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Reactions of Dimethylaminodifluorophosphine Complexes of Nickel(0) with Boron Trifluoride

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The successful isolation of $NiL(CO)_3$ and $NiL_3(CO)$ ($L = Me_2NPF_2$) is reported. Boron trifluoride reacts with $NiL_2(CO)_2$ to yield $NiL_2(CO)_2 \cdot nBF_3$, where $n = 1.44$ at –128 °C and 1.11 at 2 °C, and with NiL_4 to yield $NiL_4 \cdot nBF_3$, where $n = 2.6$ at –100 °C, $n = 1.78$ at –3 °C and $n = 1.24$ at +20 °C. Nuclear magnetic resonance and infrared spectral data is presented which indicates that the BF_3 coordinates to the nitrogen of the coordinated Me_2NPF_2 ligands. Mass spectral data for the adducts has also been obtained.

Introduction

Among the more interesting of the trivalent phosphorus fluorides are the dialkyldiaminofluorophosphines. Such ligands offer two potential Lewis donor sites and indeed it has been demonstrated that Me_2NEF_2 (E = P, As) can bind to Lewis acids by either of the two donor sites, depending on the nature of the Lewis acid [1, 2].

Schmutzler [3] and Nixon and co-workers [4, 5] have prepared and studied the various dimethylaminodifluorophosphine complexes of Ni(0), but while the species NiL_4 and $NiL_2(CO)_2$ ($L = Me_2NPF_2$) have been isolated and characterised well, the $NiL(CO)_3$ and $NiL_3(CO)$ have only been obtained *in situ* and not been isolated. We here wish to report the isolation of these last two species and also the reactions of the $NiL_4(CO)_{4-n}$ complexes with boron trifluoride.

Results and Discussion

Nickel tetracarbonyl and $(CH_3)_2NPF_2$ react regardless of the order of addition or stoichiometry to produce $NiL_2(CO)_2$. No matter how much L is added to $Ni(CO)_4$ only $NiL_2(CO)_2$ and (if enough L is added and the reaction heated) NiL_4 are formed, and it is impossible by using stoichiometric control of L to produce directly $NiL(CO)_3$ or $NiL_3(CO)$ [3]. If $NiL_2(CO)_2$ is stored for 4 to 8 weeks significant amounts (20 to 30%) of $NiL(CO)_3$ and $NiL_3(CO)$ are formed as a mixture with the original $NiL_2(CO)_2$. This behaviour had been noticed by Nixon, Murray and Schmutzler [6] for $L = Me_2NPF_2$, Et_2NPF_2 and $C_5H_{10}NPF_2$ and by Clark [7] for $L = PF_3$. The rate of rearrangement for $L = PF_3$ is much faster [6] than for L = dialkylaminofluorophosphine. Clark [7] was able to separate $Ni(PF_3)(CO)_2$ and $Ni(PF_3)_2(CO)_2$ and $Ni(PF_3)_3(CO)$ by vapour phase chromatography, but attempts to separate and prove the independent existence of $NiL_3(CO)$ and $NiL(CO)_3$ where $L = Me_2NPF_2$ have been unsuccessful prior to this work [3, 6, 8–10]. Nixon and Schmutzler [6, 8] have attributed this observed rearrangement to a dissociative process to form CO or L where the rate of dissociation is much slower in the case of the dialkylaminofluorophosphines as compared to PF_3. However, since the rearrangement is observed also *in vacuo* and no free L or CO is observed by us it is unlikely that the reaction proceeds via the dissociative mechanism suggested by Nixon and Schmutzler. The $NiL(CO)_3$, $NiL_2(CO)_2$ and $NiL_3(CO)$ are nicely separated by high pressure liquid chromatography which proves the independent existence of $NiL_3(CO)$ and $NiL(CO)_3$ as opposed to their existence as equilibrium species in solution which could not be isolated as independent species.

Our results from the n.m.r. measurements are similar to those reported by other workers [3, 11], *viz*: NiL_4(δ_F + 38.9, δ_P – 167, J_{P-F} 1104, $NiL_3(CO)$ (δ_F + 41.6, J_{P-F} 1137), $NiL(CO)_3$ (δ_F + 44.8, J_{P-F} 1157), $NiL_2(CO)_2$ (δ_F + 43.3, δ_P – 168.5, J_{P-F} 1150).

From the study done by Fleming and Parry [1] it is known the BF_3 will add to the nitrogen of $(CH_3)_2NPF_2$. When $(CH_3)_2NPF_2$ displaces two CO ligands in $Ni(CO)_4$ to form $NiL_2(CO)_2$ the $(CH_3)_2NPF_2$ has been shown by Schmutzler [3] to coordinate to the

Ni through the phosphorus. There is now an extended π network from the nitrogen to the phosphorus ($2p\pi \rightarrow 3d\pi$), backbonding from the Ni to the $P(3d\pi_{Ni} \rightarrow 3d\pi_P)$ and also backbonding from the Ni to the antibonding orbitals of CO. If BF_3 coordinates to the nitrogen of $Ni(PF_2NMe_2)_2(CO)_2$ this should affect the whole extended π network, and cause noticeable changes in several of the stretching frequencies of the complex.

The BF_3 uptake study described in the experimental section was done to determine how much BF_3, n, the $NiL_2(CO)_2 \cdot nBF_3$ adduct contained over a large temperature range (−128 to +3 °C). At −128 °C the excess BF_3 has a vapour pressure of about 45 torr and with this vapour pressure it is possible to condense off into a −178 °C trap all the uncomplexed BF_3. At −128 °C, n = 1.44, indicating that more than one species is present in the reaction product [*i.e.* $NiL_2(CO)_2$, $NiL_2(CO)_2 \cdot nBF_3$ (n = 1, 2)]. Uptake of BF_3 studies at temperatures lower than −128 °C could not be carried out since it would be impossible experimentally to remove the excess uncomplexed BF_3. At +2 °C the moles of BF_3 present in the reaction product is 1.11.

If the BF_3 coordinates through the oxygen of the CO in $NiL_2(CO)_2$ and not at all through the nitrogen of the L, minimal uptake of BF_3 by NiL_4 would be expected. If the BF_3 coordinates with both the N and O sites of $NiL_2(CO)_2$, a maximum value of n = 4 would result from the uptake study. For this reason, a BF_3 uptake study was performed with NiL_4. NiL_4 has four nitrogen and no carbonyl donor sites available for coordination to BF_3. At −100 °C n = 2.6 for $NiL_4 \cdot nBF_3$. This indicates that the nitrogen of L in NiL_4 readily takes up BF_3 and is thus likely that the nitrogen of L also takes up BF_3 in $NiL_2(CO)_2$. Therefore at −100 °C there must be either/or $NiL_4 \cdot 3BF_3$ and $NiL_4 \cdot 4BF$ present in the reaction mixture; of course, some $NiL_4 \cdot BF_3$ and $NiL_4 \cdot 2BF_3$ could also be present. Again, as was the case with $NiL_2(CO)_2$ it was impossible to force the uptake of BF_3 to n = 4 by lowering the reaction warm-up temperature much lower than −100 °C since the vapour pressure of the excess uncomplexed BF_3 gets too low to allow easy removal of the excess BF_3. The reaction of BF_3 with either $NiL_2(CO)_2$ or NiL_4 was shown by mass balance and infrared to be totally reversible indicating that no rearrangement had taken place:

$$NiL_4 + nBF_3 \rightleftarrows NiL_4 \cdot nBF_3$$

$$NiL_2(CO)_2 + nBF_3 \rightleftarrows NiL_2(CO)_2 \cdot nBF_3$$

For neat $NiL_2(CO)_2 \cdot nBF_3$ with slight BF_3 overpressure the ^{19}F n.m.r. shows two sets of gross doublets and a broad singlet. The first set of gross doublets has a chemical shift of +43.7 ppm and a P–F coupling constant of 1150 Hz due to the ligand that has no BF_3 coordinated to it and the second doublet with a shift of +45.8 ppm and P–F coupling constant of 1184 Hz due to the ligand with BF_3 coordinated to it. The very broad upfield singlet at +141.8 is assigned to BF_3 (probably due to overlapping peaks of coordinated and uncoordinated BF_3*). The ^{31}P spectrum shows two overlapping triplets, one triplet has δ_P −168.5 ppm and J_{P-F} = 1150 Hz due to the ligand without BF_3 and the second triplet has δ_P −166.3 ppm and J_{P-F} = 1184 Hz. In comparing ^{19}F nmr data of Cavell [11] for Me_2NPF_2 with the ^{19}F nmr data of Fleming and Parry [1] for $Me_2NPF_2 \cdot BF_3$ there is an increase in δ_F (shifts to higher field) and J_{P-F} when BF_3 coordinates to L. Also the ^{31}P

TABLE I. Comparison of Major Assigned Infrared Bands.

Band Assignment	L[a]	$NiL_2(CO)_2$	$NiL_2(CO)_2 \cdot nBF_3$	NiL_4	$NiL_4 \cdot nBF_3$
N–CH_3 ν_s	2805	2810	2810 (dim.)[b]	2810	2810 (dim.) (almost absent)
C–O ν_s A_1		2060	n = 1 2076 n = 2 2098		
C–O ν_s B_1		2009	c		
N–P–F_2 ν_s	702	706	712 (br)	710	696 (br)[d]
P–F	812	828	883	842	835
ν_a' ν_s	772	775	790	770	750
B–N ν_s			610		580

[a] L = Me_2NPF_2. [b] dim. = greatly diminished in intensity compared to 1185. [c] B_1 bands overlapping, broadened and B_1 region shifted to higher wave number. [d] br = broadened.

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*A referee has also pointed out that it is possible that the broadness could be due to the fact that fluorine is attached to boron which has a quadrupole.

shift data show a decrease in δ_P when BF_3 coordinates to L. This same trend is noted for the coordination of BF_3 to $NiL_2(CO)_2$. Below 25 °C the $NiL_2(CO)_2 \cdot nBF_3$ adduct begins to form solid particles in solution thereby decreasing the concentration of adduct in solution. Also at lower temperatures the solubility of $NiL_2(CO)_2 \cdot nBF_3$ in $NiL_2(CO)_2$ or CH_2Cl_2 is insufficient to run the ^{19}F spectrum. Attempts to dissolve the solid adduct in acetone produced only $NiL_2(CO)_2$ and $(CH_3)_2C{=}O \cdot BF_3$. The $NiL_4 \cdot nBF_3$ adduct was insufficiently soluble in all solvents commonly used for ^{19}F spectra. Attempts to dissolve the $NiL_4 \cdot nBF_3$ in acetone produced a solution of NiL_4 and $(CH_3)_2C{=}O \cdot BF_3$ indicating that the oxygen of acetone is a better Lewis base than the nitrogen of the complex toward the hard Lewis acid BF_3. If one adds BF_3 to a solution of either $NiL_2(CO)_2$ or NiL_4 in CH_2Cl_2, solid BF_3 adduct product precipitates out without any detectable BF_3 adduct remaining in solution.

The major characteristic bands of the infrared spectra of Me_2NPF_2 (L), $NiL_2(CO)_2$, $NiL_2(CO)_2 \cdot nBF_3$, NiL_4 and $NiL_4 \cdot nBF_3$ are listed in Table I. The tentative assignments of the new compounds made in this study have been based on those made by other workers [1, 3, 7, 12, 13]. Braunholtz [13] has shown for a large number of compounds of the type $\rangle N{-}CH_3$ an absorption band of medium to strong intensity is present between 2760 and 2820 cm^{-1} due to the symmetrical stretch of a methyl group attached to a nitrogen whose lone pair is not involved in coordination. The presence or absence of this band in the 2760–2820 cm^{-1} range provides a valuable diagnostic test for this group. For L, $NiL_2(CO)_2$ and NiL_4, the $N{-}CH_3$ ν_s band is present indicating the nitrogen lone pair is not coordinated. The band is greatly diminished in intensity in $NiL_2(CO)_2 \cdot nBF_3$ and $NiL_4 \cdot nBF_3$ indicating that some of the nitrogen lone pairs of these two compounds are forming adducts with BF_3 causing the band intensity to diminish. If n = 2 for $NiL_2(CO)_2 \cdot nBF_3$ or n = 4 for $NiL_4 \cdot nBF_3$ the band would be expected to disappear completely. The band in the region 600–560 cm^{-1} has been attributed to a B–N symmetrical stretch by using ^{10}B and ^{11}B isotope studies [1]. Bands appear in this region for $NiL_2(CO)_2 \cdot BF_3$ and $NiL_4 \cdot nBF_3$ giving further evidence for the existence of a B–N bond in these three compounds. The A_1 C–O symmetrical stretch for $NiL_2(CO)_2$ is at 2060 cm^{-1}. When BF_3 is added to $NiL_2(CO)_2$ two new A_1 bands appear at 2070 and 2098 cm^{-1} tentatively assigned to $NiL_2(CO)_2 \cdot nBF_3$ where n = 1 and 2 respectively. The B_1 C–O stretching region undergoes a similar shift to higher frequency but these bands overlap making assignment impossible. The shift to higher frequency of the two new A_1 bands indicates that as the BF_3 coordinates to the nitrogen of $NiL_2(CO)_2$, the nitrogen lone pair is no longer available to undergo 2p → 3d bonding with the empty d orbitals on phosphorus. This makes the phosphorus a better acceptor from the nickel which causes the nickel to donate more of its d electrons into the empty d orbitals on phosphorus at the expense of donating some of these electrons to the antibonding orbitals of the carbonyl. Since fewer electrons are now being donated to the antibonding orbitals of the carbonyl, the carbonyl bond order increases and this is reflected in the shift to higher A_1 carbonyl stretching frequencies for $NiL_2(CO)_2 \cdot nBF_3$.

TABLE II. Infrared Carbonyl Stretching Frequencies and Assignments for $NiL_{4-n}(CO)_n$ (n = 1, 2, 3).

	ν_{C-O} cm^{-1}	Assignment
$NiL(CO)_3$	2102 m	A_1
	2092 w, sh	$Ni(C^{13}O)(C^{12}O)_2L$
	2028s	E*
	1996 w, sh	$Ni(C^{13}O)(C^{12}O)_2L$
$NiL_2(CO)_2$	2060 s	A_1
	2050 w, shoulder	$Ni(C^{13}O)(C^{12}O)L_2$
	2009 s	B_1
	1975 w	$Ni(C^{13}O)(C^{12}O)L_2$
$NiL_3(CO)$	2018 s	A_1
	1970 w	$Ni(C^{13}O)L_3$

s = strong; m = medium; w = weak; sh = shoulder.
*Has some E-band splitting due to low symetry of L.

The P–F stretching frequencies (ν_a and ν_s respectively) are shifted to higher frequency in going from L to $L \cdot BF_3$. This indicates a strengthening of the P–F bond in $L \cdot BF_3$. When BF_3 coordinates to the nitrogen, the nitrogen can no longer $2p\pi \rightarrow 3d\pi$ bond to the phosphorus. This causes the phosphorus to take a greater share of the electrons in the P–F bond which makes the bond stronger and more covalent which is reflected in the shift of the P–F stretching bands to higher frequency. The same trend is noted in going from $NiL_2(CO)_2$ to $NiL_2(CO)_2 \cdot nBF_3$ which can be explained in the same terms (although the magnitude of the shift is slightly less for the $NiL_2(CO)_2$ case compared to L). One sees an opposite trend in a shift to low frequencies for the P–F stretch in going from NiL_4 to $NiL_4 \cdot nBF_3$. The reason for this is not clear. Perhaps this partly reflects a steric effect in NiL_4 which is not seen in $NiL_2(CO)_2$ or L.

Table II lists the infrared carbonyl stretching frequencies for $NiL(CO)_3$, $NiL_2(CO)_2$ and $NiL_3(CO)$ and assignments are made by comparison with those of Loutelier and Bigorne [12] for the corresponding series of PF_3 compounds. By comparing the A_1 mode which is in all three, one sees a decrease in ν_{A_1} from $NiL(CO)_3$ to $NiL_3(CO)$ indicating that as more Me_2NPF_2 replace CO, the coordinating phosphorus is a poorer π acceptor of electrons from Ni and consequently as poorer π acceptor L's are added, more

TABLE III. Mass Spectrum of $NiL_2(CO)_2 \cdot nBF_3$ (E.I. Mode).

m/e	Ion	Relative Intensity
476	$NiL_2(CO)_2 \cdot 2BF_3^+$	16
408	$NiL_2(CO)_2 \cdot BF_3^+$	6
380	$NiL_2(CO) \cdot BF_3^+$	12
340	$NiL_2(CO)_2^+$	5
312	$NiL_2(CO)^+$	2
284	NiL_2^+	2
199	$NiL(CO)^+$	3
181	$L \cdot BF_3^+$	8
171	$NiL(CO)^+$	2
113	L^+	100

TABLE IV. Mass Spectrum of $NiL_4 \cdot nBF_3$ (E.I. Mode).

m/e	Ion	Relative Intensity
578	$NiL_4 \cdot BF_3^+$	2
510	NiL_4^+	20
465	$NiL_3 \cdot BF_3^+$	18
397	NiL_3^+	60
352	$NiL_2 \cdot BF_3^+$	7
284	NiL_2^+	70
181	$L \cdot BF_3^+$	4
171	NiL^+	30
113	L^+	100

Ni d-electrons are being donated into the antibonding orbitals of the C–O as one goes from the L_1 to the L_3. The increased donation of electrons by Ni into C–O antibonding orbitals causes a decrease in the C–O bond order and hence a shift to lower frequencies of the A_1 C–O stretch as one goes from L_1 to L_3. The E mode has some splitting due to the low symmetry of L.

The complete mass spectrum of $NiL_2(CO)_2 \cdot nBF_3$ run in the E.I. mode is listed in Table III. The mass spectrum shows evidence for the existence of the species $NiL_2(CO)_2 \cdot 2BF_3$ and $NiL_2(CO)_2 \cdot BF_3$. It is interesting to note that the preferred breakdown pattern of the adducts is the loss of $L \cdot BF_3$ from the $NiL_2(CO) \cdot BF_3^+$ ion to form $NiL(CO)^+$ instead of the loss of CO to form $NiL_2 \cdot BF_3^+$. There is no evidence for the loss of L when an $L–BF_3$ group is present also. Another mass spectrum run on an aged sample of $NiL_2(CO)_2$ showed the presence of the species $NiL_3(CO)^+$ m/e = 425 and $NiL(CO)_3^+$ m/e = 225. BF_3 addition to this mixed aged sample showed presence of $NiL_3(CO)_3 \cdot 2BF_3^+$ m/e = 561, $NiL_3(CO) \cdot BF_3$ m/e = 493 and $NiL(CO)_3 \cdot BF_3$ m/e = 323.

The complete mass spectrum of $NiL_4 \cdot nBF_3$ run in the E.I. mode is listed in Table IV. The mass spectrum shows evidence for the existence of $NiL_4 \cdot BF_3$. It is known from the BF_3 uptake studies that either/or $NiL_4 \cdot 4BF_3$ and $NiL_4 \cdot 3BF_3$ may be present. The relative intensity of m/e 578 ($NiL_4 \cdot BF_3^+$) is only 2%. $NiL_4 \cdot 4BF_3^+$ would have an m/e = 782 and $NiL_4 \cdot 3BF_3^+$ would have an m/e = 714. The high mass of these two species would cause a low volatility under the conditions that the spectrum was run and consequently were not seen as $NiL_4 \cdot 4BF_3$ or $NiL_4 \cdot 3BF_3$, but BF_3 was pumped off until $NiL_4 \cdot BF_3$ was present which was sufficiently volatile at 10^{-7} torr to be seen.

Experimental

Starting Materials

Nickel tetracarbonyl was obtained from Strem Chemical Co. in a 100 g gas cylinder pressurized with carbon monoxide to 15 psi. The $Ni(CO)_4$ was frozen at −178 °C (liquid in trap) and the remaining CO gas was pumped off prior to the initial use. PF_3 was obtained from Ozark-Mahoning. Commercial BF_3 and $(CH_3)_2NH$ were obtained from Matheson and were shown by gas phase infrared to be essentially pure.

Dimethylaminodifluorophosphine

Using a modified version of Cavell's procedure [11], gaseous dimethylamine was bled into a previously evacuated 5000-ml bulb on the vacuum line to a pressure of 500 torr and was then closed off. PF_3 was added to the rest of the vacuum line at a pressure of 700 torr. The closed off stop cock to the 5000-ml bulb was opened and this over-pressure of PF_3 was then bled into the bulb containing the dimethylamine while the line pressure was maintained at a pressure of about 700 torr by the continued addition of PF_3 to the line. The PF_3 addition was periodically stopped to check for continued reaction via pressure drop and was discontinued after no pressure drop was noted after stopping the addition of PF_3 to the line. This procedure assured that all the dimethylamine had reacted and that there was an excess of PF_3 present since the vapour pressure of the product is less than 300 torr at ambient temperature [12].

The volatile product, $(CH_3)_2NPF_2$, was separated from the excess PF_3 by high vacuum, low temperature fractionation through traps cooled to −45, −78, −178 °C consecutively. The PF_3 passes through to the −178 °C trap while the $(CH_3)_2NPF_2$ stops in the −45° and −78 °C traps. The $(CH_3)_2NPF_2$ was identified and checked for purity by comparing its infrared with that of Cavell's [11].

This modification of Cavell's method has the advantage of allowing one to prepare large quantities of the dimethylaminodifluorophosphine at one time.

$Ni(Me_2NPF_2)_4$ and $Ni(Me_2NPF_2)_2(CO)_2$

These were prepared by standard literature methods [3, 4].

Isolation of $NiL_3(CO)$ and $NiL(CO)_3$

A sample of a mixture of $NiL_n(CO)_{4-n}$ (n = 1, 2, 3) was dissolved in spectral grade hexane to make an approximately 20% (by volume) solution. The hexane solution was purged with dry nitrogen. The liquid chromatograms were carried out on a Waters Associate L.C. run at 1600 psi and at a flow rate of 1.5 ml/min. Three peaks were detected using the refractive index detector. The first corresponded to the $NiL(CO)_3$, the second to $NiL_2(CO)_2$ and the third to $NiL_3(CO)$. The identification was made by ^{19}F nmr. The chromatogram peaks were well separated and the liquid chromatogram output was collected in N_2 filled polyethylene bottles as each peak was seen on the refractive index detector. This process was repeated about 8 times with all l.c. outputs corresponding to peak 1, peak 2 and peak 3 being respectively combined. The solutions were concentrated by evaporation of some of the hexane solvent by bubbling dry N_2 through the solution until the final volume was about 5 ml. Infrared spectra were made with the concentrated solutions of the samples using a 0.1 mm KBr liquid infrared cell. The spectra were recorded on a very slow scan time using an ultra fine tip pen and were calibrated using the sharp 1601.4 cm^{-1} band of polystyrene file.

The major infrared peaks are tabulated and assigned in the Results and Discussion.

The compound $NiL(CO)_3$ was volatile and had significant vapor pressure at room temperature. $NiL_2(CO)_2$ and $NiL_3(CO)$ had essentially no vapor pressure at room temperature and were essentially non-volatile at a 10^{-2} torr pressure at room temperature.

Reaction of $NiL_2(CO)_2$ with BF_3

A 75 ml Fischer–Porter reactor was evacuated and tared. The reactor was then opened in a dry N_2 filled glove bag. Freshly prepared $NiL_2(CO)_2$ (L = Me_2NPF_2) was added, the reactor was again evacuated and it was then determined that 5.00 X 10^{-3} mol of $NiL_2(CO)_2$ had been added. The reactor and contents were then cooled to –178 °C and BF_3 (5.0 X 10^{-2} mol) was condensed into the reactor and allowed to interact with the $NiL_2(CO)_2$ for 1 hr. The reactor and contents were then allowed to warm to –128 °C and allowed to interact for an additional hour. The excess, uncomplexed BF_3 was slowly condensed off at –128 °C until no noticeable additional BF_3 pressure was given off under a static vacuum of <1 torr for a period of 15 minutes. The Fischer–Porter reactor containing the $NiL_2(CO)_2 \cdot nBF_3$ adduct was then sealed and allowed to warm to room temperature and the mol, n, of BF_3 added was determined by mass gain: n = 1.44 at –128 °C. The above procedure was repeated at –80 °C and +2 °C in place of –128 °C and it was determined by mass gain that n = 1.2 at –80 °C and n = 1.11 at +2 °C. The BF_3 addition could be totally reversed by pumping on the adduct overnight at room temperature. The reversibility was shown by both mass balance and identical infrared spectra before the BF_3 was added and after the BF_3 was all pumped off. The various above BF_3 adducts are solids which show in the infrared the characteristic B–N stretching vibration at 610 cm^{-1} (B–N stretch region 560–660 cm^{-1} [1]).

The ^{19}F nmr spectrum run neat at room temperature with a slight overpressure of BF_3 consisted of two doublets and a broad singlet, one doublet was centered at 43.7 ppm (J_{P-F} = 1150 cps) and the other was centered at 45.8 ppm (J_{P-F} = 1184 cps). The very broad singlet was at 141.8 ppm. Attempts to run low temperature nmr either neat or in CH_2Cl_2 proved unsuccessful due to the precipitation of solid adduct which made meaningful resolution impossible.

The ^{31}P nmr spectrum run on this same sample showed basically two overlapping triplets, one centered at –168.5 ppm (J_{P-F} = 1150 cps) and the other centered at about –166.3 ppm (J_{P-F} = 1184 cps).

Reaction of NiL_4 with BF_3

A 75 ml Fischer–Porter reactor was evacuated and tared. The reactor was then placed in a dry N_2-filled glove bag. A concentrated solution of freshly filtered (to remove any insoluble oxidation product) NiL_4 in CH_2Cl_2 was added to the reactor. The CH_2Cl_2 solvent was slowly pumped off on the vacuum line leaving behind the NiL_4 (2.59 X 10^{-3} mol). The evacuated reactor and contents were then cooled to –178 °C and BF_3 (5.0 X 10^{-3} mol) was condensed into the reactor and allowed to interact with the NiL_4 for 1 hr. The reactor and contents were then allowed to warm to –100 °C and were allowed to interact for an additional hour. The excess, uncomplexed BF_3 was slowly condensed off at –100 °C until no noticeable additional BF_3 pressure was given off under a static vacuum of <1 torr for a period of 15 min. The Fischer–Porter reactor containing the $NiL_4 \cdot nBF_3$ adduct was then sealed and allowed to warm to room temperature and the mol, n, of BF_3 added were determined by mass gain: n = 1.78 at –3° and n = 1.24 at +20 °C. The BF_3 addition could be totally reversed by pumping on the adduct overnight at room temperature. The reversibility was shown by both mass balance and identical infrared spectra before the BF_3 was added and after the BF_3 was all pumped off. The n = 2.6 adduct is a solid, the n =

1.78 and n = 1.24 adducts are very viscous oils having almost the consistency of glass slightly above its softening temperature.

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