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Electron Donor–Acceptor Properties in the Bonding of Olefins and Other Unsaturated Molecules to Zerovalent Nickel

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Complexes of the type Ni(*t*-BuNC)$_2$(olefin) have been prepared with over 150 different olefins. The isocyanide stretching frequencies have been measured and related to the electron-withdrawal properties of the olefins. Over 50 complexes of other unsaturated molecules such as imines, diazenes, ketones, nitroso compounds, and acetylenes have been studied similarly. The effects of substituent change are cumulative and an empirical relationship has been developed to predict ν_{NC}. The relative strengths of the metal–olefin bonds have been measured calorimetrically and the effects of changing substituents are again found to be cumulative. The electron-withdrawal properties of the olefins are relatively inductive in nature while the overall bond strengths are more closely related to resonance effects.

Introduction

It is now evident that electron donor–acceptor properties and the steric requirements of various ligands coordinated to a transition metal complex will influence the chemical behavior of that complex. We have recently reviewed the structural aspects of metal complexes with unsaturated molecules.[1] The Dewar–Chatt–Duncanson[2] concept of olefins being σ donors and π acceptors has been used to explain most observed features in olefin bonding and has been shown to be readily applicable to the bonding of other types of unsaturated molecules.[3,4]

There have been a number of discussions in the literature on the importance of π back-bonding in the coordination of unsaturated molecules to transition metals. ESCA has been used to assign relative degrees of oxidation in a series of platinum complexes.[5] Subsequent detailed calculations[6,7] have borne out the gross features of the Dewar–Chatt–Duncanson model. As expected, back-bonding becomes more important as the electronegativity of the unsaturated molecule increases and as the availability of electron density on the metal increases.

A number of recent papers have dealt with the effects of substituents on the bonding and physical properties of coordinated olefins. A series[8] of papers has shown that the upfield chemical shift of ^{13}C NMR resonances of coordinated olefins is an indication of the degree of π-electron density back-bonded from the metal to the olefin; more highly activated olefins or electron-rich metals cause greater upfield shifts. In a system having an electron-rich metal such as zerovalent nickel,[9] electron-withdrawing substituents give more stable complexes, with resonance effects being more important than inductive effects. Similar results were observed in an iron(0) system.[10] When a silver(I) system was studied,[11] it was found that electron withdrawal destabilized the complexes and inductive effects were more important than resonance effects. The σ-donor properties of the olefin became the dominant feature of the bonding. Recent calorimetric studies of silver(I),[12] palladium(II),[13] and platinum(II)[14] monoolefin complexes have also demonstrated different olefin selectivities by different metals. To better understand the nature of these differences and thus the nature of a metal–olefin bond, we have undertaken a detailed infrared and calorimetric study of some zerovalent nickel–olefin complexes.

Experimental Section

Materials and Apparatus. All operations were carried out in the nitrogen atmosphere of a Vacuum Atmospheres drybox. Tetrahydrofuran was distilled from sodium/benzophenone under argon just prior to use. Toluene was dried over Linde 4A molecular sieves and purged with nitrogen. Many of the olefins, acetylenes, diazenes, ketones, imines, and nitroso compounds were available commercially. The others were available from the many fine organic chemists in this department or were easily prepared by standard techniques. Bis(1,5-cyclooctadiene)nickel[15] and *t*-BuNC[16] were prepared by standard techniques. These compounds and commercial PPh$_3$ were used to prepare the nickel complexes by appropriate modifications of the literature technique.[17] Complexes were recrystallized and gave satisfactory analyses.

Infrared Studies. The infrared studies were done with 0.05 M THF solutions. Spectra were recorded with a Perkin-Elmer 221 spectrometer calibrated with CO gas and have an estimated error of 2 cm^{-1}. In many cases, the nickel complexes were not prepared on a synthetic scale but rather were prepared on a spectroscopic scale by reacting a solution of 0.10 M "Ni(*t*-BuNC)$_2$" (actually 0.011 M Ni(*t*-BuNC)$_4$, 0.022 M Ni$_4$(*t*-BuNC)$_7$) with the appropriate ligand in THF.

All complexes involving unusual olefins or other molecules where there might be some ambiguity as to the mode of coordination were prepared on a synthetic scale and fully characterized by conventional techniques. The values of $\nu_{N\equiv C}$ measured in the solid state were found to be in reasonable agreement with those in solution.

Calorimetry. The calorimetric apparatus and technique have been described previously.[18] A known quantity of the complex, Ni(PPh$_3$)$_2$(olefin) (approximately 0.4 mmol), was dissolved in 200 mL of toluene and incrementally titrated with neat (CF$_3$)$_2$C═C(CN)$_2$. Estimated error = 4 kJ mol^{-1}. In all cases, evolution of heat was rapid. In several cases, a solution of Ni(PPh$_3$)$_2$(C$_2$H$_4$) was treated with the desired olefin as an internal check; in several of these cases evolution of heat was too slow to give meaningful results. All results reported were done by the first technique.

Discussion

Electronic Effects. Various methods for measuring the electronic properties of ligands coordinated to transition metals have been devised. Tolman[19] developed a widely accepted ranking of phosphorus ligand donor–acceptor properties based on measurement of the A$_1$ carbonyl stretching frequency of complexes Ni(CO)$_3$(PX$_1$X$_2$X$_3$). The frequency can be accurately predicted by adding the contributions $\mathbf{x}_i$ of the substituents X$_i$. We now present a new measure of ligand donor–acceptor properties based on measurement of the isocyanide stretching frequencies of the complexes Ni(*t*-BuNC)$_2$L. In this system, L can equal one bidentate or two monodentate nitrogen, phosphorus, or arsenic ligands, or one olefin, acetylene, diazene, ketone, or imine ligand.

As a test of the model, we have prepared a representative series of phosphorus ligand complexes, Ni(*t*-BuNC)$_2$(P)$_2$ (where P are various phosphorus ligands). The values of ν_{NC} measured for these complexes are given in Table I; Figure 1 shows the correlation with Tolman's $\nu_{C\equiv O}$. The reasonably good correlation indicates that the two techniques measure the same property, the electron donor–acceptor characteristics of the coordinated ligands. As the phosphorus ligands donate less electron density to the metal, ν_{NC} increases indicating less electron density on the metal available for back-bonding into the antibonding orbitals of the isocyanide ligands. As a measure of phosphorus ligand electronic effects, this technique has the distinct disadvantage of lower accuracy because the bandwidths of coordinated isocyanide vibrational modes are

Table I. Values of ν_{NC} for a Series of Phosphorus Ligands in $Ni(t\text{-}BuNC)_2(P)_2$

	P	ν_{NC}	
1	PEt_3	2025	1970
2	$PPhMe_2$	2031	1982
3	PPh_3	2048	2000
4	$PPh_2(OEt)$	2057	2020
5	$PPh(OEt)_2$	2076	2037
6	$PPh(OMe)_2$	2090	2042
7	$P(OMe)_3$	2098	2050
8	$P(OPh)_3$	2125	2100

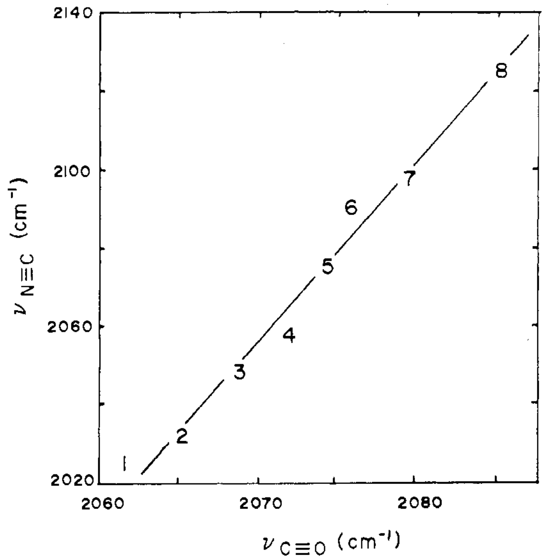
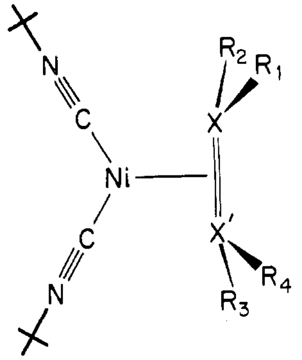


Figure 1. $\nu_{N\equiv C}$ vs. $\nu_{C\equiv O}$ for a variety of phosphorus ligands.

greater than those of carbonyls. The new technique finds its utility in the assignment of donor–acceptor properties of unsaturated molecules coordinated to zerovalent nickel and in demonstrating their relation to the electronic properties of other ligands in related complexes.

First, it is necessary to determine the range of ν_{NC} and its relation to the electron density on the nickel center in orbitals capable of interaction with the π-acceptor orbitals of the isocyanides. This is done by looking at the two known tetrakis(isocyanide) complexes, $Ni^0(t\text{-}BuNC)_4$[20] and $[Ni^{II}(t\text{-}BuNC)]^{2+}$,[21] which have ν_{NC} of 2000 and 2250 cm^{-1}, respectively. The former complex is zerovalent nickel and the removal of two electrons from the nickel center to obtain the latter complex raises ν_{NC} by 250 cm^{-1}. All of the complexes studied have ν_{NC} between these two extremes, corresponding to partial removal of electron density from the metal orbitals involved in π bonding with the isocyanides.

The olefin (X = X′ = carbon) and "heteroolefin" (X, X′ = carbon, nitrogen, oxygen) complexes studied were of the type



where the coordination is trigonal planar if the olefin is considered to be a monodentate ligand. The structures of these olefin and "heteroolefin" complexes have been reviewed in ref 1. The values of ν_{NC} for olefin complexes are given in Table II[22] and the results for other unsaturated molecules are given in Table III. Because the proper symbols for the two isocyanide vibrations change as the symmetry of the olefin changes, they will be referred to simply as $\nu_{NC}{}^1$ and $\nu_{NC}{}^2$ for all complexes.[23]

The most common type of Ni^0 olefin complex is of the stoichiometry NiL_2(olefin) (where L = phosphorus or isocyanide ligand), although complexes of the types $NiL_2(\text{olefin})_2$ and NiL_3(olefin) are known. Maleic anhydride (MA) forms all three types of nickel(0) complexes with L = $t\text{-}BuN{\equiv}C$. If one considers the series $NiL_x(MA)_y$:[20]

	$\nu_{N\equiv C}$		
$Ni(t\text{-}BuNC)_4$		2000	
$Ni(t\text{-}BuNC)_3(MA)$	2150	2120	2115
$Ni(t\text{-}BuNC)_2(MA)$	2161	2128	
$Ni(t\text{-}BuNC)_2(MA)_2$	2185	2170	

it is apparent that introduction of the first olefin has a greater effect than introduction of the second. Removing one isocyanide from $NiL_3(MA)$ increases $\nu_{CN}{}^1$ of the two remaining isocyanides, but it is not possible to attribute this solely to an increase in electron density on the metal because the complex goes from four-coordinate tetrahedral to three-coordinate trigonal planar (if the olefin is considered to be a monodentate ligand). This change in coordination geometry could account for the 11 cm^{-1} change in $\nu_{NC}{}^1$. Thus while it might have been better to compare $Ni(t\text{-}BuN{\equiv}C)_2(P)_2$ with $Ni(t\text{-}BuN{\equiv}C)_2(\text{olefin})_2$, the greater variety of bis(isocyanide) monoolefin complexes is a more important factor.

Several of the compounds listed in Tables II and III have been reported.[20,24–26] Any discrepencies between the isocyanide stretching frequencies reported here and the earlier results can be attributed to misassignment of cyanide and isocyanide bands for some cyanoolefin complexes, differences in calibration, and the dissociation of the olefin complex (for unactivated olefins) to free olefin and $Ni_4(t\text{-}BuNC)_7$ in the absence of an excess of olefin. We have evidence which indicates this last complication can take place in Nujol or even in the solid state if the complexes are not scrupulously purified and dried before storage. The problem was corrected for unactivated olefins by using excess olefin to shift the equilibrium

$$\text{"}Ni(t\text{-}BuNC)_2\text{"} + \text{olefin} \rightleftharpoons Ni(t\text{-}BuNC)_2(\text{olefin})$$

to the right. In general, this was necessary with complexes having $\nu_{NC}{}^1 < 2150$ cm^{-1}; for some complexes with $\nu_{NC}{}^1 < 2135$ cm^{-1} it was necessary to use saturated THF solutions for solid olefins and neat olefin for some of those which are liquid. We were not able to measure ν_{NC} for the ethylene complex because of its low formation constant. Calculated (vide infra) values are included in Table II for completeness.

No dimethylamino or amino and few vinyl olefins have been included in Table II. Various deactivated olefins were investigated but they either formed no complex or coordinated by some means other than the vinyl group.

It has been reported[25] that the attempted preparation of $Ni(t\text{-}BuNC)_2(F_2C{=}CF_2)$ results in the metallocyclopentane product $Ni(t\text{-}BuNC)_2(-(CF_2)_4-)$. We also observed this reaction but were able to detect the intermediate olefin adduct by working quickly at reduced temperature, using a stoichiometric quantity of olefin. The bands attributable to the simple olefin complex disappear with time as the new bands of $Ni_4(t\text{-}BuNC)_7$ and the metallocycle grow in.

The large range of values for ν_{NC} tabulated in Table II demonstrates that the effects of consecutive addition of any particular substituent are approximately incremental. This effect is apparent in Figure 2. There are apparent saturation

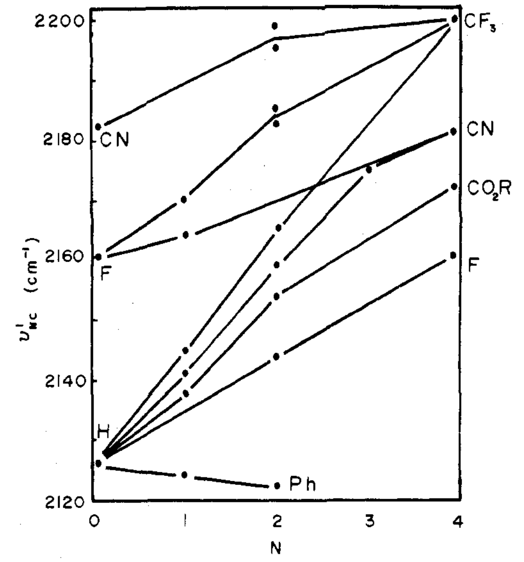


Figure 2. ν_{NC}^1 for a variety of olefins demonstrating the cumulative effects of substitution.

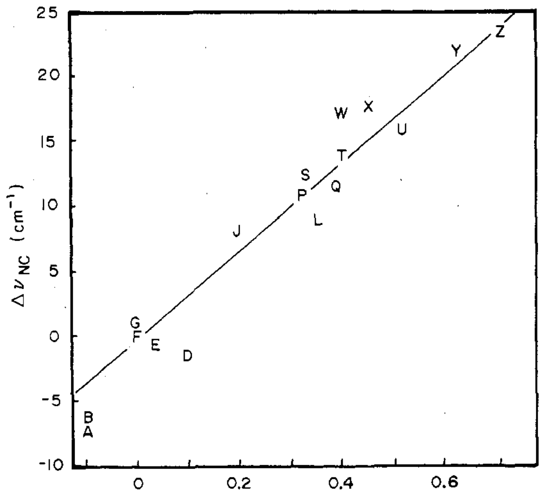


Figure 3. $\Delta\nu_{NC}^1$ vs. σ for selected substituents (35% **R**; see text).

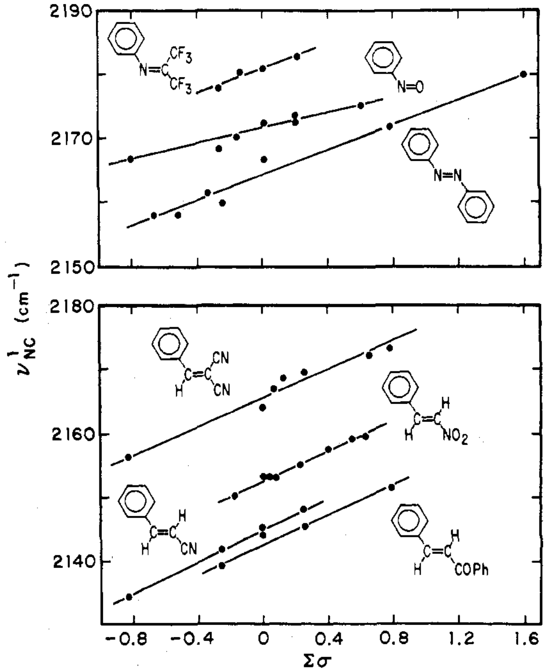


Figure 4. ν_{NC}^1 vs. the summation of the appropriate Hammett parameters for selected olefins, imines, diazenes, and nitroso compounds.

effects with addition of the third or fourth of a particular substituent, symbiotic effects between different groups, and isomer effects, but these are small when compared to the cumulative effects of added substituents. Thus it is possible to assign substituent contributions for electron withdrawal by olefins as has been done for phosphorus ligands. These contributions to ν_{CN}^1 were calculated using a least-squares routine for the more common substituents listed in Table IV. The equation fit was

$$\nu_{NC}^{\text{olefin}} = \nu_{NC}^{C_2H_4} + \sum^{i=1,4} p_i \qquad (1)$$

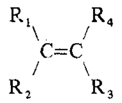
and the contribution of a hydrogen atom was zero by definition. All observations were given equal weighting. Contributions for substituents which appear only one or two times in the data were not included in the least-squares fitting but were calculated on the basis of the least-squares results. The results are given in Table IV. Observed values of ν_{NC}^1 and those calculated using eq 1 agree within 5 cm^{-1}. A similar calculation was carried out for ν_{NC}^2; all calculated and observed values of ν_{NC}^2 agree within 9 cm^{-1}.

It is informative to study the correlation between the calculated substituent contributions and a commonly used free-energy relationship. The Swain and Lupton[27] field (**F**) and resonance (**R**) components to substituent effects allow something to be said about the nature of the effect. It has already been observed[9] that the stability of a series of nickel olefin complexes correlates with the σ_p^+ constants which are 66% resonances in the terminology of Swain and Lupton. Other workers have observed better correlations with σ_M and σ_p (22% R and 53% R respectively) for complexes of Ag$^+$ and Fe^0,[10] respectively. In this system the best correlation with $\Delta\nu_{NC}$ for the olefin substituents is achieved using a combination of **F** and **R** having 35% sensitivity to resonance effects (Figure 3).

We also studied the dependence of ν_{NC}^1 on substituents on the aryl group of a number of different series of aryl olefins and found a good correlation with the sum of the appropriate Hammett parameters[28] (Figure 4). For each class of aryl olefins the dependence of ν_{NC}^1 on $\sum\sigma_{M,P}$ is the same. The intercepts of the various plots are dependent on the other substituents on the vinyl group. The slope of 12 cm^{-1} for cinnamonitriles, chalcones, β-nitrostyrenes, and α-cyanocinnamonitriles can be compared to one of 32 cm^{-1} for the various substituents bonded directly to the olefin. Thus, the electronic effects of substituents bonded to the ring are almost 40% of those bonded directly to the olefin, implying a delocalization of electron density throughout the entire olefin. The slope of 12 cm^{-1} can be used in the calculation of ν_{NC}^1 and the corresponding value for ν_{NC}^2 is also 12 cm^{-1}. It would have been expected that the value for ν_{NC}^2 would be larger than the value for ν_{NC}^1 because Table II shows a greater range of ν_{NC}^2 values, but this was not observed. This low value may be attributed in part to the greater errors in prediction of ν_{NC}^2.

The delocalization throughout the entire olefin of electron density removed from the metal by the π-acceptor orbitals of the olefin can be explained qualitatively on the basis of frontier orbitals.[29] Using cyano olefins as an example, the donor HOMO is localized mostly on the double bond but the acceptor LUMO has a moderate interaction with the cyano groups. As the number of cyano groups is increased, the LUMO becomes more nitrile in nature. Bonding to the metal has the net effect of transferring some electron density from the more localized HOMO into the delocalized LUMO; as this takes place, the two orbitals must approach each other in energy. Thus while it must be kept in mind that the frontier

Table II. Values of ν_{NC} and Stabilization Energies for a Variety of Olefins



	Olefin							
No.	R_1	R_2	R_3	R_4	$\nu_{NC}{}^{1\,a}$	$\nu_{NC}{}^{2\,a}$	ν_{CN}	$-\Delta H^b$
9	Ph	H	Ph	H	2122	2087		−5.9
10	Ph	H	H	H	2124	2088		
11	H	H	H	H	2128	2190		0.0
12	COH	Me	H	H	2129	2102		
13	CO_2Me	Me	H	H	2130	2093		
14	CO_2Et	H	Me	H	2130	2107		
15	$CONH_2$	Me	H	H	2130	2088		
16	COMe	H	Me	Me	2131	2093		
17	CO_2Me	H	Me	H	2131	2093		8.9
18	H	$CO-(CH_2)_2-CH_2$		H	2132	2194		
19	$CONH_2$	H	H	H	2133	2088		
20	H	$CO-CH_2-CH_2$		H	2133	2097		
21	H	$CO-(CH_2)_3-CH_2$		H	2134	2093		
22	$4\text{-}Me_2NC_6H_4$	H	CN	H	2134	2100	2189	
23	$CONH_2$	H	Ph	H	2135	2098		
24	CH=CHMe	H	CO_2Et	H	2136	2100		
25	$P(S)Me_2$	H	H	H	2137	2099		
26	C_6F_5	H	H	H	2138	2099		
27	CH=CHMe	H	COH	H	2138	2100		
28	CO_2Me	H	H	H	2138	2110		
29	COMe	H	H	H	2139	2099		
30	$4\text{-}MeOC_6H_4$	H	COPh	H	2139	2104		
31	CN	H	H	Et	2140	2098	2193	
32	CN	H	Et	H	2140	2100	2195	
33	CF_3	Me	H	H	2140	2100		
34	CO_2Me	H	Ph	H	2140	2104		19.2
35	COH	H	H	H	2140	2105		
36	CN	Me	H	H	2141	2101	2192	
37	CN	H	H	Me	2141	2102	2193	
38	CN	H	H	H	2141	2102	2198	18.9
39	COMe	H	Ph	H	2141	2103		22.2
40	$4\text{-}MeOC_6H_4$	H	CN	H	2141	2105	2192	
41	CN	H	Me	H	2142	2102	2195	
42	COH	H	Ph	H	2143	2107		
43	F	H	F	H	2144	2109		−6.7
44	Ph	H	COPh	H	2144	2110		
45	$4\text{-}FC_6H_4$	Ph	Ph	CF_3	2145	2102		
46	CO_2Et	CO_2Et	Me	H	2145	2104		
47	$SiCl_3$	H	H	H	2145	2104		
48	Ph	Ph	H	COH	2145	2105		
49	CF_3	H	H	H	2145	2105		
50	Me	CH_2-CHCN		H	2145	2107	2197	
51	$4\text{-}ClC_6H_4$	H	COPh	H	2145	2108		
52	CH_2CH_2CN	CN	H	H	2145	2110	2190, 2250	
53	$3,4\text{-}CH_2O_2C_6H_3$	H	CN	H	2145	2110	2193	
54	Ph	H	CN	H	2145	2112	2194	15.1
55	$4\text{-}ClC_6H_4$	CF_3	Ph	Ph	2146	2105		
56	$CF_2-CF_2-CH_2$		H	H	2146	2110		
57	Ph	Ph	CN	Ph	2148	2110	2195	
58	$4\text{-}ClC_6H_4$	H	CN	H	2148	2114	2200	
59	CO_2Et	CO_2Et	H	Ph	2150	2112		
60	SO_2Me	H	H	H	2150	2114		
61	$3,4\text{-}(MeO)_2C_6H_3$	H	NO_2	H	2150	2115		
62	$4\text{-}NO_2C_6H_4$	H	COPh	H	2151	2117		
63	CF_3	Ph	Ph	F	2152	2114		
64	CO_2Me	CF_3	Ph	Ph	2153	2116		
65	Ph	H	NO_2	H	2153	2118		
66	$3\text{-}F\text{-}4\text{-}MeOC_6H_3$	H	NO_2	H	2153	2118		
67	$2\text{-}MeO\text{-}5\text{-}BrC_6H_3$	H	NO_2	H	2153	2118		
68	$4FC_6H_5$	CF_3	F	Ph	2153	2118		
69	CN	OCOMe	H	H	2153	2118	2204	
70	$4ClC_6H_4$	H	NO_2	H	2154	2117		23.8
71	CO_2Me	H	H	CO_2Me	2154	2120		46.1
72	$C_4H_3O^c$	H	NO_2	H	2155	2119		
73	CH=CHCN	H	CN	H	2155	2124	2200, 2218	
74	Ph	CF_2-CF_2		Ph	2156	2121		
75	$4\text{-}Me_2NC_6H_4$	H	CN	CN	2156	2139	2200, 2208	
76	$2\text{-}BrC_6H_4$	H	NO_2	H	2157	2123		
77	CN	CN	SMe	SMe	2157	2124	2201, 2190	
78	CN	Cl	H	H	2157	2130	2201	

Table II (*Continued*)

No.	Olefin				$\nu_{NC}{}^{1\,a}$	$\nu_{NC}{}^{2\,a}$	ν_{CN}	$-\Delta H^b$
	R_1	R_2	R_3	R_4				
79	H	CO-NEt-CO		H	2158	2120		
80	3-NCC_6H_4	H	NO_2	H	2158	2123	2230	
81	4-$MeOC_6H_4$	CF_3	4-$MeOC_6H_4$	CF_3	2158	2123		54.1
82	3,4-$Cl_2C_6H_3$	H	NO_2	H	2158	2124		
83	2-ClC_6H_4	H	$CONH_2$	CN	2158	2125	2195	
84	Me	CO-O-CO		Me	2158	2126		
85	CF_3	H	F	F	2158	2135		
86	CO_2Me	H	CO_2Me	H	2159	2120		
87	CN	H	CN	H	2159	2136	2202	62.9
88	F	F	F	F	2160	2120		−3.7
89	COPh	H	COPh	H	2160	2127		
90	H	CO-CH_2-CO		H	2160	2128		78.8
91	H	CO-O-CO		H	2161	2128		
92	CF_3	Ph	Ph	CF_3	2161	2128		
93	H	CF_2-CF_2		H	2162	2124		36.6
94	4-$MeOC_6H_4$	CF_3	CF_3	4-$MeOC_6H_4$	2162	2125		
95	CF_3	CF_3	Ph	Ph	2163	2128		
96	CF_3	CF_3	Ph	$C_4H_3S^c$	2163	2130		
97	CN	CN	Ph	H	2164	2138	2200, 2210	
98	CN	F	F	F	2164	2142	2190	
99	CF_3	H	CF_3	H	2165	2128		
100	1-$C_{10}H_7$	H	CN	CN	2165	2142	2209, 2202	
101	OMe	CF_2-CF_2		F	2167	2128		
102	2,5-$(MeO)_2C_6H_3$	H	CN	CN	2167	2136	2210, 2200	
103	CN	CN	Ph	Ph	2167	2140	2209, 2203	
104	4-FC_6H_4	H	CN	CN	2167	2142	2207, 2200	
105	OMe	F	CF_3	F	2168	2134		
106	OMe	CF_2-CF_2		Cl	2168	2137		
107	3-$MeOC_6H_4$	H	CN	CN	2168	2138	2215, 2205	
108	4-ClC_6H_4	H	CN	CN	2169	2144	2214, 2207	
109	CF_3	F	F	F	2170	2130		
110	CF_3	H	CF_3	F	2170	2137		
111	CF_3	CF_3	Ph	F	2172	2140		
112	4-NCC_6H_4	H	CN	CN	2172	2143	2222, 2214	
113	CO_2Et	CO_2Et	CO_2Et	CO_2Et	2173	2140		88.0
114	4-$NO_2C_6H_4$	H	CN	CN	2173	2145	2208, 2200	
115	Ph	CF_2-CO		Cl	2173	2145		
116	CF_2-CF_2		F	F	2174	2148		
117	4-$Me_2NC_6H_4$	C_2F_5	CN	CN	2174	2150	2210	
118	CN	CN	CN	Ph	2174	2152	2228, 2222	
119	CN	CN	CN	H	2175	2154	2227, 2220	
120	CF_3	CF_3	CF_3	Ph	2177	2148		
121	Ph	CF_3	CN	CN	2178	2155	2198	
122	F	CF_2-CF_2		F	2179	2148		
123	CF_3	CF_2Cl	CN	CN	2179	2152	2218	
124	F	CF_2-CF_2-CF_2		F	2181	2153		
125	Cl	CF_2-CF_2		Cl	2182	2152		
126	CN	CN	CN	CN	2182	2154	2234, 2220	78.3
127	F	CF_2-$(CF_2)_2$-CF_2		F	2182	2157		
128	CF_3	CF_3	F	F	2183	2155		
129	CF_3	CO-O-CO		H	2184	2158		
130	CF_3	F	CF_3	F	2185	2152		
131	CF_3	CF_3	CN	CN	2195	2174	2216	97.3
132	CF_3	CN	CF_3	CN	2200	2173	2220	
133	CF_3	CF_3	CF_3	CF_3	2200	2173		80.8

[a] For the complex Ni(*t*-BuNC)$_2$(olefin) (cm^{-1}) estimated error is 2 cm^{-1}. [b] For the reaction $Ni(PPh_3)_2(C_2H_4)$ + olefin → $Ni(PPh_3)_2$(olefin) + C_2H_4 (kJ/mol) estimated error is 4 kJ mol^{-1}. [c] C_4H_3O = 2-furyl, C_4H_3S = 2-thyenyl, $C_{10}H_7$ = 1-naphthyl.

orbital approach is normally to be limited to kinetic effects, it does provide a useful model for the overall bonding. There are undoubtedly cases where changes in the olefin orbitals upon bonding are sufficient to render this approach inappropriate. One such example would be halo olefins for which it has been observed that distortions from olefin geometry are most pronounced.[1]

The effects of ring size on stability constants have been noted in earlier studies. We found that for perfluorocycloolefins there is a small but steady increase in ν_{NC} as ring size increases (**122**, **124**, **126**). The small change makes it impossible to draw conclusions because the change is in the order expected for chain lengthening in acyclic olefins ($\Delta\nu_{NC}$ for C_2F_5 is greater than for CF_3). The acyclic olefin **130** causes an even greater shift.[3] Tetrafluorocyclobutenes (**74**, **93**, **101**, **106**, and **122**) form a well-behaved series of complexes. The 1,2-CF_2CF_2 contributes 31.1 and 33.4 cm^{-1} to $\nu_{NC}{}^1$ and $\nu_{NC}{}^2$, respectively, considerably less than the contributions of two trifluoromethyl groups. This weakened π-acceptor capability may be due partly to the strained nature of the olefin. The greatly strained 1,1-CF_2CF_2 of perfluoromethylenecyclopropane (**116**) weakens the back-bonding even more; this unstable complex undergoes further reaction on standing to give what is presumably a ring-opening product. In a series of cycloalkenones (**18**, **20**, and **21**), ring size again has a very minimal effect on the π-acceptor properties. The primary effects on electron withdrawal are due to the substituents, and perturbations such as ring strain are secondary. Considerably more work will be

Table III. Values of ν_{NC} for a Variety of Unsaturated Molecules in $Ni(t\text{-}BuNC)_2(Un)$ (cm^{-1})

Acetylenes ($R_1C{\equiv}CR_2$)

	R_1	R_2	ν_{NC}^1	ν_{NC}^2
134	Et	Et	2122	2095
135	Ph	Me	2125	2090
136	Ph	Ph	2138	2100
137	Ph	COMe	2144	2109
138	Ph	COH	2145	2113
139	Ph	C_6F_5	2147	2110
140	CO_2Me	CO_2Me	2160	2123
141	CF_3	CF_3	2169	2134

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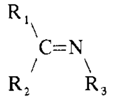
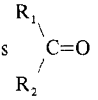


$R_1(R_2)C{=}NR_3$

	R_1	R_2	R_3	ν_{NC}^1	ν_{NC}^2
142	CF_3	CF_3	Me	2168	2130
143	CF_3	CF_3	OMe	2170	2138
144	CF_2Cl	CF_2Cl	H	2171	2135
145	CF_3	CF_3	$4\text{-}MeOC_6H_4$	2178	2148
146	CF_3	CF_3	OH	2179	2149
147	CF_3	CF_2H	H	2180	2143
148	CF_3	CF_3	$4\text{-}MeC_6H_4$	2180	2149
149	CF_3	CF_3	H	2182	2150
150	CF_3	CF_3	Ph	2182	2154
151	CF_3	CF_3	$4\text{-}ClC_6H_4$	2183	2158
152	CF_3	CF_3	$OCOCF_3$	2206	2183

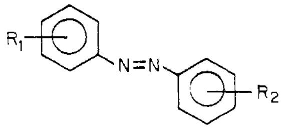
Ketones



$R_1(R_2)C{=}O$

	R_1	R_2	ν_{NC}^1	ν_{NC}^2
153	CF_3	$ON{=}C(CF_3)_2$	2155	2132
154	CO_2Me	Me	2158	2118
155	CO_2Et	Ph	2163	2124
156	CO_2Me	Ph	2164	2128
157	CF_3	Me	2165	2120
158	CF_3	Ph	2169	2130
159	CN	Ph	2173	2138
160	CO_2Et	CO_2Et	2173	2140
161	C_2F_5	F	2180	2144
162	$CF_2{=}CF$	F	2182	2154
163	CF_3	CF_3	2188	2153

Azobenzenes

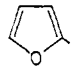


	R_1	R_2	ν_{NC}^1	ν_{NC}^2
164	$4\text{-}NH_2$	H	2158	2132
165	4-MeO	4-MeO	2158	2129
166	$3,5\text{-}Me_2$	$3,5\text{-}Me_2$	2160	2138
167	4-Me	4-Me	2161	2130
168	H	H	2167	2132
169	$4\text{-}NO_2$	H	2172	2144
170	$4\text{-}NO_2$	$4\text{-}NO_2$	2180	2155

Nitrosobenzenes R-NO

	R	ν_{NC}^1	ν_{NC}^2
171	$4\text{-}Et_2NC_6H_4$	2165	2130
172	$4\text{-}Me_2NC_6H_4$	2166	2131
173	$4\text{-}MeOC_6H_4$	2168	2134
174	$4\text{-}MeC_6H_4$	2170	2136
175	Ph	2172	2138
176	$4\text{-}ClC_6H_4$	2173	2140
177	$4\text{-}CO_2EtC_6H_4$	2174	2143
178	$3,4\text{-}Cl_2C_6H_3$	2175	2143
179	C_6F_5	2179	2152
180	CF_3	2190	2176
181	Dioxygen	2196	2178

Table IV. Contributions to ν_{NC}^1 and ν_{NC}^2 for a Variety of Olefin Substituents (cm^{-1})

		$\Delta\nu_{NC}^1$	$\Delta\nu_{NC}^2$
A	Et	−7	−9
B	Me	−6.2	−9.1
C	CH=CHMe	−3	−5
D	SMe	−2	−8
E	Ph	−0.6	−0.7
F	H	0	0
G	OMe	1.0	−0.8
H		4	2
I	$CONH_2$	6.8	5.1
J	F	8.2	9.4
K	$C_6H_4NO_2$	9	9
L	OCOMe	9	7
M	$P(S)Me_2$	9	9
N	C_6F_5	10	9
O	CH=CHCN	11	13
P	Cl	11.1	15.3
Q	CO_2Et	11.4	14.2
R	COH	11.5	18.4
S	CO_2Me	12.4	14.6
T	COPh	14.0	18.2
U	CN	15.9	21.1
V	$SiCl_3$	17	14
W	COMe	17.3	21.0
X	CF_3	17.7	20.4
Y	SO_2Me	22	24
Z	NO_2	23.5	27.7

Ethylene basis $\nu_{NC}^1 = 2128$, $\nu_{NC}^2 = 2090$

needed before these effects can be fully delineated.

The isocyanide stretching frequencies for complexes having C=C, C=N, C=O, N=N, N=O, and O=O groups π bonded to zerovalent nickel are reported in Table III. It was not possible to clearly establish the basis ν_{NC}^1 for the nonsubstituted (perhydro) species because very few of the unsaturated molecules had even one hydrogen substituent. This was the case for acetylenes because the attempted use of monosubstituted acetylenes resulted in cluster species which were not characterized. In the other species, the hydro moieties simply were not available. Nonetheless, by comparison of similarly substituted species the following estimates of ν_{NC}^1 can be made: 2128, 2150, 2160, 2170, 2175, and 2196 cm^{-1} for $H_2C{=}CH_2$, $H_2C{=}NH$, $H_2C{=}O$, $HN{=}NH$, $HN{=}O$, and $O{=}O$, respectively. These effects can be attributed to the increasing electronegativity of the double-bond atoms. As the electronegativity increases, the π-acceptor character becomes increasingly important to the overall bonding. The analogy between $={C(CN)_2}$ and $=O$ in organic molecules has already been discussed at length.[30] We find that the analogy is also useful in this system. Cyano or trifluoromethyl groups increase the apparent electronegativity of C and N such that R_2C, RN, and O are equivalent and RC and HN are equivalent when R = CF_3 or CN. Thus $(CF_3)_2C{=}C(CF_3)_2$, $(CF_3)_2C{=}O$, CF_3NO, and $O{=}O$ result in ν_{NC}^1 of 2200, 2188, 2190, and 2196 cm^{-1}, respectively.

The π-acceptor capabilities of acetylenes are enhanced by the extra orbitals of the triple bond. Thus, an estimate of ν_{NC}^1 = 2136 cm^{-1} for unsubstituted acetylene is readily explicable. A comparison of ν_{NC}^1 for selected acetylene and similarly substituted olefin complexes (Figure 5) demonstrates that the isocyanide stretching frequencies of the acetylene complexes are less sensitive to substitution than are those of the olefin complexes. This and the higher value of ν_{NC}^1 for acetylene relative to ethylene indicate that while carbon–carbon triple bonds are better π-acceptor ligands than olefins, the back-bonded electron density remains more localized in coordinated triple bonds.

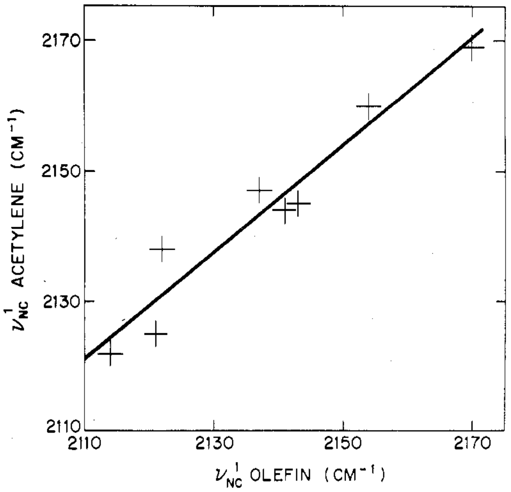


Figure 5. Relation between $\nu_{NC}{}^1$ for complexes of selected acetylenes and complexes of similarly substituted olefins.

It has already been shown that there is a good correlation between the effects of substituents on the aryl group of aryl olefins and the sums of the appropriate Hammett parameters. This is also true for aryl groups attached to the heteroatomic bridges, but as the heteroatomic bridges become more electronegative, the slopes of the appropriate Hammett correlations (Figure 4) decrease. The values observed for olefins, imines, diazenes, and nitrosobenzenes are 12, 10, 9, and 6 cm^{-1}, respectively. Thus, as the electronegativity of the coordinated double bond increases, the dependence of $\nu_{NC}{}^1$ on the aryl substituents decreases. The aryl group does not compete as well with the more electronegative bridge for the back-bonded electron density; there is less delocalization of this electron density to the aromatic portion of the molecule. A similar result has been noted in a series of π-carboxo complexes[26] where the sensitivity to substitutent changes was 80% of that for similarly substituent olefins.

Enthalpic Studies

The above effects are an indication of the electron transfer between the metal and the coordinated olefin. It was felt that there should be some relationship between these effects and the strength of the metal–olefin bond. To test this hypothesis, a series of calorimetric measurements were made. The reaction studied was

$$\mathrm{Ni(PPh_3)_2(olefin)} + \mathrm{(CN)_2C{=}C(CF_3)_2} \xrightarrow{-\Delta H} \mathrm{Ni(PPh_3)_2((CN)_2C{=}C(CF_3)_2)} + \text{olefin}$$

This system was chosen for several reasons. The starting complexes are easily prepared using a standard technique; the complexes are stable to dissociation in solution in the absence of other ligands; the reaction is fast, giving more reliable data than would be obtained from a slower reaction. While it would have been nice to use complexes of the type Ni(t-BuNC)$_2$ (olefin), there is a complicating equilibrium to Ni$_4$(t-BuNC)$_7$ and free olefin for the more weakly bound olefins. Reaction of olefins with Ni(PPh$_3$)$_2$(C$_2$H$_4$) was also studied but unactivated olefins react too slowly to give reliable results. More highly activated olefins react more rapidly; cyanoolefin and nitroolefin reactions were among the most rapid. This kinetic effect may be related to the frontier orbitals and suggests an interesting area of research.

The observed heats of reaction tabulated in Table II range over 100 kJ mol^{-1} in metal–olefin bond strengths. The only metal–olefin system studied to date which has a larger range of ΔH is the platinum analogue.[31-33] In the platinum system, the range between C$_2$H$_4$ and TCNE is 156 ± 8 kJ mol^{-1} compared with 78 kJ mol^{-1} in the nickel system.

Table V. Contributions to Stabilities of Olefin Complexes (kJ mol^{-1})

Me	−13	CN	20
Ph	−3	CO$_2$R	22
F	−2	COMe	25
H	0	CF$_3$	25
		NO$_2$	27

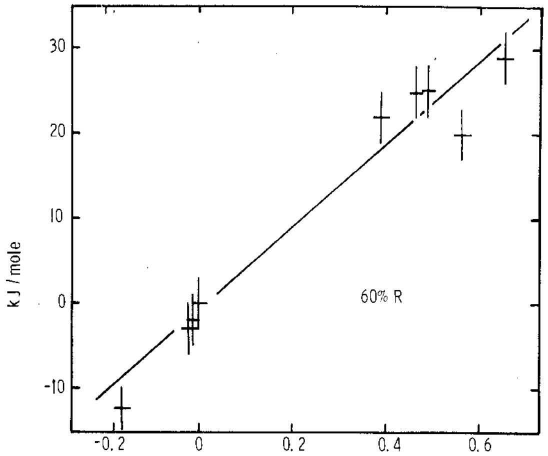


Figure 6. $\Delta(-\Delta H)$ vs. σ for selected substituents (60% **R**; see text).

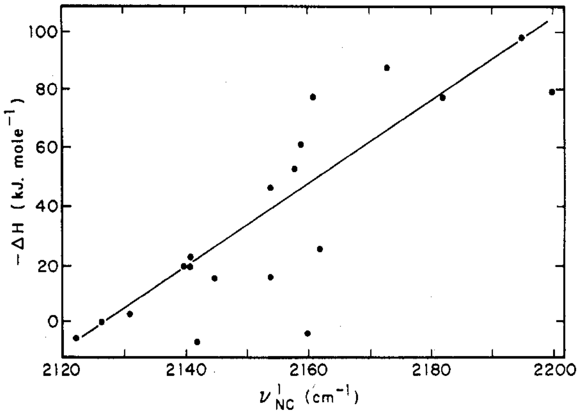


Figure 7. Stability vs. $\nu_{NC}{}^1$ for selected olefins in the complex Ni(t-BuNC)$_2$(olefin).

As was the case for ν_{NC}, olefin substituents have a cumulative effect on the metal–olefin bond strength. Thus, it is possible to calculate contributions to the heats of reaction for the various substituents. The values in Table V have relatively large errors associated with them because far fewer heats of reaction for olefins were measured. Nonetheless, the heats of reaction can be calculated reasonably well. It is found that the correlation between these values and the contributions to ν_{NC} is not exceptionally good but a reasonable correlation is observed when the enthalpic contributions are compared with a mixture of Swain and Lupton coefficients having sensitivity to resonance effects of approximately 60% **R** (Figure 6). This is in agreement with the correlation of ΔG with $\sigma_p{}^+$ (66% **R**) by Tolman[9] for a similar system. Thus while the electronic factors involving metal orbitals which contribute to variations in the isocyanide stretching frequencies are largely inductive in nature, the overall bonding is more sensitive to resonance effects.

These results shed some light on an interesting effect in olefins bearing fluoro or methoxy groups. Figure 7 displays the correlation between $\nu_{NC}{}^1$ and $-\Delta H$; the points falling well below the line are those involving fluoro substituents. Because these groups are resonance donating but inductively withdrawing in nature, seemingly anomalous results are obtained.

Using tetrafluoroethylene (**88**) as an example, ν_{NC}, which is dependent on inductive effects indicates that **88** is a good π-acceptor ligand. This is in contrast to the measured stability of the complex which is more strongly influenced by resonance effects. Thus, it becomes clear in this case that enhanced back-bonding is offset by weakened forward bonding and there is little net change in bond strength upon fluorine substitution.

Another seemingly anomalous situation exists in the stabilities of **127b**, **131b**, and **133b**. One would expect the stability of the complex containing the mixed substituent olefin bis(trifluoromethyl)dicyanoethylene to fall between the stabilities of the TCNE and tetrakis(trifluoromethyl)ethylene complexes. That this is not the case might be attributed to a saturation effect in the tetrakis complexes but at present this is not clear.

Using unsaturated molecules other than olefins, the stabilities of the complexes relative to ethylene parallel the isocyanide stretching frequencies. Thus, diphenylacetylene and azobenzene complexes are 15.5 and 35.6 kJ mol^{-1} more stable than the ethylene complex. This is in good agreement with conclusions drawn from structural results earlier. The enhanced back-bonding capabilities of these new bridges enable them to form stronger complexes. It is found[31] that ΔH for diphenylacetylene in the platinum analogue is -82 ± 12 kJ mol^{-1}. Thus, as for olefin complexes, zerovalent platinum forms an appreciably stronger bond to molecules having good π-acceptor characteristics.

Conclusions

The results of the nickel–olefin studies indicate that in the coordination of an olefin to an electron-rich nickel atom inductive effects are important in the distribution of electron density between the nickel atom and the coordinated olefin; resonance effects are more important in determination of the metal–olefin bond strength. The electron distribution and the metal–olefin bond strength are strongly influenced by the nature and number of substituents on the olefin. The effects are cumulative and can be predicted by an empirical method. The electron density transferred from the metal to the π-acceptor orbitals of the double bond is not localized on the double bond but delocalized throughout the olefin. Thus, in aryl olefin complexes, substituent changes on the aryl group have almost 40% of the effect of substituent changes directly on the olefin. These observations are not incompatible with the generalized Dewar–Chatt–Duncanson model for olefin bonding. It is clear that substituent effects play a very important part in olefin bonding and must be dealt with by any more detailed model. The degree of electron transfer forms a broad continuum, though that portion localized on the coordinated double bond is limited.

When other unsaturated molecules are coordinated to the nickel atom, the π-acceptor properties of the double bonds are dependent on the electronegativity of the bridging atoms. The effects of substituent changes decrease as the electronegativity of the bridge increases. The "heteroolefinic" bridges $C{=}N$, $C{=}O$, $N{=}N$, and $N{=}O$ are respectively 83, 80, 75, and 50% as sensitive to substituent effects as are olefins. Thus, the "heteroolefins" have a higher concentration of electron density on the coordinated double bond; this electron density is not delocalized to substituents as much as is observed with olefins.

The same phenomenon is observed with acetylenes. The greater back-bonding is not attributed to the greater electronegativity of sp hybridized carbon atoms relative to sp^2 but rather to the extra set π^* orbitals of the triple bond. Again there is a greater localization of electron density on the triple bond and the sensitivity to substituent effects is only 80% as great as observed for similarly substituted olefins.

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Registry No. **1**, 63688-70-0; **2**, 63713-98-4; **3**, 56386-31-3; **4**, 63688-71-1; **5**, 63688-72-2; **6**, 63688-73-3; **7**, 63688-74-4; **8**, 63688-75-5; **9a**, 63729-72-6; **9b**, 12151-25-6; **10a**, 63688-76-6; **11a**, 63688-77-7; **11b**, 23777-40-4; **12a**, 63688-78-8; **13a**, 63688-79-9; **14a**, 63679-37-8; **15a**, 63702-02-3; **16a**, 63679-38-9; **17a**, 63679-39-0; **17b**, 63679-40-3; **18a**, 63679-41-4; **19a**, 63679-42-5; **20a**, 63679-43-6; **21a**, 63679-44-7; **22a**, 63679-45-8; **23a**, 63679-46-9; **24a**, 63679-47-0; **25a**, 63679-48-1; **26a**, 63679-49-2; **27a**, 63679-50-5; **28a**, 63688-59-5; **29a**, 63688-60-8; **30a**, 63688-61-9; **31a**, 63688-62-0; **32a**, 63729-71-5; **33a**, 63688-63-1; **34a**, 63688-64-2; **34b**, 63688-65-3; **35a**, 63688-66-4; **36a**, 63713-99-5; **37a**, 63783-41-5; **38a**, 63688-67-5; **38b**, 63688-68-6; **39a**, 63688-69-7; **39b**, 63576-75-0; **40a**, 63702-19-2; **41a**, 63702-21-6; **42a**, 63679-25-4; **43a**, 63679-26-5; **43b**, 63702-20-5; **44a**, 63679-27-6; **45a**, 63679-28-7; **46a**, 63679-29-8; **47a**, 63679-30-1; **48a**, 63679-31-2; **49a**, 63679-32-3; **50a**, 63679-33-4; **51a**, 63679-34-5; **52a**, 63679-35-6; **53a**, 63679-36-7; **54a**, 63679-10-7; **54b**, 63679-11-8; **55a**, 63679-12-9; **56a**, 63679-13-0; **57a**, 63679-14-1; **58a**, 63679-15-2; **59a**, 63679-16-3; **60a**, 63679-17-4; **61a**, 63679-18-5; **62a**, 63679-19-6; **63a**, 63679-20-9; **64a**, 63679-21-0; **65a**, 63679-22-1; **66a**, 63679-23-2; **67a**, 63679-24-3; **68a**, 63688-46-0; **69a**, 63688-47-1; **70a**, 63688-48-2; **70b**, 63688-49-3; **71a**, 35914-95-5; **71b**, 36351-97-0; **72a**, 63688-50-6; **73a**, 63688-51-7; **74a**, 63688-52-8; **75a**, 63688-53-9; **76a**, 63688-54-0; **77a**, 63688-55-1; **78a**, 63688-56-2; **79a**, 63688-57-3; **80a**, 63688-58-4; **81a**, 63678-91-1; **81b**, 63679-00-5; **82a**, 63679-01-6; **83a**, 63679-02-7; **84a**, 63679-03-8; **85a**, 63679-04-9; **86a**, 63729-70-4; **87a**, 63701-61-1; **87b**, 63679-05-0; **88a**, 63679-06-1; **88b**, 30138-17-1; **89a**, 63679-07-2; **90a**, 63679-08-3; **90b**, 63679-09-4; **91a**, 32649-38-0; **92a**, 63678-89-7; **93a**, 63678-90-0; **93b**, 63702-14-7; **94a**, 63678-91-1; **95a**, 63678-92-2; **96a**, 63678-93-3; **97a**, 63678-94-4; **98a**, 63678-95-5; **99a**, 63678-96-6; **100a**, 63678-97-7; **101a**, 63702-15-8; **102a**, 63678-98-8; **103a**, 63702-16-9; **104a**, 63678-99-9; **105a**, 63702-17-0; **106a**, 63678-76-2; **107a**, 63678-77-3; **108a**, 63678-78-4; **109a**, 34779-37-8; **110a**, 63678-79-5; **111a**, 63678-80-8; **112a**, 63678-81-9; **113a**, 63702-18-1; **113b**, 63678-82-0; **114a**, 63678-83-1; **115a**, 63678-84-2; **116a**, 63678-85-3; **117a**, 63678-86-4; **118a**, 63678-87-5; **119a**, 63678-88-6; **120a**, 63678-65-9; **121a**, 63678-66-0; **122a**, 63678-67-1; **123a**, 63678-68-2; **124a**, 63702-03-4; **125a**, 63678-69-3; **126a**, 24917-37-1; **126b**, 63678-70-6; **127a**, 63702-04-5; **128a**, 63678-71-7; **129a**, 63678-72-8; **130a**, 63678-73-9; **131a**, 34779-36-7; **131b**, 63678-74-0; **132a**, 63678-75-1; **133a**, 63678-58-0; **133b**, 63678-59-1; **134**, 63678-60-4; **135**, 63678-61-5; **136**, 32802-08-7; **137**, 63678-62-6; **138**, 63702-05-6; **139**, 63678-63-7; **140**, 63678-64-8; **141**, 57903-01-2; **142**, 63702-06-7; **143**, 63702-07-8; **144**, 63702-08-9; **145**, 63702-09-0; **146**, 63702-10-3; **147**, 63678-45-5; **148**, 63678-46-6; **149**, 63678-47-7; **150**, 63678-48-8; **151**, 63678-49-9; **152**, 63678-50-2; **153**, 63702-12-5; **154**, 63702-13-6; **155**, 63678-51-3; **156**, 63678-52-4; **157**, 63678-53-5; **158**, 63678-54-6; **159**, 63678-55-7; **160**, 63678-56-8; **161**, 63678-57-9; **162**, 63678-37-5; **163**, 63678-38-6; **164**, 63678-39-7; **165**, 63678-40-0; **166**, 63678-41-1; **167**, 63678-42-2; **168**, 32714-19-5; **169**, 63702-11-4; **170**, 63678-43-3; **171**, 63678-44-4; **172**, 57761-86-1; **173**, 57718-91-9; **174**, 57718-90-8; **175**, 57718-89-5; **176**, 57718-87-3; **177**, 63678-35-3; **178**, 57718-86-2; **179**, 63702-01-2; **180**, 63678-36-4; **181**, 19633-19-3.

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(23) For an ethylene complex, the symmetry would be C_{2v} and $\nu_{NC}{}^1$ and $\nu_{NC}{}^2$ would be A_1 and B_1. Substitution reduces the symmetry to C_2 (trans disubstitution), C_s (gem or cis disubstitution), or C_1 (mono or trisubstitution).

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Chemistry of Tetravalent Nickel and Related Species. 3.[1] Characterization and Cyclic Voltammetry of New NiN_6 Species Based on Tridentate Ligands

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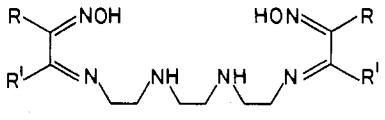
High-spin octahedral (NiN_6 core; $Dq \approx 1250\ cm^{-1}$) nickel(II) complexes of type $Ni(HRR'T)_2X_2$ (where HRR′T is a tridentate ligand of class *N*-β-aminoethylisonitroso ketimine and X = ClO_4, NO_3) are readily oxidized by concentrated nitric acid to yield the diamagnetic nickel(IV) species $Ni(RR'T)_2X_2$. Cyclic voltammetry (CV) of $Ni(RR'T)_2(ClO_4)_2$ has been thoroughly done in well-buffered aqueous media over a wide range of pH. Below pH 6.0, CV data show a single reversible two-electron, two-proton transfer process followed by an irreversible chemical decomposition of the nickel(II) species. The rate constant for this decomposition reaction has been determined to be $0.16\ s^{-1}$ (283 K) from CV data. In the pH range 7.0–9.0, two distinct reversible one-electron processes are observed corresponding to Ni(IV)–Ni(III) and Ni(III)–Ni(II) couples. The first of these has no proton involvement while the other involves one proton. The $E°'_{298}$ values for the various couples have been accurately determined from CV data. Representative results are as follows: $Ni(Me_2T)_2{}^{2+}$–$Ni(HMe_2T)_2{}^{2+}$, 0.71 V; $Ni(Me_2T)_2{}^{2+}$–$Ni(Me_2T)_2{}^{+}$, 0.40 V; $Ni(Me_2T)_2{}^{+}$–$Ni(HMe_2T)(Me_2T)^{+}$, 0.66 V; $Ni(Me_2T)_2{}^{+}$–$Ni(Me_2T)_2$, 0.07 V (estimated). The nickel(II) species involved in each of the above couples is what is expected from acid dissociation (oxime protons) data of $Ni(HMe_2T)_2{}^{2+}$ ($pK_1 = 7.80$; $pK_2 = 10.00$).

Introduction

The highest known oxidation state of nickel is IV. Only a very limited number of nickel(IV) species have been identified to date. These include[2-7] σ complexes having NiN_6, NiO_6, NiF_6, $NiAs_4X_2$, NiP_4X_2, NiS_6, and $NiSe_6$ coordination spheres and η^5 complexes derived from cyclopentadienyl, dicarbollide, and related anions. Our present concern lies with σ-NiN_6 species.[3] The only structurally definitive works[8] done till now concern two ligand systems: tridentate 2,6-diacetylpyridine dioxime[9,10] and hexadentate[1,11-13] $H_2RR'L$, **1**. It is believed[12] that in nickel(IV) complexes of these ligands, the negative charge on the oximato oxygen plays an important role in bringing about partial neutralization of the positive charge on the metal atom through inductive transmission and σ donation. In view of the interesting chemical and electrochemical results[1,11-13] obtained with complexes of **1**, it is of interest to investigate the behavior of the closely related chelate system derived from tridentate donors of type *N*-β-aminoethylisonitroso ketimine (**2**). The major results of this investigation are presented below. In what follows, the ligand **2** will be abbreviated as HRR′T. When R = R′, the abbreviation will be HR_2T.



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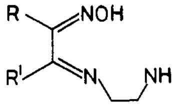

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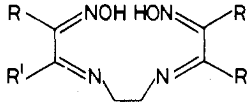

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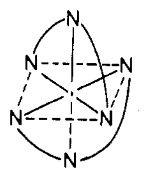

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Results and Discussion

A. Ligands and Their Nickel(II) Complexes. Three ligands of type **2**, viz., HMe_2T, HEtMeT, and HMeEtT, were obtained by condensing 1 mol of ethylenediamine with 1 mol of the appropriate isonitroso ketone. When 2 mol of isonitroso ketone is used, ligands of type **3** are obtained.[14] Ligands of type **2** are reported here for the first time. They show characteristic NH (3340–3150 cm^{-1}), OH (2650–2550 cm^{-1}), and C⩦N + C⩦C (1650–1610 cm^{-1}) stretches in the infrared spectra. The low frequency and broadness of the OH stretch suggest that the systems are strongly hydrogen bonded.

Red-brown nickel(II) species of type $Ni(HRR'T)_2{}^{2+}$ are readily obtained by reaction of nickel(II) salts with HRR′T in ethanolic solution. Nitrates and perchlorates of these cations have been isolated. These act as 1:2 electrolytes[15] in nitro-