the transition metals by virtue of the large variety of homogeneous catalytic reactions involving acetylenes and olefins in which it is involved. Polymerization

and cyclization of acetylenes,¹ cyclization of butadiene,² formation of 1,4-hexadiene from butadiene

(1) W. Reppe and W. K. Schwenkendiek, *Justus Liebig's Ann. Chem.*, **560**, 104 (1948).

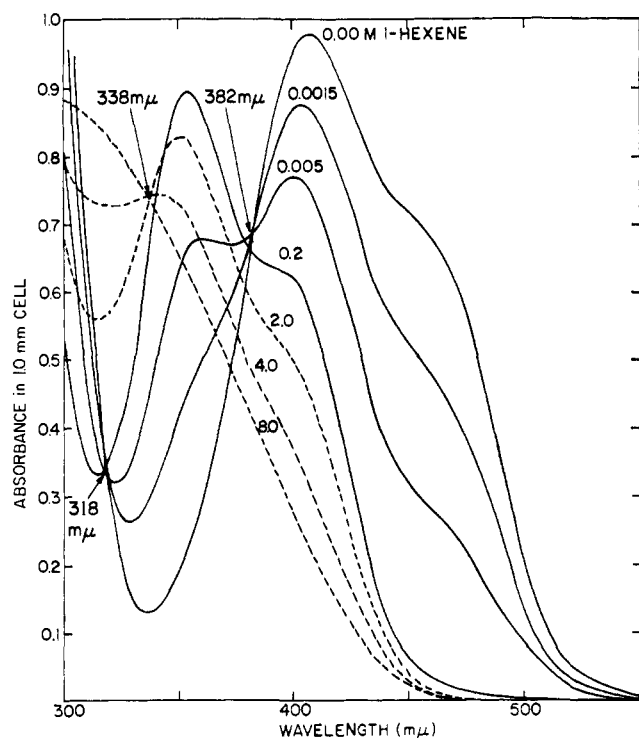
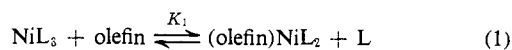


Figure 1. Optical spectra of benzene solutions at 25° containing $2.20 \times 10^{-3} M$ $Ni[P(O-o-tolyl)_3]_2$ and increasing concentrations of 1-hexene. The last solution with 8.0 M olefin contains neat 1-hexene.

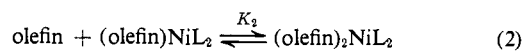
and ethylene,³ olefin isomerization,⁴ and acrylonitrile polymerization⁵ are among the reported examples.

Studies of olefin complexes of nickel are also important in understanding the nature of transition metal-olefin bonding generally. Zerovalent nickel lies toward the end of a spectrum of metal-olefin bond types characterized by strong electron donation from metal d to olefin π^* orbitals, as illustrated by structural, vibrational, and nmr data on (olefin) $Ni[P(O-o-tolyl)_3]_2$ complexes in the preceding paper.⁶ In this paper we consider the implications of this type of bonding on equilibrium constants for reaction 1 for a variety of



olefin structures where $L = P(O-o-tolyl)_3$.

Spectrophotometric evidence is also presented for the formation of bis(olefin) complexes in concentrated solutions of olefins by reaction 2.



Experimental Section

Most of the olefins were research grade and were used without further purification. Acrylonitrile, methyl acrylate, methyl vinyl ketone, styrene, and vinyl acetate were freshly distilled before use; maleic anhydride was sublimed.

Solutions were prepared with nitrogen-purged solvents in an N_2 atmosphere in a Vacuum Atmospheres drybox with less than 5 ppm O_2 (1.5 M Et_2Zn in n -heptane did not smoke). Outside the drybox solutions were handled in serum capped vessels and transferred with N_2 flushed syringes.

(2) G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **2**, 105 (1963).

(3) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 6777 (1970).

(4) C. A. Tolman, *J. Amer. Chem. Soc.*, **94**, 2994 (1972).

(5) M. Uchino and S. Ikeda, *J. Organometal. Chem.*, **33**, C41 (1971).

(6) For part II in the series, see C. A. Tolman and W. C. Seidel, *J. Amer. Chem. Soc.*, **96**, 2774 (1974).

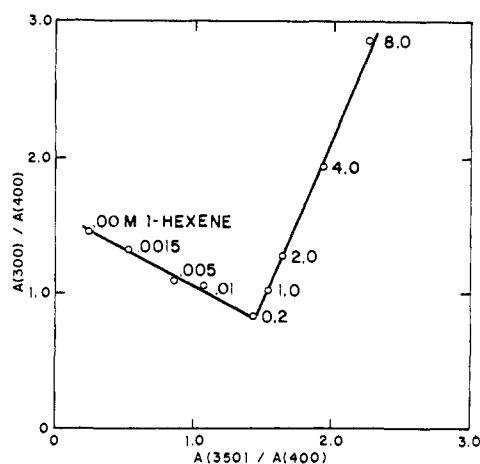


Figure 2. Graphical analysis for the number of absorbing species by the method of Coleman, Varga, and Mastin⁷ in the reaction of 1-hexene with $Ni[P(O-o-tolyl)_3]_2$.

Infrared spectra were determined with a Perkin-Elmer 221 spectrometer and calibrated with CO gas (2143 cm^{-1}) and polystyrene (1601 cm^{-1}). Methylene chloride solutions were contained in nitrogen flushed 0.1-mm NaCl microcavity cells from Barnes Engineering Co., Inc.

Optical spectra were determined with a Cary 14 spectrophotometer. For most of the spectra at 25° the sample compartment was thermostated at 25° and a serum capped 1-mm cell was used. For spectra at other temperatures a jacketed 1-mm cell was maintained at the desired temperature, determined to $\pm 0.5^\circ$ with a 36 gauge copper constantan thermocouple in the center of the cell, by circulating water from a Forma constant temperature bath through the cell jacket.

Equilibrium constants for olefin complex formation were determined spectrophotometrically. A series of benzene solutions was prepared containing $\sim 2 \times 10^{-3} M$ $Ni[P(O-o-tolyl)_3]_2$ and variable concentrations of an olefin ranging usually from about 0.5×10^{-3} to 5 M, usually in steps of factors of 2–3. The absorbance data were analyzed graphically for the number of absorbing species as described by Coleman, Varga, and Mastin.⁷

Spectra of a series of solutions containing 1-hexene are shown in Figure 1 and the corresponding graphical analysis is in Figure 2. The straight line segments in Figure 2 correspond to simple reactions involving only two chromophores, reaction 1 in the region of low olefin concentration and reaction 2 above 0.2 M olefin. The calculation of K_1 and K_2 is illustrated in Table I.

In the case of gaseous olefins it was convenient to add the gas by syringe through the rubber serum cap of a quartz cell as described for the reaction of C_2H_4 with $Ni[P(C_6H_5)_3]_2$.⁸ The 1.0-mm cell used here had a total volume of 3.56 cc and contained 2.0 ml of $\sim 2 \times 10^{-3} M$ nickel complex. The amount of olefin added to the cell was determined assuming it behaved as a perfect gas, with a molar volume of 24.4 l. at 25° and 1 atm. The concentration in solution was found by correcting for the amount of olefin present as nickel complex and the distribution between liquid and vapor phases. The fraction of free olefin in the liquid phase f was given by the relation

$$f = 2.0 \times \text{sol} / (2.0 \times \text{sol} + 1.56)$$

where sol is the solubility of olefin in benzene in cc/cc. Gas solubilities were taken from the literature or estimated from saturation vapor pressures using data tabulated by Cramer.⁹ Because of the small vapor volume employed in our experiments, the correction factor f was never much smaller than 1.0. Concentrations of gaseous olefins in solution did not usually exceed 0.1 M.

Some olefins coordinated so strongly that addition of olefin to a solution of NiL_3 gave essentially a spectrophotometric titration with a sharp point. Direct determination of K_1 was possible only if $K_1 \lesssim$

(7) J. S. Coleman, L. P. Varga, and S. H. Mastin, *Inorg. Chem.*, **9**, 1015 (1970).

(8) C. A. Tolman, W. C. Seidel, and D. H. Gerlach, *J. Amer. Chem. Soc.*, **94**, 2669 (1972).

(9) R. Cramer, *J. Amer. Chem. Soc.*, **89**, 4621 (1967).

Table I. Calculation of K_1 and K_2 for Reactions A and B

Soln no.	$10^3[1-H]_{\text{total}}$	A. 1-hexene + $\text{NiL}_3 \xrightleftharpoons{K_1} (\text{1-hexene})\text{NiL}_2 + \text{L}^a$					K_1^e
		$10^3[1-H]^b$	$A(450)$	$10^3[\text{NiL}_3]^c$	$10^3[(1-H)\text{NiL}_2]^d$		
1	0	0.00	0.725	2.20	0.00		
2	1.5	0.79	0.515	1.49	0.71	0.43	
3	5.0	3.66	0.32	0.86	1.34	0.57	
4	200	198	0.07	0.0485	2.15	0.48	
	∞	∞	(0.055) ^f	0.00	2.20		
Av 0.50 ± 0.07							
Soln no.	$[1-H]_{\text{total}}$	B. 1-hexene + $(1-H)\text{NiL}_2 \xrightleftharpoons{K_2} (1-H)_2\text{NiL}_2^a$				$K_2, i M^{-1}$	
		$A(318)$	$10^3[(1-H)_2\text{NiL}_2]^g$	$10^3[(1-H)\text{NiL}_2]^h$			
4	0.2	0.36	0.00	2.20			
5	1.0	0.47	0.32	1.88	0.17		
6	2.0	0.59	0.67	1.53	0.22		
7	4.0	0.765	1.19	1.01	0.30		
8 ⁱ	8.0	0.86	1.59	0.79	0.25		
	∞	(1.11) ^k	2.20	0.00			
Av 0.24 ± 0.04							

^a $2.20 \times 10^{-3} M \text{Ni}[\text{P}(\text{O}-o\text{-tolyl})_3]_3$ in benzene at 25°; 1.0-mm cell. ^b $[1-H] = [1-H]_{\text{total}} - [(1-H)\text{NiL}_2] M$. ^c $[\text{NiL}_3] = [A(450) - A_{\infty}(450)] / [0.725 - A_{\infty}(450)] \times 2.20 \times 10^{-3} M$. ^d $[(1-H)\text{NiL}_2] = 2.20 \times 10^{-3} M - [\text{NiL}_3] M$. ^e $K_1 = [(1-H)\text{NiL}_2][\text{L}] / [1-H][\text{NiL}_3] = [(1-H)\text{NiL}_2]^2 / [1-H][\text{NiL}_3]$. ^f $A_{\infty}(450)$ was determined by successive approximation to make the calculated K_1 for solution no. 4 equal to the average K_1 . ^g $[(1-H)_2\text{NiL}_2] = [A(318) - 0.36] / [A_{\infty}(318) - 0.36] \times 2.20 \times 10^{-3} M$. ^h $[(1-H)\text{NiL}_2] = 2.20 \times 10^{-3} - [(1-H)_2\text{NiL}_2] M$. ⁱ $[(1-H)_2\text{NiL}_2] / [1-H][(1-H)\text{NiL}_2] M^{-1}$. ^j In neat 1-hexene. $[\text{Ni}]_{\text{total}} = 2.38 \times 10^{-3} M$ for this solution. ^k $A_{\infty}(318)$ was determined by successive approximation to make the calculated K_2 for solution no. 8 equal to the average K_2 .

Table II. Calculation of K_1 for the Reaction $\text{mac} + \text{NiL}_3 \xrightleftharpoons{K_1} (\text{mac})\text{NiL}_2 + \text{L}^a$

Soln no.	Added[L]	K_1					
		$10^3[\text{mac}]_{\text{total}}$	$10^3[\text{mac}]^b$	$A(372)$	$10^3[(\text{mac})\text{NiL}_2]^c$	$10^3[\text{NiL}_3]^d$	$10^2 K'^e$
1	0.5	0.0	0.00	0.07	0.00	1.92	
2	0.5	1.5	0.72	0.28	0.78	1.14	4.8
3	0.5	3.0	2.74	0.41	1.26	0.66	3.5
4	0.5	6.0	4.40	0.50	1.60	0.32	5.7
5	0.0	6.0	4.1	0.585	1.92	0.00	
Av 4.7 ± 0.6							

^a $1.92 \times 10^{-3} M \text{Ni}[\text{P}(\text{O}-o\text{-tolyl})_3]_3$ with 0.5 M added $\text{P}(\text{O}-o\text{-tolyl})_3$ in benzene at 25°; 1.0-mm cell. ^b $[\text{mac}] = [\text{mac}]_{\text{total}} - [(\text{mac})\text{NiL}_2]$. ^c $[(\text{mac})\text{NiL}_2] = [A(372) - 0.07] / (0.585 - 0.07) \times 1.92 \times 10^{-3} M$. ^d $[\text{NiL}_3] = 1.92 \times 10^{-3} M - [(\text{mac})\text{NiL}_2] = [\text{NiL}_3] + [\text{NiL}_4]$. ^e $K' = [(\text{mac})\text{NiL}_2][\text{L}] / [\text{NiL}_3][\text{mac}] = [(\text{mac})\text{NiL}_2][\text{L}] / [\text{NiL}_3][\text{mac}] \times [\text{NiL}_3] / ([\text{NiL}_3] + [\text{NiL}_4]) = K_1 \times [\text{NiL}_3] / ([\text{NiL}_3] + [\text{NiL}_4])$. Taking $K_a = 25 M^{-1}$ at 25°, $K_1 = 6.3 \pm 0.8 \times 10^3$.

10. In cases where $K_1 \geq 10$, it was determined either by adding $\text{P}(\text{O}-o\text{-tolyl})_3$ to drive equilibrium 1 to the left or by competing the olefin in question with another olefin whose K_1 was known. In case L was added, account was taken of formation of NiL_4 ¹⁰ in equilibrium 3, using a value of $K_a = 25 M^{-1}$ at 25°.¹¹ The method



is illustrated in Table II for the reaction of methyl acrylate (mac) in the presence of 0.5 M added $\text{P}(\text{O}-o\text{-tolyl})_3$. No ligand was added to the last solution in order to get the spectrum corresponding to complete conversion of nickel to (olefin) NiL_2 complex.

Results

Addition of olefins to red-orange benzene or methylene chloride solutions of $\text{Ni}[\text{P}(\text{O}-o\text{-tolyl})_3]_3$ usually caused an immediate color change to yellow. In case the olefin contained a conjugated carbonyl or cyanide group, formation of an olefin complex was indicated in the infrared spectrum by a shift of ν_{CO} or ν_{CN} to lower frequency by 12–44 cm^{-1} , as shown in Table III. Coordination of olefin in several cases caused a marked enhancement in the intensity of these bands, New

(10) In the absence of added L the concentration of NiL_4 can be ignored in these $2 \times 10^{-3} M$ nickel solutions since at 25° it never exceeds $2.5 \times 10^{-5} M$.

(11) This value was found by interpolation of data¹² at other temperatures.

(12) L. W. Gosser and C. A. Tolman, *Inorg. Chem.*, **9**, 2350 (1970).

Table III. Infrared Spectral Data on ν_{CO} or ν_{CN} for (Olefin) $\text{Ni}[\text{P}(\text{O}-o\text{-tolyl})_3]_3$ Complexes in CH_2Cl_2

Olefin ^d	(Olefin) NiL_2		Free olefin		Change	
	ν^a	Log ϵ^b	ν	Log ϵ	$\Delta\nu$	$\Delta \log \epsilon$
TCNE	2232	1.9	2253	1.8		
	2205 sh	1.7	2217	1.6		
	2120 br ^c	2.7				
MA ^e	1733	3.2	1777	3.2	-44	0.0
	1805	3.0	1845	2.4	-40	0.5
FMN	2210	2.6	2240	1.4	-30	1.2
DMM	1710	3.1	1730	3.0	-20	0.1
ACN ^e	2194	2.5	2227	1.7	-33	0.8
MAC	1714	3.4	1726	2.9	-12	0.5
MVK	1645	0.45	1680	0.38	-35	0.1

^a Frequency in cm^{-1} . Uncertainty $\pm 3 \text{ cm}^{-1}$. ^b Log ϵ in $\text{cm}^{-1} M^{-1}$. Uncertainty ± 0.1 . ^c The TCNE complex is probably not an olefin complex (see text). ^d Abbreviations used: TCNE, tetracyanoethylene; MA, maleic anhydride; FMN, fumaronitrile; DMM, dimethyl maleate; ACN, acrylonitrile; MAC, methyl acrylate; MVK, methyl vinyl ketone. ^e (Olefin) NiL_2 complex isolated in ref 6.

bands observed after addition of excess maleic anhydride (MA) or acrylonitrile (ACN) to NiL_3 had the same frequency and extinction coefficient as the isolated (MA) NiL_2 and (ACN) NiL_2 complexes.⁶

Table IV. Equilibrium Constants for Acyclic Olefins and Electronic Spectra^a of (Olefin)Ni[P(O-*o*-tolyl)₃]₂ Complexes in Benzene at 25°

Olefin	K_1^b	K_2, M^{-1}^c	λ_{max}	$10^3\epsilon_{max}$	λ_{sh}	$10^3\epsilon_{sh}$
1 Maleic anhydride ^{l,m}	4.0×10^{10}	<i>d</i>	295	13.1	345	4.8
2 <i>trans</i> -NCCH=CHCN	1.6×10^{10}	~ 0	<i>j</i>		337	3.8
3 <i>cis</i> -CH ₃ OCOCH=CHCOOCH ₃	4.8×10^{10}	~ 0	305 ^h	6.8	350	4.0
4 CH ₂ =CHCN ^l	4.0×10^{10}	0.9 ± 0.3	326 ⁱ	4.6	362	3.7
5 CH ₂ =CHCOOCH ₃	6.3×10^{10}	<i>d</i>	320 ^h	4.8	372	3.0
6 CH ₂ =CHCOCH ₃	2.5×10^{10}	<i>d</i>	310	6.3	<i>j</i>	
7 CH ₂ =CHC ₆ H ₅ ^l	1.0×10^{10}	0.05 ± 0.01	312	10.5	390	3.9
8 CH ₂ =CHCH ₂ OCH ₃	1.4	0.3 ± 0.1	350	4.1	386	3.1
9 1-Hexene	5.0×10^{-1}	0.24 ± 0.04	354	4.2	392	3.0
10 CH ₂ =CHOCOCH ₃	4.6×10^{-1}	<i>d</i>	341	3.9	377	2.9
11 CH ₂ =CHCH ₂ Si(CH ₃) ₃	2.0×10^{-1}	~ 2	358	4.0	399	3.3
12 <i>trans</i> -PhCH=CHPh	8.0×10^{-2}	~ 0	<i>j</i>		400	4.6
13 CH ₂ =CHC(CH ₃) ₃	1.6×10^{-2}	~ 0	359	4.3	395	3.2
14 CH ₂ =CHO(CH ₂) ₃ CH ₃	3.1×10^{-3}	~ 0	356	≥ 3.3	~ 392	≤ 2.7
15 <i>trans</i> -2-Hexene	2.7×10^{-3}	~ 0.5			<i>k</i>	
16 <i>cis</i> -2-Hexene	2.3×10^{-3}	~ 0	~ 360		~ 396	
17 2-Methyl-1-pentene	1.2×10^{-3}	~ 0	~ 359		~ 399	
18 CH ₃ CH=C(CH ₃) ₂	$\sim 3 \times 10^{-4}$				<i>k</i>	
19 <i>trans</i> -(CH ₃) ₃ CCH=CHC(CH ₃) ₃	$\sim 10^{-4}$					

^a Wavelengths in $m\mu$ (± 2), extinction coefficients in $cm^{-1} M^{-1}$ ($\pm 10\%$). ^b $K_1 = [(olefin)NiL_2][L]/[NiL_3][olefin]$. Uncertainty generally $\pm 15\%$. ^c $K_2 = [(olefin)_2NiL_2]/[(olefin)NiL_2][olefin]$. ^d Not determined. ^e Determined in competition with added acrylonitrile and assuming $K_1 = 4.0 \times 10^4$ for ACN. ^f Determined in competition with styrene and assuming $K_1 = 10$ for styrene. ^g Determined with added L = P(O-*o*-tolyl)₃ and assuming $K_2 = 25 M^{-1}$ for NiL₃. ^h Band appears only as a shoulder. ⁱ There was also an absorbance max at 296 $m\mu$ ($\epsilon 4.8 \times 10^3$). ^j Not observed. ^k K_1 was so small compared to K_2 that a good spectrum of (olefin)NiL₂ was not obtained, ^l (Olefin)-NiL₂ complex isolated in ref 6. ^m Even though maleic anhydride is a cyclic olefin it is included here for ease of comparison with other functionally substituted olefins.

Tetracyanoethylene did not give the spectrum expected for a simple olefin complex. Rettig and Wing¹³ have pointed out that a wide variety of TCNE olefin complexes show a single ν_{CN} band at about 2200 cm^{-1} . Addition of TCNE to a solution of NiL₃ gives a dark brown solution with at least three bands in the CN stretching region, a strong band at 2120 and weak bands at 2232 and 2205 cm^{-1} . We conclude that our TCNE in complex is not olefin bonded and so it was not studied further.

The qualitative relative stabilities of olefin complexes were determined by infrared experiments in which olefins were added to CH₂Cl₂ solutions of another olefin complex. In most cases equilibrium was rapidly achieved. Table III is ordered to show increasing ease of displacement on descending the table. Addition of acrylonitrile to solutions of (C₂H₄)NiL₂ or (C₂F₄)NiL₂¹⁴ caused immediate and quantitative replacement of the C₂H₄ or C₂F₄ by ACN, with the appearance of the characteristic ν_{CN} band of (ACN)NiL₂ at 2194 cm^{-1} . Greater stability of the ACN complex compared to that with C₂H₄ is reflected in shortening of an Ni-C bond in the former by 0.10 Å.^{14b}

Quantitative determination of equilibrium constants was carried out spectrophotometrically as described in the Experimental Section. Addition of increasing concentrations of an olefin to a solution of Ni[P(O-*o*-tolyl)₃]₂ caused spectral changes which were attributed to (olefin)NiL₂ formation by eq 1. The simple nature of the reaction at low olefin concentrations is indicated by the isosbestic points at 318 and 382 $m\mu$ in the 1-hexene spectra of Figure 1. Addition of maleic anhydride, acrylonitrile, styrene, and ethylene to solutions of NiL₃ gave electronic spectra identical with those of the isolated (olefin)NiL₂ complexes.⁶ With high

olefin concentrations ($>1 M$) several of the olefins (Table IV) caused additional spectral changes which we have ascribed to formation of bis(olefin) complexes (eq 2). In the case of 1-hexene (Figure 1) a new isosbestic point was obtained at 338 $m\mu$. The featureless spectrum obtained in 8 *M* 1-hexene is similar in appearance to that of (COD)NiL₂, where infrared and nmr experiments⁶ have shown that the 1,5-cyclooctadiene is chelating and that both phosphite ligands remain coordinated if the solutions are not too dilute.¹⁵ In view of the tendency of (COD)NiL₂ to dissociate L in highly dilute solutions, we cannot be certain in all cases that (olefin)₂NiL species¹⁶ are not present to some degree at high olefin concentrations.

Equilibrium constants at 25° and electronic spectral data for a number of acyclic monoenes are given in Table IV. Values of ~ 0 for K_2 indicate that no bis(olefin) complex was detected in 3–5 *M* olefin¹⁷ or in a solution saturated with some of the less soluble olefins such as fumaronitrile or *trans*-stilbene.

Values of K_1 for gaseous olefins are given in Table V. No evidence for bis(olefin) complexes were obtained for these olefins, but their concentrations in solution did not usually exceed 0.1 *M*. The value of K_1 for C₂F₄ was difficult to determine accurately, owing to the slowness of its reactions and to secondary reaction to form cyclo-(C₄F₈)NiL₂.⁶ The reactions of C₂F₄ with NiL₃ or of acrylonitrile with (C₂F₄)NiL₂ went to completion at a 1:1 ratio of added olefin-nickel. Thus, limits can be set such that $50 < K_1 < 300$ for C₂F₄ at 25°. K_1 for C₂H₄ is 250. Thus, C₂F₄ and C₂H₄ give complexes with comparable stabilities. We attempted to

(15) (COD)NiL₂ does not obey Beer's law and in very dilute solutions ($\sim 10^{-4} M$) shows shoulders at 340 and 390 $m\mu$ which have been assigned⁶ to (COD)NiL.

(16) Complexes of this type have been isolated with L = P(C₆H₁₁)₃ by P. W. Jolly, I. Thatchenko, and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, 10, 328 (1971).

(17) An upper limit of 0.03 M^{-1} can be set on K_2 in most cases, assuming that conversion of 10% of the nickel to (olefin)₂NiL₂ in 3 *M* olefin would have been detected.

(13) M. F. Rettig and R. M. Wing, *Inorg. Chem.*, 8, 2685 (1969).

(14) (a) Prepared in solution by allowing a solution of NiL₃ and tetrafluoroethylene to stand for 1 hr at 25°. See ref 6. (b) L. S. Guggenberger, *Inorg. Chem.*, 12, 499 (1973).

Table V. Equilibrium Constants for Gaseous Olefins and Electronic Spectra of (Olefin)Ni[P(O-*o*-tolyl)₃]₂ Complexes in Benzene at 25°

Olefin	K_1	$10^{-3} \times \text{sat. pressure, mm}^e$	Solubility, ^f cc/cc	f^a	λ_{max}	$10^3 \epsilon_{\text{max}}$	λ_{sh}	$10^3 \epsilon_{\text{sh}}$
20 CH ₂ =CHCF ₃	1.0×10^3 ^b			1.00 ⁱ	335	4.3	366	3.3
21 C ₂ H ₄ ^k	2.5×10^2 ^b	51.5	(3.4) ^g	0.81	350	4.5	383	3.5
22 C ₂ F ₄	$\sim 10^2$		1.43	0.65	315	3.3	359 ^d	3.2
23 CH ₂ =CHF	9.0×10^1 ^b	21.0	8.4	0.92	340	4.1	381	2.9
24 CH ₂ =CHCl	1.6×10^1 ^b	2.9	59	0.99	339	4.1	378	2.7
25 CH ₂ =CHCH ₃	5.3×10^{-1}	8.7	20	0.96	354	>3.3 ^c	390	>2.5 ^c
26 1-Butene	5.2×10^{-1}	2.2	80	0.99	354	>3.1 ^c	390	>2.4 ^c
27 CHF=CF ₂	4.1×10^{-1} ^b		4.3 ^h	0.85	326	>3.1	365	>2.3
28 <i>trans</i> -CHF=CHF	6.5×10^{-2}		12.1 ^h	0.94	~ 345 ⁱ			

^a Fraction of uncomplexed olefin present in the liquid phase $f = 2.0 \times \text{sol} / (1.56 + 2.0 \times \text{sol})$. ^b Determined in competition with added styrene and assuming $K_1 = 10$ for styrene. ^c O₂ was accidentally admitted before complete conversion to (olefin)NiL₂. ^d Sharp maximum. ^e Taken from compilation in ref 9. ^f Sol = $3.4 \times 51.5 \times 10^3 / \text{sat. pressure (mm)}$ except as noted otherwise. ^g A. Seidel, "Solubilities of Organic Compounds," Vol. II, 3rd ed, Van Nostrand, New York, N. Y., p 96. ^h Solubilities measured in toluene at 25°, ref 9. ⁱ Assumed in the absence of solubility data. ^j K_1 was too small to force all of the nickel into (olefin)NiL₂. ^k (C₂H₄)Ni[(P(O-*o*-tolyl)₃]₂ was isolated by W. C. Seidel and C. A. Tolman, *Inorg. Chem.*, **9**, 2354 (1970).

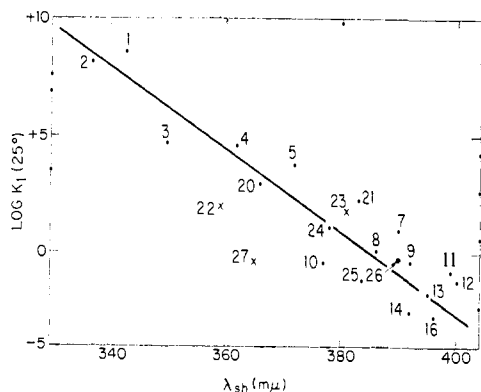
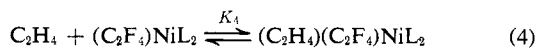


Figure 3. Correlation of $\log K_1$ (25°) with λ_{sh} of (olefin)Ni[P(O-*o*-tolyl)₃]₂. Olefin numbers refer to Tables IV and V. C₂H_{4-n}F_n complexes are designated by x.

displace C₂F₄ by ethylene. Addition of C₂H₄ to a solution of (C₂F₄)NiL₂ gave isosbestic points at 308 and 385 m μ , indicating a simple reaction with only two chromophoric species; however, the final spectrum was *not* that of (C₂H₄)NiL₂ but showed a shoulder with an inflection at 330 m μ . Presumably the reaction observed was that shown in eq 4, with $K_4 = 235 \pm$



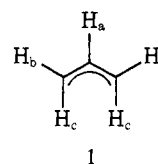
50 M⁻¹ at 25°. Simple and quantitative displacement of C₂F₄ by acrylonitrile was indicated by both ultraviolet and infrared spectra.

Solutions with vinyl chloride were unstable; the initially yellow solutions turned green on standing for a few hours at 25°, and uv bands assigned to (C₂H₃Cl)-NiL₂ were lost. The reaction was not characterized further but probably involved cleavage of the C-Cl bond. Similar reactions of C₂F₃Cl with zerovalent nickel complexes are well known.¹⁸ With allyl chloride no uv bands assignable to an olefin complex were observed even in a freshly prepared solution. The spectrum showed an absorption maximum at 312 m μ ($\epsilon = 2.8 \times 10^3$) and a second very broad maximum at 420 m μ ($\epsilon = 0.8 \times 10^3$), reminiscent of the spectrum of π -C₄H₇Ni[P(OEt)₃]₃⁺.¹⁹ The formation of a π -allyl complex with rapid cleavage of the C-Cl bond of allyl

(18) J. Ashley-Smith, M. Green, and F. G. A. Stone, *J. Chem. Soc. A*, 3019 (1969).

(19) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 6777 (1970).

chloride was confirmed by a proton nmr experiment. H_a in 1 appeared as a triplet of triplets at τ 5.52 with



$J_{\text{ab}} = 8$ Hz, $J_{\text{ac}} = 14$ Hz. H_b and H_c appeared as broad doublets at 6.74 and 4.9. Similar parameters have been reported for π -C₃H₅Ni[P(OC₆H₅)₃]₂Br.²⁰

Several features of the data in Tables IV and V are noteworthy. The values of K_1 cover an extremely large range, $\sim 10^{12}$. Olefin complex stability is markedly enhanced by electron-withdrawing substituents, such as cyano or carboxyl, and reduced by electron-donating alkyl groups. The electronic effect of the substituents on the double bond is reflected in the wavelength of the lowest energy electronic transition, as shown by the plot of $\log K_1$ against λ_{sh} in Figure 3.

Closer examination of electronic effects shows that the resonance interaction of a substituent on the double bond is far more important than the inductive interaction in determining the stability of the olefin complex. An oxygen in the side chain of allyl methyl ether increases K_1 by a factor of 3 over that of 1-hexene, as expected for an electronegative oxygen atom. Moving the oxygen next to the double bond in vinyl butyl ether, however, *decreases* K_1 from that of 1-hexene by a factor of 160. Resonance donation of electrons by oxygen overpowers inductive withdrawal. A similar effect is observed with fluorine. Nonconjugated fluorines in CH₂=CHCF₃ stabilize the olefin complex while fluorines directly attached to the double bond in vinyl fluoride and *trans*-1,2-difluoroethylene destabilize it. The importance of resonance effects is indicated by the rather good correlation between $\log K_1$ and $\Sigma\sigma_{\text{p}}^+$ in Figure 4. For olefins with more than one substituent the σ_{p}^+ values of the various groups were simply added. The substituent parameter σ_{p}^+ is 66% R and 34% F, in the terminology of Swain and Lupton.²¹ From the slope $\rho = +5.5$.

(20) D. Walter and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **5**, 897 (1966).

(21) C. G. Swain and E. C. Lupton, Jr., *J. Amer. Chem. Soc.*, **90**, 4328 (1968).

Table VI. Equilibrium Constants for Cyclic Olefins and Electronic Spectra of (Olefin)NiL₂ in Benzene at 25°

Olefin	K ₁	K ₂ , M ⁻¹	λ _{max}	10 ³ ε _{max}	λ _{sh}	10 ³ ε _{sh}	Strain energies, ^c kcal/mol	K ₁ for Ag ⁺ ^d
29 Norbornene	4.4	1.22 ± 0.05	356	4.6	400 ^a	3.0	27.2	62
30 <i>cis</i> -Cyclooctene	6.2 × 10 ⁻²	0.19 ± 0.01	359	4.3	396	3.2	7.4	14.4
31 Cyclopentene	2.6 × 10 ⁻²	<i>b</i>	360	4.2	395	2.9	6.8	7.3
32 Cycloheptene	2.3 × 10 ⁻²	0.62 ± 0.02	355	4.1	395	3.0	6.7	12.8
33 Cyclohexene	3.5 × 10 ⁻⁴	~0	~367		~395		2.5	3.6

^a Appeared as a slight maximum. ^b Not determined. ^c Strain energies of cyclic olefins from P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.*, **92**, 2377 (1970). ^d Data for Ag⁺ at 40° from ref 23.

The success of the correlation in Figure 4 for non-fluorinated olefins suggests that substituent effects are roughly additive in our system. The magnitude of K₁ is increased by factors of ~500 for each -H replaced by -CN and ~20 for each -COOCH₃ and decreased by factors of ~50 and ~300 for -C₆H₅ and alkyl. The similar values of K₁ for propylene, 1-butene, and 1-hexene (olefins 25, 26, and 9) show that the length of the alkyl chain is unimportant. Equilibrium constants also appear to be quite insensitive to positional isomerism as shown by the closely similar values of K₁ for *trans*-2-hexene, *cis*-2-hexene, and 2-methyl-1-pentene (olefins 15-17). Surprisingly, the *trans* isomer is slightly more stable than the *cis*. A greater stability of *trans* isomers has also been reported for some silver ion complexes.²²

The fluoro olefins behaved in a peculiar way. Increasing *n* in the series C₂H_{4-n}F_n (olefins 23, 28, 27, and 22) caused K₁ to decrease, pass through a minimum, and rise to a value comparable to that of C₂H₄ with C₂F₄. It was as if the first few fluorine atoms destabilized the olefin complex through resonance electron donation but that their ability to donate was finally overcome by their strongly inductive character as more fluorines were added.

Equilibrium constants for some cyclic olefins are given in Table VI. The electronic spectra are essentially independent of ring size. Values of K₁ are nicely correlated with the strain energies listed in the table suggesting that bonding of strained rings is enhanced by partial relief of strain on coordination. This effect has also been noted by Muhs and Weiss²³ in the stability constants of Ag⁺ complexes. Their values of K₁ fall roughly in the same order but vary by only a factor of 17 on going from norbornene to cyclohexene. Our values of K₁ vary by more than 10⁴. Apparently relief of strain occurs to a much greater extent in the Ni(0) compounds.

Equilibrium constants were measured at additional temperatures of 40, 55, and 70° in a few cases. Plots of log K₁ against 1/T were linear to within experimental error and were used to determine the values of ΔH and ΔS shown in Table VII. The entropy changes are essentially zero for replacement of one olefin by another or of one L by olefin. This indicates that the equilibrium constants directly reflect changes in ΔH and therefore the strengths of the nickel-olefin bonds. The 10¹² range of K₁ values in Table IV corresponds to 17 kcal/mol difference in bond strengths between

(22) T. Okuyama, T. Fueno, and J. Furukawa, *Bull. Chem. Soc. Jap.*, **42**, 3106 (1969).

(23) M. A. Muhs and F. J. Weiss, *J. Amer. Chem. Soc.*, **84**, 4697 (1962).

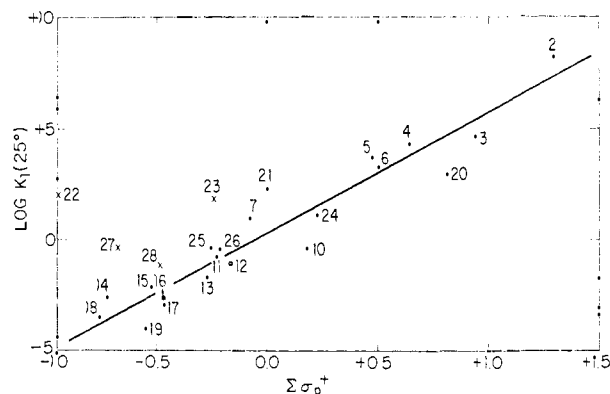


Figure 4. Correlation of log K₁ (25°) with Σσ_p⁺. Values of σ_p⁺ are from ref 21. x designates C₂H_{4-n}F_n complexes.

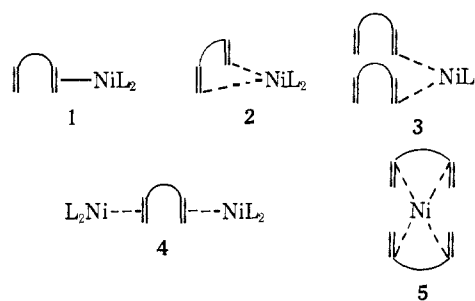
Table VII. Thermodynamic Data^a from Temperature Dependence of Equilibrium Constants

Reaction	ΔH, kcal/mol	ΔS, eu
ACN + (MA)NiL ₂ ⇌ MA + (ACN)NiL ₂	6 ± 3	2 ± 10
1-hexene + NiL ₃ ⇌ (1-hexene)NiL ₂ + L	1 ± 1	2 ± 3
cyclohexene + NiL ₃ ⇌ (cyclohexene)NiL ₂ + L	5 ± 1	1 ± 3

^a In benzene.

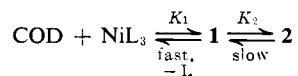
maleic anhydride at one extreme and *trans*-di(*tert*-butyl)ethylene at the other.

Reactions of some dienes with Ni[(*O*-*o*-tolyl)₂]₃ were briefly investigated. Dienes can conceivably bond to Ni(0) in a variety of ways, some of which are indicated below.



Addition of 1,5-cyclooctadiene to a solution of NiL₃ caused an immediate slight color change, followed by a slow (~5 min) change of the orange solution to nearly colorless in 0.2 M COD. Spectra of equilibrated solutions at various diene concentrations showed an isobestic point at 356 mμ, with only tailing absorbance above 300 mμ with 0.2 M diene. Since cyclooctene

reacts very rapidly ($K_1 = 0.06$), the slow reaction with COD is believed to involve coordination of the second double bond, converting a complex of type 1 to 2.

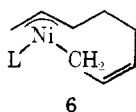


The overall equilibrium constant $K_1K_2 = 7.5 \pm 0.5$. This value may be compared with the corresponding value of $K_1K_2 = 1.2 \times 10^{-2}$ for cyclooctene. The factor of 600 in the product, which probably arises mostly in K_2 , is attributable to chelation.

Norbornadiene reacts rapidly with NiL_3 to give spectra without isosbestic points and with shoulders at 340 and 396 $\text{m}\mu$. The NiL_3 was consumed before the ratio of NBD-Ni reached 1:1. These observations suggest a mixture of olefin complexes, probably containing 1, 2, and 4. Behavior different from that of COD is a consequence of strain in norbornadiene, which makes each double bond coordinate more strongly. K_1 for norbornene is 4.4.

4-Vinylcyclohexene behaved very much like 1-hexene, giving $(\text{VCH})\text{NiL}_2$ with λ_{max} at 354 $\text{m}\mu$ ($\epsilon 4.8 \times 10^3$) and λ_{sh} at 396 $\text{m}\mu$ ($\epsilon 2.7 \times 10^3$) with $K_1 = 0.33 \pm 0.03$. This K_1 is slightly smaller than that of 1-hexene, in spite of the presence of two double bonds, and suggests that the exocyclic C=C is the primary coordination site, with K_1 diminished as a result of the secondary β carbon. Binding at the endocyclic C=C is unimportant because of the small K_1 ; that of cyclohexene itself is only 3.5×10^{-4} .

1,3-Butadiene behaved in a peculiar way. Spectra obtained soon after bubbling BD through a solution of NiL_3 did not look like those of typical olefin complexes but showed a shoulder at 386 $\text{m}\mu$ ($\epsilon 2.5 \times 10^3$) and a long sloping tail extending beyond 600 $\text{m}\mu$. Proton nmr spectra of a similar solution showed the gradual appearance of COD and VCH, formed in a catalytic cyclodimerization reaction, which had a half-life of 15 min at 54°. The electronic spectrum is attributed to a π -allyl nickel complex of type 6. A related struc-



ture with $\text{L} = \text{P}(\text{C}_6\text{H}_{11})_3$ has been identified in solution by Jolly, Thatchenko, and Wilke.²⁴

Discussion

One fundamental problem in studies of stabilities of olefin complexes is deciding to what extent substituent effects are steric in origin and to what extent electronic. Several features of our results indicate that steric effects of olefin substituents are rather *unimportant* in our system.

1. There are good correlations between $\log K_1$ and λ_{sh} or $\Sigma\sigma_{\text{p}^+}$. Both suggest the importance of electronic effects.

2. Substituent effects are approximately additive. If steric effects were important, there should be marked deviations from additivity in the direction of *destabiliz-*ing olefins with more than one substituent.

(24) P. W. Jolly, I. Thatchenko, and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, 10, 329 (1971).

3. Bulky olefins such as *tert*-butylethylene and trimethylethylene (13 and 18) form $(\text{olefin})\text{NiL}_2$ complexes whose stability is reasonable based on the expected electronic effects.

4. Many of the fairly bulky olefins, such as *trans*-2-hexene, are able to form bis(olefin) complexes.

The significance of both resonance and inductive interactions of substituents on olefins has been recognized by others. von Gustorf, *et al.*,²⁵ found a good correlation between the qualitative stability of (olefin)- $\text{Fe}(\text{CO})_4$ complexes or of ν_{CO} with σ_{p} , which is 53% *R*.²¹ Net electron donation by $-\text{OC}_2\text{H}_5$ in $(\text{CH}_2=\text{CHOC}_2\text{H}_5)\text{Fe}(\text{CO})_4$ was indicated by low carbonyl stretching frequencies and the thermal instability of the complex.

Fueno, *et al.*,²⁶ found a good correlation between $\log K_1$ for argentation of a series of vinyl compounds and σ_{m} , which is 22% *R*.²¹ Thus in the Ag^+ system, inductive substituent effects appear to be more important than resonance. The value of $\rho = -5.07$ indicates that electron-withdrawing groups *destabilize* the silver complexes. Methyl acrylate and methyl vinyl ketone gave less stable complexes than did propylene.

Perhaps the most striking feature of our results when compared to equilibrium studies in other systems is the extreme sensitivity of the Ni(0) equilibrium constants to structural modifications of the olefins. This high selectivity is illustrated in Table VIII, where equilibrium

Table VIII. Selectivity of Various Transition Metal Complexes. Relative Equilibrium Constants at 25°

Olefin	$(\text{C}_2\text{H}_4)\text{Ag}^+{}^a$	acacRh- $(\text{C}_2\text{H}_4)_2{}^b$	$(\text{C}_2\text{H}_4)\text{NiL}_2{}^c$
C_2H_4	(1.0)	(1.0)	(1.0)
$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	0.35	0.09	2×10^{-3}
<i>cis</i> - $\text{CH}_3\text{CH}=\text{CHCH}_3$	0.24	0.004	0.9×10^{-5}
<i>trans</i> - $\text{CH}_3\text{CH}=\text{CHCH}_3$	0.06	0.002	1.1×10^{-5}

^a Data at 40° from ref 23. ^b Reference 9. ^c This work. Data are for hexenes rather than butenes.

constants of alkyl-substituted ethylenes are compared to those of ethylene. Stability constants for coordination to Ag^+ decrease by a factor of ~ 3 for each alkyl group placed on the double bond. The corresponding factor in the Rh(I) system is ~ 20 . In the Ni(0) system, each alkyl group decreases K_1 by about 300. The sensitivity to substituent effects is also apparent in Figure 4, whose slope indicates a value of $\rho = +5.5$.

The nature of the bonding in these nickel complexes and the sensitivity of formation constants to substituent effects can be understood in terms of a model which considers the bonding between the metal and the olefin to arise primarily from interactions between the highest occupied molecular orbital (HOMO) of the olefin and the lowest unoccupied molecular orbital (LUMO) of NiL_3 ²⁷ and between the NiL_3 HOMO and the olefin π^* LUMO. The former interaction can be considered as donation of olefin π electrons to the metal and the latter as donation of metal electrons to the olefin π^*

(25) E. K. von Gustorf, M. C. Henry, and D. J. McAdoo, *Justus Liebigs Ann. Chem.*, 707, 190 (1967).

(26) T. Fueno, O. Kajimoto, and J. Furukawa, *Bull. Chem. Soc. Jap.*, 41, 782 (1968).

(27) Strictly speaking we should consider a hypothetical NiL_2 with the ligand atoms in the positions they will occupy in the olefin complex.

orbital in the Dewar–Chatt–Duncanson²⁸ picture. Excellent discussions on the bonding of olefins and acetylenes to transition metals have been given by Hartley²⁹ and Greaves, *et al.*³⁰

A relationship between the stability of olefin complexes and the energy level separation Δ_{π^*} between metal d and olefin π^* orbitals was apparently first recognized by Schrauzer,³¹ in explaining the ability of acrylonitrile or acrolein to form (olefin)₂Ni complexes. von Gustorf, *et al.*,³² suggested a correlation of Δ_{π^*} with the qualitative stability of (olefin)Fe(CO)₄ complexes.³² Yamamoto, *et al.*,³³ found a rather good correlation between log *K* for formation of (olefin)Ni(dipy) complexes and olefin π^* energies E_{π^*} obtained from molecular orbital calculations.

Experimentally derived values of E_{π} and E_{π^*} for a number of olefins are given in Table IX. E_{π} was taken

Table IX. IP and $\pi \rightarrow \pi^*$ Data on Olefins

No. ^a	Olefin	IP, ^b eV	Ref	$\pi \rightarrow \pi^*$, ^c eV	Ref	$-E_{\pi^*}$, eV
2	Fumaronitrile	11.15	<i>d</i>	5.64	<i>e</i>	5.51
4	Acrylonitrile	10.91	<i>f</i>	6.43	<i>o</i>	4.48
6	Methyl vinyl ketone	10.10	<i>g</i>	5.95	<i>g</i>	4.15
7	Styrene	8.47	<i>f</i>	4.33	25	4.14
9	1-Hexene	9.46	<i>f</i>	7.00	<i>h</i>	2.46
10	Vinyl acetate	9.19	<i>f</i>	6.1	<i>i</i>	3.1
12	<i>trans</i> -Stilbene	7.95	<i>j</i>	3.71	<i>k</i>	4.24
14	CH ₂ =CHO(CH ₂) ₃ CH ₃	8.93	<i>l</i>	6.43	<i>m</i>	2.50
15	<i>trans</i> -2-Hexene	9.13	<i>n</i>	6.84	<i>o</i>	2.29
16	<i>cis</i> -2-Hexene	9.13	<i>n</i>	6.98	<i>o</i>	2.15
17	2-Methyl-1-pentene	9.12	<i>n</i>	6.58	<i>o</i>	2.54
18	CH ₃ CH=C(CH ₃) ₂	8.67	<i>f</i>	6.98	<i>h</i>	1.69
21	C ₂ H ₄	10.52	<i>f</i>	7.28	<i>h</i>	3.24
22	C ₂ F ₄	10.52	43	8.88	44	1.64
23	CH ₂ =CHF	10.58	43	7.44	44	3.14
24	CH ₂ =CHCl	10.00	<i>f</i>	6.4	25	3.6
25	Propylene	9.73	<i>f</i>	7.10	<i>p</i>	2.63
26	1-Butene	9.58	<i>f</i>	7.10	<i>h</i>	2.48
27	CHF=CF ₂	10.53	43	7.61	44	2.92
28	<i>trans</i> -CHF=CHF	10.38	43	7.28	44	3.10

^a Numbering used in Tables IV and V. ^b Ionization potential, adiabatic if available. ^c Separation of energy levels from uv spectra. ^d H. Bock and H. Stafast, *Chem. Ber.*, **105**, 1158 (1972). ^e J. Halpern, W. D. Closson, and H. B. Gray, *Theor. Chim. Acta*, **4**, 174 (1966). ^f K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, **2**, 369 (1962). ^g Data are given for acrolein in ref 25. ^h L. C. Jones, Jr., and L. W. Taylor, *Anal. Chem.*, **27**, 228 (1955). ⁱ Estimated as described in the text. ^j Reference 35, p 160. ^k R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962). ^l Data for methyl vinyl ether in reference in footnote *f*. ^m M. Procházka and M. Paleček, *Collect. Czech. Chem. Commun.*, **32**, 3149 (1967). ⁿ Given in footnote *f* for the corresponding butene. ^o Given in footnote *h* for the corresponding pentene. ^p Given in reference in footnote *h* for 1-butene.

to be minus the ionization potential of the free olefin, where the energy zero corresponds to complete removal of an electron. The separation $E_{\pi^*} - E_{\pi}$ was determined from uv data. In the case of vinylacetate we were un-

(28) (a) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C79 (1951); (b) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(29) F. R. Hartley, *Angew. Chem., Int. Ed. Engl.*, **11**, 596 (1972).

(30) E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Can. J. Chem.*, **46**, 3879 (1968).

(31) G. N. Schrauzer, *Chem. Ber.*, **94**, 6421 (1961).

(32) The actual parameter they used was Δ_{π^*} divided by the free olefin ionization potential.²⁵

(33) T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, **93**, 3360 (1971).

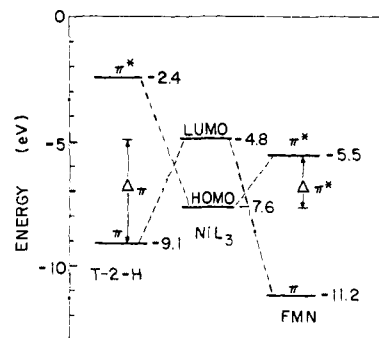


Figure 5. Energy level diagram showing the relative positions of the highest occupied and lowest unoccupied MO's of Ni[P(O-*o*-tolyl)₃]₃, *trans*-2-hexene (T-2-H), and fumaronitrile (FMN).

able to find an assignment of the uv spectrum so the $\pi \rightarrow \pi^*$ energy was estimated from data on *trans*-1-substituted 1,3-butadienes.³⁴ Plotting the $\pi \rightarrow \pi^*$ energies from other sources (Table IX) for monoenes CH₂=CHX against Fueno's data³⁴ for dienes *trans*-CH₂=CHCH=CHX gave a straight line with $(\pi \rightarrow \pi^*)_{\text{monoene}} = 2.44(\pi \rightarrow \pi^*)_{\text{diene}} - 6.87$ eV. The diene $\pi \rightarrow \pi^*$ value of 5.32 eV for X = -OCOCH₃ gave 6.1 eV for vinyl acetate.

Figure 5 shows the positions of the energy levels of the highest occupied and lowest unoccupied molecular orbitals of *trans*-2-hexene and fumaronitrile with respect to those of Ni[P(O-*o*-tolyl)₃]₃. The HOMO level of NiL₃ is taken as -7.6 eV, the ionization energy of atomic nickel.³⁵ The LUMO of NiL₃ is estimated at 2.8 eV above this, since the longest wavelength electronic transition of NiL₃ is at about 450 mμ.¹²

We assume that the bonding interaction between Ni and the olefin involves primarily those orbitals whose levels are shown in Figure 5. Interaction of the olefin π and nickel LUMO (separation Δ_{π}) gives two new levels lower and higher in energy. The lower bonding MO is largely on the olefin but does transfer some electron density to the metal. Interaction of the nickel HOMO and olefin π^* (separation Δ_{π^*}) also gives two new levels, the lower bonding MO residing mostly on the metal but transferring some electron density to the olefin π^* . The stabilization energy, given by second-order perturbation theory, which results from the interactions is given by eq 5.^{36a} *A* and *B* involve geometrical

$$SE = A/\Delta_{\pi} + B/\Delta_{\pi^*} \quad (5)$$

factors and orbital overlap. In the case of *trans*-2-hexene Δ_{π} (4.3 eV) is smaller than Δ_{π^*} (5.2 eV). Replacing the two alkyl groups by -CN lowers both π and π^* so that Δ_{π^*} (2.1 eV) is much smaller than Δ_{π} (6.4 eV).

Reducing the energy level separation Δ_{π^*} should increase the electron transfer from metal d to olefin π^* . The resulting loss of electron density on the metal is shown by ESCA measurements on the isolated (olefin)-NiL₂ complexes.^{36b}

(34) T. Fueno and K. Yaraguchi, *J. Amer. Chem. Soc.*, **94**, 1119 (1972).

(35) V. I. Vedenyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L. Frakevich, "Bond Energies, Ionization Potentials, and Electron Affinities," St. Martin's Press, New York, N. Y., 1966, p 152.

(36) (a) An analogous treatment has been used by N. D. Epitotis, *J. Amer. Chem. Soc.*, **94**, 1924 (1972), for electrocyclic cycloaddition reactions of olefins. (b) C. A. Tolman, W. M. Riggs, W. J. Linn, C. M. King, and R. C. Wendt, *Inorg. Chem.*, **12**, 2770 (1973).

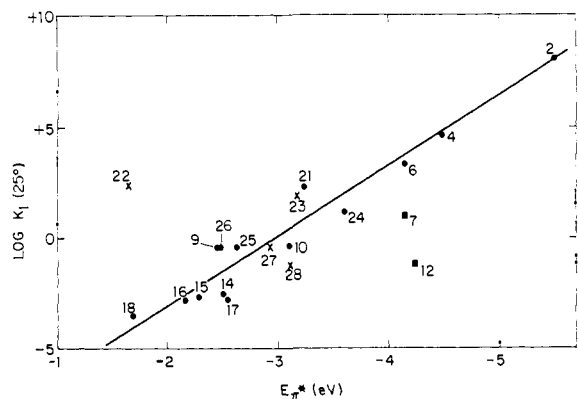


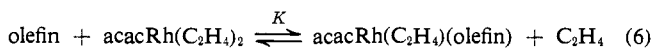
Figure 6. Correlation of $\log K_1$ (25°C) with the energy of the lowest unoccupied orbital of the free olefin. $C_2H_4-nF_n$ olefins are designated by x and $C_2H_4-n(C_6H_5)_n$ by ■.

It can be seen from Table IX that the energy of the π^* level, E_{π^*} , is more sensitive to structural change than is E_{π} . For example, E_{π} changes by 2.5 eV on going from trimethylethylene to fumaronitrile while E_{π^*} changes by 3.8 eV. It may be that B in eq 5 is generally larger than A . Both factors tend to increase the selectivity of a metal with a higher HOMO. The extreme sensitivity of K_1 in the nickel(0) system to structural modifications in the olefin is a consequence of the low ionization potential of Ni(0) and resulting small energy level separation Δ_{π^*} .

As the metal HOMO is lowered in the series Ni(0) \gtrsim Fe(0) \gtrsim Pt(0) $>$ Rh(I) $>$ Pt(II) $>$ Ag⁺, Δ_{π^*} is increased, there is less electron donation from metal to olefin π^* , and the selectivity of the metal for different olefins is expected to decrease. This expectation is in accord with the results in Table VIII.

Figure 6 shows the relationship between $\log K_1$ and E_{π^*} for a number of olefins. The rather good correlation lends support to the bonding picture proposed. Styrene and *trans*-stilbene (points 7 and 12) fall badly off the line. For these molecules E_{π} is high and E_{π^*} low as a consequence of extensive electron delocalization in the extended π systems. Special comment is also required for the fluoro olefins.

It is commonly believed that fluoro olefins form more stable metal-olefin bonds than do hydrocarbons. There is little direct experimental evidence, however, to support this view. Cramer's work⁹ on reaction 6 has



often been quoted. Cramer actually found that vinyl fluoride ($K = 0.32$) and vinylidene fluoride ($K = 0.10$) form *less stable* complexes than does ethylene. Only with C_2HF_3 ($K = 88$)³⁷ and C_2F_4 ($K = 59$) were the fluoro olefins substantially better than C_2H_4 . Very strong metal-fluoro olefin bonds have generally been inferred from preparative studies and the similarity of geminal F-F coupling constants to those found in fluorocyclopropanes.³⁸⁻⁴¹ Stronger bonding of C_2F_4

(37) For reasons which are not clear, trifluoroethylene had the largest formation constant of the $C_2H_4-nF_n$ olefins in the rhodium system but not in the nickel system.

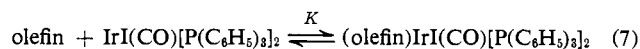
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than of C_2H_4 is also indicated by a longer $d_{C=C}$ and shorter d_{M-C} for C_2F_4 in the X-ray crystal structure of $\pi-C_5H_5Rh(C_2H_4)(C_2F_4)$.^{42a} The K for reaction 7 is



100 times as large for C_2F_4 as for C_2H_4 .^{42b}

We were extremely surprised to find that none of the fluoro olefins examined (with the exception of $CH_2=CHCF_3$) were as good as C_2H_4 in coordinating to nickel(0). While attempting to explain our results, we came across recent photoelectron spectroscopic⁴³ and far-ultraviolet studies⁴⁴ of fluoroethylenes. The E_{π^*} levels (Table IX) are higher in these fluoroethylenes than in ethylene itself while the E_{π} levels are essentially the same. Based on the bonding model developed here, C_2F_4 ($E_{\pi^*} = -1.64$ eV) is expected to be the worst π acceptor of the fluoroethylenes and to behave like trimethylethylene ($E_{\pi^*} = -1.69$) or cyclohexene ($E_{\pi^*} = -1.87$).

We suggest that the inadequacy of the model in explaining the stability of the C_2F_4 complex arises from using electronic data appropriate for the planar D_{2h} olefin. By severely bending back the fluorines from the plane containing the C-C axis, the LUMO must fall in energy and permit a strong interaction with occupied metal orbitals. The fluorines in $\pi-C_5H_5Rh(C_2H_4)(C_2F_4)$ are bent back to an even greater degree than has been found for cyano groups in TCNE complexes.^{42a} The structural reorganization required before tetrafluoroethylene can bond effectively may be responsible for the slowness of its reaction with NiL_3 .⁶ The use of electronic data on planar olefins is much more appropriate for other olefins where the degree of bending back is probably much less. Thus, the proton nmr spectrum⁶ of $(ACN)NiL_2$ shows values of J_{HH} for the coordinated olefin not too different from those of free acrylonitrile. The X-ray structure determination of the complex showed the CN bent back somewhat but the hydrogens were not accurately located.^{14b}

Because these nickel complexes represent an extreme of metal to olefin back bonding, it would be of some interest to know the actual metal-olefin bond strength. Equation 1 involves breaking a nickel-phosphorus bond as well as making a nickel-olefin bond. If we assume that solvation effects are unimportant

$$\Delta H_1 = D(\text{Ni-L}) - D(\text{Ni-OI}) \quad (8)$$

where $D(\text{Ni-L})$ and $D(\text{Ni-OI})$ represent metal-phosphorus and metal-olefin bond strengths. There are no data on $D(\text{Ni-L})$ in NiL_3 complexes but there is information for NiL_4 complexes. Activation energies of phosphorus ligand dissociation from NiL_4 complexes can be used to estimate Ni-P bond strengths, by assuming that activation energies for the reverse association reactions will be very small. Values of ΔH^\ddagger of 27 [L = $P(\text{OEt})_3$],⁴⁵ 28 [L = PF_3],⁴⁶ 29 [L = $P(\text{O}i\text{-toly})_3$],⁶ and 26 kcal/mol [L = $P(\text{OC}_6\text{H}_5)_3$]⁴⁷ have been

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reported. We estimate $D(\text{Ni-L}) = 30$ kcal/mol in NiL_3 since Ni-P bonds in NiL_3 should be somewhat stronger than NiL_4 as a consequence of hybridization changes on Ni and decreased steric repulsions. Assuming $\Delta S_1 \sim 0$ (Table VII) and using the well-known relation $\Delta F = \Delta H - T\Delta S = RT \ln K$ and eq 8 we obtain eq 9. On this basis we estimate $D(\text{Ni-OI})$ to be

$$D(\text{Ni-OI}) \sim 30 + RT \ln K_1 \quad (9)$$

about 25 kcal/mol for *trans*-(CH_3)₃CCH=CHC-(CH_3)₃, 33 kcal/mol for C_2H_4 , and 42 kcal/mol for *trans*-(NC)CH=CH(CN). Our value for ethylene is somewhat higher than the activation energy of 31 kcal/mol measured by Cramer⁴⁸ for dissociation of ethylene from $(\pi\text{-C}_2\text{H}_4)\text{Rh}(\text{C}_2\text{H}_4)_2$.

Summary

The results of our studies on olefin complexes of nickel indicate that electron donation from filled metal d to empty olefin π^* orbitals is extremely important in de-

termining the stability of the complexes. Steric effects of substituents are relatively unimportant compared to electronic effects, and resonance is more important than inductive interaction. Ring strain and chelation both assist olefin coordination. Reducing the ability of the metal to back bond in the series $\text{Ni}(0) \gtrsim \text{Pt}(0) > \text{Rh}(\text{I}) > \text{Pt}(\text{II}) > \text{Ag}^+$ reduces the importance of resonance and decreases the selectivity of the metal for differently substituted olefins, while at the same time reducing the C=C bond length and increasing the stretching force constant. Our data suggest that the degree to which substituents are bent back away from the metal in transition metal olefin complexes is not simply related to the metal-olefin bond strength. Tetrafluoroethylene, which shows extreme bending back in other systems, shows a bond strength to Ni(0) which is no greater than, and probably less than, that of ethylene itself.

Acknowledgment. The author wishes to thank Miss Susan Vladuchick for technical information assistance and Mr. Dallas W. Reutter for skilled laboratory assistance in carrying out this work.

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Crystal Structure and Molecular Stereochemistry of α,γ -Dimethyl- α,γ -dihydrooctaethylporphinatonickel(II)

Patrick N. Dwyer,^{1a} J. W. Buchler,^{1b} and W. Robert Scheidt*^{1a}

Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556, and The Institut für Anorganische Chemie, Rheinisch-Westfälische Technische Hochschule, D-51 Aachen, Federal Republic of Germany. Received September 25, 1973

Abstract: Crystals of α,γ -dimethyl- α,γ -dihydrooctaethylporphinatonickel(II) utilize the space group $C2/c$; the unit cell has $a = 22.456$ (6), $b = 14.980$ (6), $c = 20.615$ (8) Å, and $\beta = 96.04$ (1)° and contains eight molecules. The calculated and experimental densities are 1.197 and 1.20 g/cm³, respectively. Intensity data were collected by θ - 2θ scanning with Mo $K\alpha$ radiation, and 2890 data were retained as observed and used for the solution and refinement of structure; the conventional and weighted R values are 0.071 and 0.082, respectively. The air-stable reduced porphyrin has a folded and ruffled core which leads to an average Ni-N distance of 1.908 Å for the square-planar NiN_4 coordination group. The core of the molecule has approximate C_{2v} geometry; the two methyl groups at C- α and C- γ are in the syn-axial configuration.

Structural data for dihydroporphyrins are limited,^{2,3} although the molecular stereochemistry of a large variety of the closely related porphyrins and metalloporphyrins has been reported.^{4,5} Dihydroporphyrin derivatives may be divided into three classes according to the position of the two additional hydrogen atoms on the porphine (1) nucleus.⁶ The isophlorins have both hydrogen atoms substituted on the nitrogen atoms.^{7,8}

The phlorins have one hydrogen substituted on a nitrogen atom and one on a meso-carbon atom.^{7,8} The third class has both hydrogen atoms substituted on carbon atoms of the porphine nucleus. The three possible stable species^{6,9} are chlorin (2), α,β -dihydroporphine (3), and α,γ -dihydroporphine (4) (porphodimethene). The chlorophyll pigments of plants¹⁰ and photosynthetic algae utilize the chlorin moiety. Although 3 and its derivatives are unknown, derivatives of 4 have been suggested as intermediates in porphyrin syntheses.¹¹⁻¹⁴ These derivatives have not been isolated

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