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NEW π-CARBOXO COMPLEXES OF NICKEL(0)

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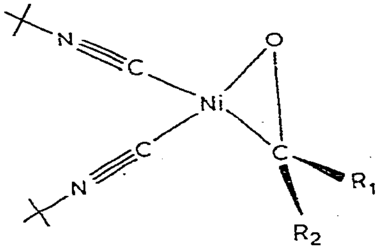
Summary

The synthesis of several new zerovalent nickel complexes containing carboxo coordinated organic molecules bearing substituents such as CN, CO_2R, CF_3, F, and $F_2C{=}CF$ demonstrates that a range of electron withdrawing functional groups is capable of effecting the necessary activation of the C=O bond to cause π-coordination.

The first complex of hexafluoroacetone was reported more than a decade ago [1]. The proposed π-coordination of the carboxo group was confirmed later crystallographically [2]. Reactions of these complexes with other unsaturated molecules to yield five membered metallocycles have received much attention [3]. More recently, π-coordinated complexes of benzaldehyde and benzophenone have been reported [4]. As part of a continuing [5] study of the electronic effects in bonding for olefin type π-complexes we have prepared a series of new π-bonded carboxo complexes of the type:



A variety of substituents withdraw enough electron density to activate the carboxo group and cause π-coordination.

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* Contribution no. 2460.

Experimental

All reactions were carried out in the nitrogen atmosphere of a Vacuum Atmospheres dry box. All solvents were dried and degassed by standard techniques prior to use. All of the carboxo compounds are commercially available; t-BuNC [6] and "Ni(t-BuNC)$_2$" [7] (actually a mixture of Ni$_4$(t-BuNC)$_7$ and Ni(t-BuNC)$_4$ having the given stoichiometry) were prepared by literature techniques. NMR spectra were obtained on Varian A-60 and XL-100 spectrometers in benzene-d_6 or toluene-d_8. Melting points are uncorrected. Infrared spectra were determined in tetrahydrofuran with a Perkin—Elmer 221 spectrometer calibrated with CO gas. Values of ν(NC) have an estimated error of 2 cm^{-1}. Analyses were performed in our microanalytical facilities. The complexes decompose upon exposure to air. The hexafluoroacetone adduct was prepared by the literature technique [8].

a. Preparation of nickel bis(t-butyl isocyanide)(π-diethyl ketomalonate)

A suspension of "Ni(t-BuNC)$_2$" (1.1 g, 5 mmol) in ether (20 ml) was treated with a slight excess of diethyl ketomalonate (1.0 g, 6 mmol) at room temperature. The red starting material dissolved and the yellow solution which formed was filtered. Evaporation of volatiles followed by recrystallization of the residue from pentane/ether at —40°C gave a yellow crystalline product which was collected and dried under vacuum. Yield 90%. M.p. 126—127°C. Anal. Found: C, 51.38; H, 7.07; N, 7.3; O, 19. $C_{17}H_{28}N_2NiO_5$ calcd.: C, 51.16; H, 7.07; N, 7.0; O, 20%.

b. Nickel bis(t-butyl isocyanide)(π-trifluoroacetophenone)

This complex was prepared using the procedure described above. The dark yellow complex was isolated in about 80% yield, m.p. 88—89°C (slow dec.). Anal. Found: C, 54.84; H, 5.84; N, 7.1; F, 13. $C_{18}H_{23}N_2NiOF_3$ calcd.: C, 54.71; H, 5.81; N, 7.0; F, 14%.

c. Nickel bis(t-butyl isocyanide)(methyl benzoylformate)

The preparation was similar to those above, giving the yellow product in about 75% yield, m.p. 147—149°C (slow dec.) Anal. Found: C, 58.82; H, 6.51; N, 7.5; O, 12. $NiC_{19}H_{26}N_2O_3$ calcd.: C, 58.65; H, 6.74; N, 7.2; O, 12%.

d. Nickel bis(t-butyl isocyanide)(π-benzoyl cyanide)

A suspension of "Ni(t-BuNC)$_2$" (1.1 g, 5 mmol) in ether was treated with a solution of benzoyl cyanide (0.65 g, 5 mmol) in ether at —40°C. The resulting yellow solution was evaporated giving a yellow solid which was recrystallized from pentane at —40°C. A solution of the yellow product in ether decomposed within hours at room temperature, precipitating golden solids which were not fully characterized. In the sample chamber of an infrared spectrophotometer decomposition was more rapid, occurring in minutes. The decomposition could be monitored by repeatedly scanning from 2300 to 1500 cm^{-1}.

Reactions of "Ni(t-BuNC)$_2$" with:

e. Methyl pyruvate. The desired Ni(0) adduct of methyl pyruvate could not be isolated even in the presence of a large excess of the ester. Evidence for its existence in solution could be obtained by the appearance of appropriate bands in the infrared spectrum as a great excess of the ligand was added to a tetrahydrofuran solution of "Ni(t-BuNC)$_2$".

f. Trifluoroacetone. Reaction of an ether solution of "Ni(t-BuNC)$_2$" with gaseous trifluoroacetone in an infrared cell gave evidence for adduct formation by appearance of the appropriate bands in the infrared spectrum at pressures around 1 atm. When the pressure was removed, trifluoroacetone was evolved and the bands of the starting material reappeared.

g. Acetophenone and acetone. Experiments similar to that described in *e* were carried out with acetophenone and acetone. No evidence of the desired adducts was obtained.

h. Trifluoroacetyl fluoride and trifluoroacryloyl fluoride. Reaction of these acyl fluorides with "Ni(t-BuNC)$_2$" at room temperature was rapid, yielding uncharacterized products. When the reactions were carried out at —40 to —60°C in an infrared cell, products having spectra appropriate for π-complexes were observed, but new bands similar to those of the room temperature species soon grew in as the π-complex bands faded.

Results

The reaction of diethyl ketomalonate with "Ni(t-BuNC)$_2$" in ether results in formation of nickel bis(t-butyl isocyanide)(π-diethyl ketomalonate). The isocyanide vibrational frequencies for this compound and all those to follow are listed in Table 1. The C=O bands attributable to the carboethoxy groups are shifted from 1760 and 1735 cm^{-1} for the free ligand to 1730 and 1710 cm^{-1} in the complex and ν(CO) of the π-bonded central carbonyl is shifted out of this range and is not assigned. The proton NMR spectrum of the product indicates that the ethyl groups are equivalent and the resonances shift 0.2 ppm up-

TABLE 1

ISOCYANIDE STRETCHING FREQUENCIES OF Ni(t-BuNC)$_2$(π-CARBOXO) COMPLEXES AND RELATED DISUBSTITUTED OLEFIN COMPLEXES[a,b]

Substituents		Carboxo		Olefin[c]		
R_1	R_2	ν^1(NC)	ν^2(NC)	Isomer	ν^1(NC)	ν^2(NC)
CO_2Me	Me[d]	[2158	2118]	*gem*	2130	2093
				trans	2131	2093
CO_2Me	Ph	2164	2128	*trans*	2140	2104
CF_3	Me	[2165	2120]	*gem*	2140	2100
CF_3	Ph	2169	2130	*gem*	2145	2110
CN	Ph	[2173	2138]	*trans*	2145	2112
CO_2Et	CO_2Et[d]	2173	2140	*cis*	2153	2120
				trans	2157	2119
CF_3	F	[2180	2144]	*gem*	2154	2121
CF_2=CF	F	[2182	2154]			
CF_3	CF_3	2188	2153	*trans*	2165	2128

[a] π-Carboxo complexes in brackets were not isolated or fully characterized. [b] In tetrahydrofuran solution. [c] From ref. 10. [d] Values of 2130 and 2154 cm^{-1} were used in Fig. 1 for the methyl carbomethoxy and bis(carboethoxy) olefins, respectively; the former because it was the *gem* isomer value and the latter because it has been observed [10] that *gem* values of ν^1(NC) are frequency closer to those of *cis*-isomers than *trans*-isomers.

field upon coordination (to 4.20 and 1.13 ppm, J(HH) 7 Hz). The t-butyl groups of the isocyanide ligands are observed at 0.88 ppm.

It is not necessary to have two activating groups on the carbonyl group as in hexafluoroacetone or diethyl ketomalonate. Trifluoroacetophenone, which is activated by only one trifluoromethyl group, also forms a π-complex with "Ni(t-BuNC)$_2$". The ^{19}F resonance of the trifluoromethyl group is shifted 7.1 ppm upfield to 64.67 ppm upon coordination; the 1 Hz coupling to the *ortho* hydrogen atoms is lost. The ^{1}H NMR resonances of the phenyl group are shifted upfield about 0.5 ppm and the t-butyl groups of the isocyanide ligands are observed at 0.84 ppm. A similar π-complex is formed with methyl benzoylformate. The ^{1}H resonance of the methyl group is shifted 0.32 ppm upfield from that in the free ligand to 3.61 ppm and the t-butyl resonance is observed at 0.83 ppm. The phenyl resonances are again shifted about 0.5 ppm upfield.

If trifluoromethyl and carboalkoxy groups activated benzoyl enough to cause π-coordination, then a cyano group should have the same effect. This was found to be the case. Benzoyl cyanide reacts with "Ni(t-BuNC)$_2$" at low temperature in pentane to give a yellow, crystalline solid which is soluble in ether/pentane. The cyanide band is shifted from 2230 to 2220 cm^{-1} upon coordination and there is no band around 1650 cm^{-1} attributable to ν(CO). The aryl proton display NMR shifts similar to those already mentioned. When the sample is allowed to warm to room temperature, bands attributable to a benzoyl C=O and Ni—C≡N grow in at 1665 and 2005 cm^{-1} respectively, indicating oxidative addition of the benzoyl cyanide bond *. As time progresses, a new band at 1952 cm^{-1} grows in. This band is attributable to a nickel carbonyl indicating CO migration from the benzoyl group to nickel. These products have not been characterized.

Reaction of stoichiometric quantities of "Ni(t-BuNC)$_2$" and methyl pyruvate gives little of the desired π-carboxo complex. Addition of a large excess of the pyruvate ester shifts the equilibrium 1 far enough to the right so that the isocyanide bands of the desired product can be observed. Similar results are obtained with trifluoroacetone. For unactivated carboxo compounds such as acetophenone and acetone no indication of complexation is observed; "Ni(t-BuNC)$_2$" dissolved in neat acetone gives no evidence of π-complex formation. This is in contrast to the reported bis(triphenylphosphine)nickel complexes of benzaldehyde and benzophenone [4]. In that system, there is no competition to form polymeric "Ni(PPh$_3$)$_2$" so complexes of unactivated carboxo compounds can be prepared. The equilibrium in solution is a complication even for the more activated carboxo compounds. Attempted molecular weight measurements indicated some degree of dissociation even for the highly activated diethyl ketomalonate complex.

$$\text{“Ni(t-BuNC)}_2\text{”} + \text{R}_1\text{R}_2\text{CO} \rightleftharpoons \text{Ni(t-BuNC)}_2(\text{R}_1\text{R}_2\text{CO}) \qquad (1)$$

Several acyl fluorides react with "Ni(t-BuNC)$_2$" at low temperature to yield what are presumably initial π-carboxo complexes. The observed isocyanide

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* Similar reactions have been observed for benzoyl halides [9]. We have also observed that benzoyl cyanide reacts cleanly with Pt(PEt$_3$)$_3$ to give *cis*-Pt(PEt$_3$)$_2$(CN)(COPh) with no observable π-bonded intermediate.

stretching frequencies are listed in Table 1. These unstable compounds undergo further reactions to yield uncharacterized products.

Discussion

It has been shown elsewhere [10] that ν^1(NC) and ν^2(NC) are indicative of the electron density on the metal center and thus of the net electron density transferred to the coordinated double bond. Figure 1 displays the correlation between the observed values of ν^1(NC) of the π-carboxo complexes and a series of complexes of similarly substituted olefins. While the carboxo compounds were necessarily 1,1, disubstituted, it was not possible to obtain all of the 1,1 disubstituted olefins. This is not a severe limitation because it has been found [10] that changes in isomerization cause much smaller variations in ν(NC) than do changes in substituents. This is nicely illustrated by the carboalkoxy olefins in Table 1. Changes in ν^1(NC) on going from *geminal* to *trans* for the carboalkoxy methyl or *cis* to *trans* for the bis(carboalkoxy) olefins causes a change of no more than 4 cm^{-1} in ν^1(NC) but substitution of the methyl by a second carboalkoxy group changes ν^1(NC) by well over 20 cm^{-1}.

The higher values of ν(NC) for the π-carboxo complexes indicate that the carboxo compounds remove a greater amount of electron density from the nickel atom than do the corresponding olefins. This would be expected solely on the basis of the greater electronegativity of the C=O double bond. The slope of 0.8 indicates that π-carboxo complexes are less sensitive to substituent changes than are the analogous π-olefin complexes. The electron-withdrawing substituents are less able to compete for the backbonded electron density, resulting in a greater localization of electron density on the double bond. Similar results have been observed for other π-bonded heteroatomic double bonds [10,11].

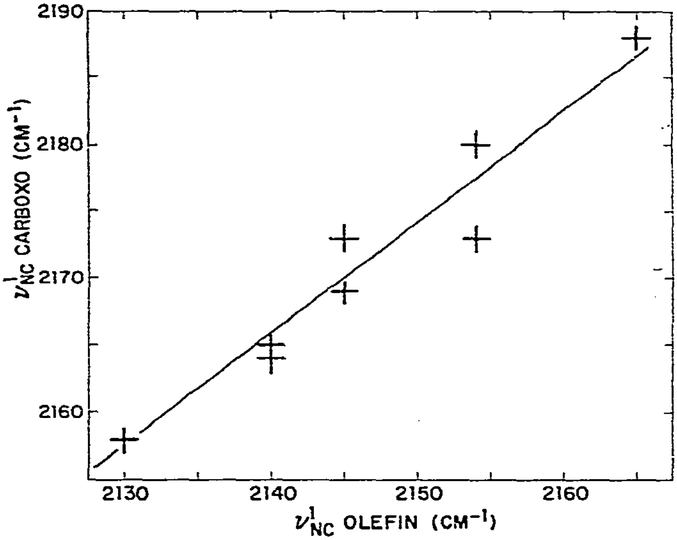

Fig. 1. Relation between ν^1(NC) for complexes of the type Ni(t-BuNC)$_2$(π-Un) where Un = carboxo compounds and similarly substituted olefins. (See Table 1 for the olefin isomers used.)

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