Journal of Organometallic Chemistry, 113 (1976) 75—83

THE NICKEL(II) CARBOXYLATE/ETHYLALUMINUM SESQUICHLORIDE/ BENZENE-1,3-BUTADIENE HOMOGENEOUS CATALYTIC SYSTEM: EVIDENCE FOR THE EXISTENCE OF A SQUARE PLANAR NICKEL(II) COMPLEX BEFORE MONOMER ADDITION

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(Received November 6th, 1975)

Summary

Nickel(II) carboxylate salts or nickel(II) chloride react with excess ethylaluminum sesquichloride or ethylaluminum dichloride in benzene to produce a diamagnetic orange-brown complex. The amount of this complex increases with an increase of the ethylaluminum dichloride content of the ethylaluminum compound, i.e., the amount is maximized when the Et/Al/Cl ratio is 1 : 1 : 2. This complex has $d \rightarrow d$ electronic absorption bands in the visible region at 520 nm (19 230 cm^{-1}) and 415 nm (24 038 cm^{-1}) with molar absorptivity coefficients of 125 ± 7 and 361 ± 25 l mol^{-1} cm^{-1}, respectively. The visible band locations, molar absorptivities, and diamagnetism are characteristic of square planar nickel(II) complexes. In the absence of monomer, the predominant complex, responsible for the observed electronic absorption bands, is slowly reduced to metallic nickel. Electronic spectra obtained as a function of time can be used to show that the reaction is first order with respect to the nickel complex. Polymerization rate data indicate that the predominant nickel(II) complex is involved in the polymerization of 1,3-butadiene to highly stereospecific *cis*-1,4-polymer.

Introduction

Nickel(II) carboxylates or nickel(II) chloride react with ethylaluminum sesquichloride ($Et_3Al_2Cl_3$) or ethylaluminum dichloride ($EtAlCl_2$) in non-coordinating aromatic solvents to produce a catalytically active solution capable of polymerizing 1,3-butadiene to a polymer which is about 90 per cent *cis*-1,4-polybutadiene. This system is also capable of dimerizing propylene to a variety of isomeric forms [1—7]. The highly stereospecific *cis*-1,4-polybutadiene produced is in most cases a low molecular weight oil suitable for use in the manufac-

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ture of synthetic rubber or lacquer [7]. This system is proposed to be similar to *bis*(π-allylnickel halide)/Lewis acid catalytic systems [14—16] due to the similarities in *cis*-1,4 content, molecular weight range, the low gel content of the polybutadiene, and theoretical considerations. After addition of monomer, the nickel(II) carboxylate/$Et_3Al_2Cl_3$ catalytic system is thought to contain a species with an active site similar to π-allylic catalytic systems. The active site in *cis*-1,4 stereoregulation of the polymerization of 1,3-butadiene has not been elucidated as yet, but it is probably either a σ-allylic or π-allylic transition metal center.

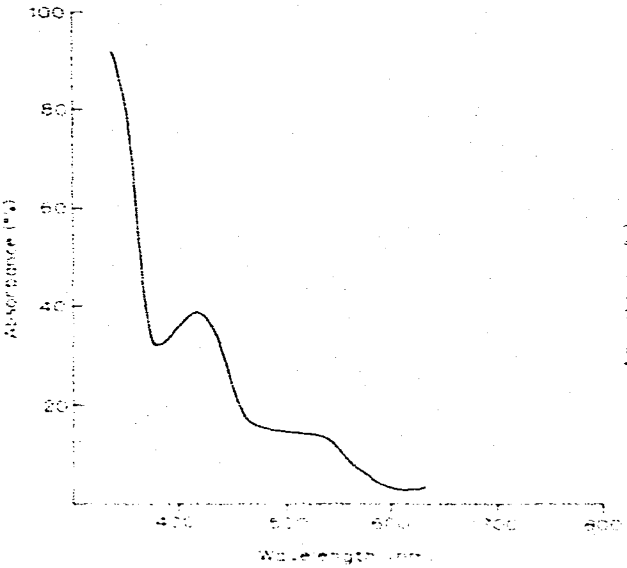
The predominant nickel species in the nickel(II) carboxylate/$Et_3Al_2Cl_3$ system before monomer addition has been proposed to be an alkylated nickel species or a nickel hydride [8], though the structure of the nickel complex present is not well established. The data that are presented in this paper were obtained in an attempt to clarify this situation.

Results and discussion

Spectral and magnetic properties of nickel(II) complexes

Octahedral (O_h) and tetrahedral (T_d) nickel(II) complexes are both paramagnetic, in contrast to square planar (D_{4h}) nickel(II) complexes which are diamagnetic. Both octahedral and tetrahedral nickel(II) complexes give $d \rightarrow d$ electronic absorption bands above and below 1000 nm (10 000 cm^{-1}), but square planar nickel(II) complexes only produce bands higher in energy than 1000 nm (>10 000 cm^{-1}). The molar absorptivities of the visible bands of a nickel(II) octahedral complex are quite low (5—30 l mol^{-1} cm^{-1}) due to the center of symmetry present in such complexes. The molar absorptivities of tetrahedral and square planar nickel(II) complexes are somewhat larger (50—500 l $mol^{-1}cm^{-1}$). The $d \rightarrow d$ electronic absorption spectrum of a square planar nickel(II) complex usually consists of a strong band in the region 670—430 nm (15 000—23 000 cm^{-1}) with molar absorptivities in the range 50—500 l cm^{-1} mol^{-1} and a second band in the region 430—370 nm (23 000—27 000 cm^{-1}) [10]. These bands are usually assigned to the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ and ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transitions, respectively. For a more detailed discussion of the spectral and magnetic properties of nickel(II) complexes of various symmetries see the references given [10—12]. The combination of visible band locations, molar absorptivities, and magnetic properties can be used to determine the symmetry of nickel(II) complexes with reasonable certainty.

The visible spectrum of the solution produced by the reaction of nickel(II) carboxylates or nickel(II) chloride with excess ethylaluminum sesquichloride or ethylaluminum dichloride (Al/Ni $\geqslant$ 6 : 1) in non-coordinating aromatic solvents is given in Fig. 1. The same visible spectrum is produced whether the nickel(II) ion is introduced as a salt of a carboxylic acid or as nickel(II) chloride. This observation can only be explained if the carboxylate groups are removed from the nickel. The complex produced by this reaction (subsequently referred to as complex I) has bands in the visible region located at 520 nm (19 230 cm^{-1}) and 415 nm (24 038 cm^{-1}). Table 1 displays the absorbances at these two band locations for various nickel concentrations. The Beer's law plots of absorbance versus nickel concentration for the two bands are linear and indicate molar absorptivity coefficients of 125 ± 7 and 361 ± 25 l mol^{-1} cm^{-1} for the 520 and 415 nm bands, respectively, (Fig. 2). These values are within the range 50—500 l mol^{-1} cm^{-1}



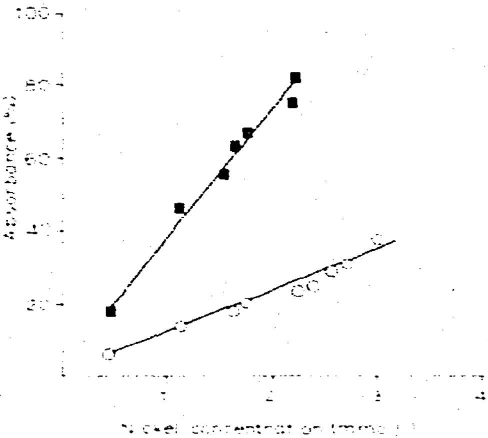


Fig. 1. Visible spectrum of the nickel(II) complex produced by the reaction of nickel(II) salts with $Et_3Al_2Cl_3$ or $EtAlCl_2$ in aromatic solvents.

Fig. 2. Beer's law plot of absorbance vs. nickel concentration. ■, absorbance at 415 nm, slope 364 l mol^{-1} cm^{-1}; ○, absorbance at 520 nm, slope 127 l mol^{-1} cm^{-1}.

usually observed for square planar nickel(II) complexes. The plots also pass through the origin indicating that the majority of the nickel is present in the form giving rise to the observed bands in the visible region.

At Al/Ni ratios of 6 : 1 or above, the spectral band locations and the molar absorptivity coefficients are constant. Whether the aluminum compound is Et_3-

TABLE 1

ABSORBANCES AT 415 AND 520 nm AT SEVERAL NICKEL CONCENTRATIONS FOR THE CATALYST SOLUTION NICKEL(II) SALT AND $Et_3Al_2Cl_3$ OR $EtAlCl_2$

Absorbance at 415 nm (%)	Absorbance at 520 nm (%)	Nickel [a] concentration (M)	Starting Al/Ni ratio
18	6	4.6×10^{-4}	7 : 1
47 [b]	15.0 [b]	1.19×10^{-3}	25 : 1
51	18.5	1.55×10^{-3}	12 : 1
58 [b]	19.2 [b]	1.56×10^{-3}	6 : 1
59	21.0	1.65×10^{-3}	7 : 1
70	24.0	2.18×10^{-3}	10 : 1
77	26.0	2.21×10^{-3}	56 : 1
—	29.5	2.37×10^{-3}	15 : 1
—	30.5	2.45×10^{-3}	10 : 1
—	38.0	2.92×10^{-3}	6 : 1

[a] Nickel concentrations were determined by atomic absorption techniques. [b] $Et_3Al_2Cl_3$ was used instead of $EtAlCl_2$ as the aluminum compound.

Al_2Cl_3 or $EtAlCl_2$ also appears to be of no significance. However, if the aluminum compound employed in the reaction is Et_2AlCl, the complex is either not formed or is formed in minimal amounts. It can be seen in Fig. 3 that approximately twice as much (ca. 14 per cent) of the starting amount of nickel(II) is converted into the benzene soluble nickel complex when the aluminum compound employed in the reaction is $EtAlCl_2$ as in the case when the aluminum compound is $Et_3Al_2Cl_3$ (Al/Ni ≥ 6 : 1). Since $Et_3Al_2Cl_3$ is an equal molar mixture of Et_2AlCl and $EtAlCl_2$, the amount of soluble nickel complex produced by the reaction is directly proportional to the $EtAlCl_2$ content of the alkylaluminum compound. This indicates that $EtAlCl_2$ is involved in the formation of the observed nickel complex.

Solvent participation in the first coordination sphere of the complex is ruled out by the observation that the same visible spectrum is obtained in benzene, ethylbenzene, chlorobenzene, and toluene. However, the complex is much more soluble in aromatic solvents than in non-aromatic solvents, and the solubility of the complex is increased by the presence of excess alkylaluminum irrespective of solvent. The solubility of the complex can be interpreted as an indication that it contains alkyl groups. An excess of $Et_3Al_2Cl_3$ should serve to drive exchange equilibrium between chloro and ethyl groups in the complex in the direction which places at least a minimal number of ethyl groups on the complex (eq. 1). Furthermore, as cited above, the data display another important indi-

$$Et_3Al_2Cl_3 + Cl\text{—}complex \geqslant 2\ EtAlCl_2 + Et\text{—}complex \qquad (1)$$

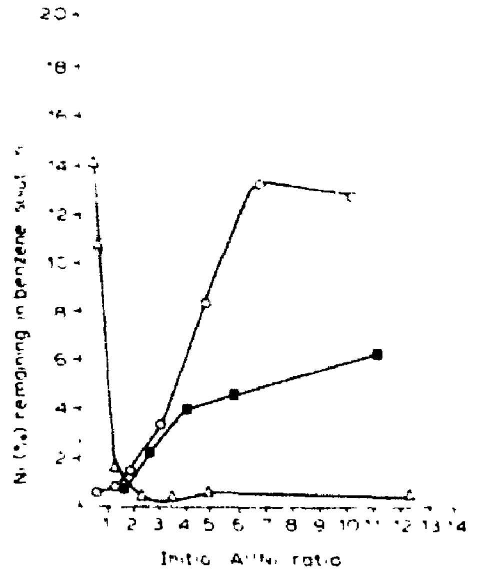


Fig. 3. Per cent nickel remaining in benzene after the reaction of nickel(II) stearate with various alkylaluminum compounds. △, Et_2AlCl; ■, $Et_3Al_2Cl_3$; ○, $EtAlCl_2$.

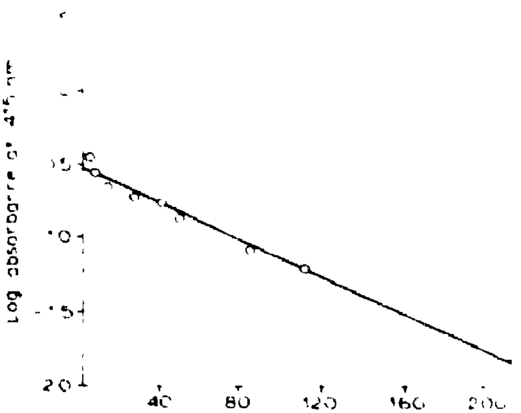
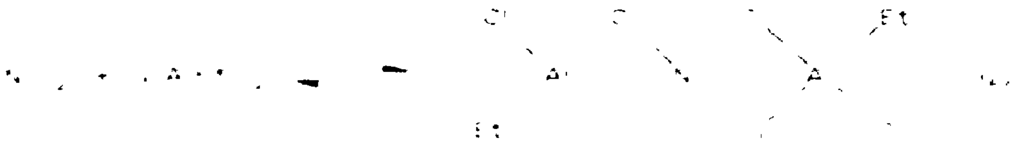


Fig. 4. First order plot for the decrease in absorbance at 415 nm vs. time for the catalyst solution produced from the reaction of nickel(II) carboxylate with ethylaluminum sesquichloride in benzene at ambient temperature. Slope $-k/2.303$; $k = 0.0065\ h^{-1} = 4.2 \times 10^{-6}\ sec^{-1}$; starting Al/Ni ratio 38 : 1; $[Al] = 3.7 \times 10^{-1}$ mol/l.

cation of a square planar structure in that the nickel(II) complex was found to be diamagnetic. The complex produced no shifts in the resonance position of an inert, external—internal reference in the nickel concentration range 2×10^{-3} to 2×10^{-2} mol/l. The diamagnetism, visible band locations, and molar absorptivities observed are all characteristic of a square planar nickel(II) complex.

Based on the spectral and magnetic data and on the fact that the amount of complex formed is directly proportional to the relative quantity of $EtAlCl_2$ present, complex I is most likely a bridge-bonded species formed from the complexation of $NiCl_2$ with $EtAlCl_2$ or its disproportionation products. Two $EtAlCl_2$ moities are depicted (eq. 2) as complexing with one $NiCl_2$ simply because a minimum of two bridge-bonded aluminum species is necessary in order to place a four coordinate environment around the nickel center.



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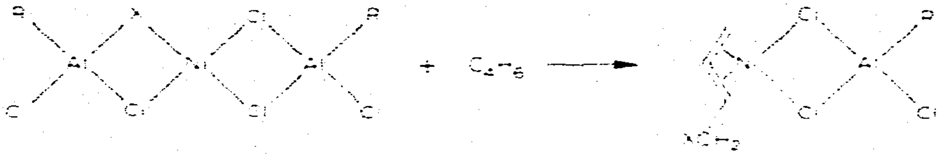
The degree of solubility of the complex suggests that it contains alkyl groups. Because the complex is only slowly reduced to metallic nickel and the electronic spectrum is characteristic of nickel(II) rather than an organonickel species, it can be predicted that any alkyl groups that may be present are not directly attached to the nickel but rather are bonded to aluminum. The aluminum, in turn, is proposed to be bridge bonded to nickel through chloro groups. A similar structure has been observed for the cobalt(II) complex, $Co(Al_2Cl_8)$, formed in benzene [13].

Attempts to isolate complex I through solvent removal and precipitation (see Experimental; Isolation and analysis) have resulted in the production of a brown precipitate which does not redissolve in benzene. The inorganic composition of this precipitate is $NiAl_{4.4}Cl_{10.2}H_{0.1}$.

The hydride content of the precipitate is so small as to seem insignificant. A small amount of nickel hydride species may be present, as reported by Obeshchalova [8], but the predominant complex does not appear to be a nickel hydride complex. The discrepancy between the nickel-to-aluminum ratio in complex I and the hydrolyzed precipitate arises from the fact that complex I contains the minimum number of aluminums necessary to place a four coordinate environment around the nickel. In reality, additional aluminum moieties may be bridge bonded to the two which are bridge bonded to nickel.

Another complicating observation is that complex I in solution is slowly reduced to metallic nickel in the absence of monomer. The disappearance of complex I was followed spectroscopically by observing the bands in the visible region. Both bands were observed to decrease with time and to maintain a reasonably constant band height ratio of about 2 : 8 : 1. Consequently it can be concluded that both bands are produced by complex I. Fig. 4 shows a plot of log of absorbance at 415 nm versus time. This first order plot is linear for the disappearance of nickel(II) with a first order rate constant of 4×10^{-6} sec^{-1}.

Due to the relatively large excess of $Et_3Al_2Cl_3$ present (Et/Ni = 114 : 1), alkylation of nickel through ligand exchange would be enhanced relative to smaller excesses. Since alkylation of nickel is prerequisite to reduction, rapid reduction could be expected. However, the rate of reduction is so relatively slow the half life of the reaction is about 44 h. The mechanism of reduction of nickel(II) acetylacetonates by organoaluminum compounds proposed by Fischer et al. [14] indicates that one of the major paths of reduction of alkylated nickel species is the formation of unstable nickel hydride intermediates. The presence of trace amounts of nickel hydride species produced as a reduction intermediate could account for the propylene dimerizing ability of this catalytic system [7], since the dimerization of olefins can be most easily explained by interaction with a metal hydride. However, the *cis*-1,4-polymerization of 1,3-butadiene, C_4H_6, is believed to be initiated by a σ-allylic or π-allylic transition metal center [15—17]. Complex I, an alkylated nickel species or a nickel hydride species are all capable of the following reaction to produce an allylic nickel center [18,19] (eq. 3).



(3)

(III)

where X = Cl, H, R and R = Me, Et

In this light, it is interesting to note that high *cis*-1,4-polymerization of 1,3-butadiene has been reported in a totally inorganic catalytic system, nickel sesquioxide/aluminum trichloride [20].

In the catalytic system, nickel(II) carboxylate/$Et_3Al_2Cl_3$, direct spectroscopic evidence of the interaction of the square planar nickel(II) complex and 1,3-butadiene has yet to be obtained due to the obscuring of the visible region by an in-

TABLE 2

INFLUENCE OF SEVERAL CATALYTIC SYSTEMS ON THE RATE OF POLYMERIZATION 1,3-BUTADIENE

Catalytic system	C_4H_6 concentration (M)	Ni concentration (M)	Conversion (%)	Time (min)	% *cis*-1,4 microstructure	Reference
Nickel(II) stearate/$Et_3Al_2Cl_3$ [a]	0.76	3.12×10^{-3}	85	10.35	92	[d]
Nickel(II) stearate/$Et_3Al_2Cl_3$ [a]	0.38	3.12×10^{-3}	64	10.17	92	[d]
(π-crotylNiCl)$_2$/$AlCl_3$	2.5	2.5×10^{-3}	70	30	90	13
(π-AllylNiCl)$_2$/$TiCl_4$	2.5	2.5×10^{-3}	81	60	92	21
(π-crotylNiBr)$_2$/$TiCl_4$	2.5	2.5×10^{-3}	51	15	89	21
π-AllylNiTFA [b]	1.2	2.0×10^{-3}	10	15	96 [c]	19

[a] Temp. 36°C. In the π-allyl systems, the temperature is usually 30°C. [b] TFA = trifluoroacetic acid. [c] The solvent is cyclohexane in this instance and benzene in all others. [d] This work.

tense band centered in the ultraviolet region that is produced upon butadiene addition to the catalyst solution. However, polymerization rate studies show that this catalyst system polymerizes 1,3-butadiene at a rate only slightly greater than those reported for *bis*(π-crotylNiCl)/Lewis acid modified catalyst systems at similar nickel and 1,3-butadiene concentrations (see Table 2). Several studies have shown that each nickel center in the π-crotyl systems is catalytically active to the same degree [21,22]. If the mechanisms of polymerization are similar in both systems (nickel(II) salt/$Et_3Al_2Cl_3$ and *bis*(π-crotylnickel halide)/Lewis acid), then the predominant nickel complex in the nickel(II) carboxylate/$Et_3Al_2Cl_3$ system must be involved in the polymerization of 1,3-butadiene in order to explain this similar rate of polymerization.

Conclusions

The predominant nickel species remaining in solution after the reaction of nickel(II) stearate or nickel(II) chloride with excess $Et_3Al_2Cl_3$ or $EtAlCl_2$ in non-coordinating aromatic solvents is seen to be the same in each case. Spectral and magnetic data indicate that the predominant catalytically active soluble nickel species present is a square planar nickel(II) complex. The complex appears to be formed from the complexation of $NiCl_2$ with $EtAlCl_2$ based on the observation that the maximum amount of soluble complex is formed when $EtAlCl_2$ is used. Polymerization rate data indicate that the predominant nickel(II) complex is involved in the stereospecific polymerization of 1,3-butadiene. In all probability this square planar nickel(II) complex is converted into a catalytically active nickel center after the introduction of 1,3-butadiene.

Experimental

All reactions and transfers were carried out under dry, deoxygenated nitrogen in an inert atmosphere box. The non-coordinating aromatic solvents were dried and deoxygenated by fractional recrystallization (from benzene) followed by fractional distillation over sodium and benzophenone under dry nitrogen.

Measurement of visible spectra

Each solution was centrifuged and the clear supernatant was added to a 1.0 cm quartz UV cell fitted with an air tight teflon stopper. The region 1500—350 nm (6 666—28 571 cm^{-1}) was scanned on a Beckman DK-1 or a Varian Cary 17 UV-visible spectrophotometer using dry benzene in the reference cell. The two moderately overlapping bands observed at 520 nm and 415 nm were resolved by graphical methods assuming the bands to be Gaussian in shape. Molar absorptivity coefficients were determined from a Beer's law plot.

Determination of nickel and aluminum

The nickel and aluminum concentrations were determined by atomic absorption using an Instrumentation Laboratories Model IL 253 spectrometer. A nitrous oxide/acetylene flame and an oxygen/acetylene flame were used in the determination of aluminum and nickel, respectively. A known amount of each solution was diluted so as to be in the concentration range 2—30 ppm and was hydrolyzed using dilute nitric acid. The absorbance values were determined from the average of three time averaged readings. Each unknown was bracketed by standards of slightly lower and higher concentrations.

Determination of magnetic properties

Magnetic properties of the catalyst solutions were investigated using the coaxial double-tube NMR method of Evans [9]. The concentration range used was 2×10^{-3}–2×10^{-2} *M*. A Varian A-60D NMR spectrometer was used.

Polymerization rates of 1,3-butadiene were followed by an NMR method whereby the relative areas under the methylene peaks of the monomer at δ 4.9 ppm and the methyne peak of the polymer at δ 5.4 ppm were used to determine the concentrations of monomer and polymer at various times. A known amount of 1,3-butadiene in benzene was added via syringe to a NMR tube containing a measured amount of catalyst solution with a known nickel concentration. The tube was shaken vigorously for a few seconds, and the NMR spectrum was then obtained as a function of time.

Chemicals

Nickel(II) stearate was obtained from Research Organic/Research Inorganic Chemical Corporation and was used without further purification but was dried for 14 h at 60°C under vacuum. Nickel(II) oleate was obtained from Pfaltz and Bauer, Inc. and was also vacuum dried. Anhydrous nickel(II) chloride was obtained from Research Organic/Research Inorganic Chemical Corporation and was used without further purification.

The aluminum compounds diethylaluminum chloride (Et_2AlCl_2), ethylaluminum sesquichloride ($Et_3Al_2Cl_3$) and ethylaluminum dichloride ($EtAlCl_2$) were obtained from Texas Alkyls or Alfa Inorganics in lecture bottles as pure liquids. The alkylaluminum compounds were analyzed for aluminum and chloride contents and their NMR spectra were obtained before use.

Isolation and analysis

The nickel complex remaining in solution after reaction was concentrated by vacuum removal of solvent at 60° C. Dry, deoxygenated cyclohexane or cycloheptane was added to precipitate the complex and was used to repeatedly wash the precipitate to remove excess alkylaluminum. The precipitate was weighed, hydrolyzed with distilled water and analyzed for Ni, Al, Cl, and H^-. Nickel and aluminum were analyzed by atomic absorption methods. Chloride was analyzed by Volhard titration. Hydride content was determined by measuring the amount of liberated hydrogen gas upon hydrolysis.

A Dupont CEC 21-490 mass spectrometer was also used in the determination of hydride content. A Schlenk flask was sealed to a special adapter designed for attachment to the mass spectrometer. The flask was evacuated and refilled with hydrogen gas at several known pressures. For each pressure the recorder response at mass number two was used to prepare a calibration chart of intensity versus hydrogen pressure. Then the isolated precipitate was added to the Schlenk flask inside a dry box filled with dry nitrogen evacuating the flask and injecting a small amount of distilled H_2O to hydrolyze the precipitate, and measuring the mass spectrometer response at mass number two. After removal from the dry box, the flask was evacuated, a small amount of distilled water was injected to hydrolyze the precipitate and the mass spectrometer response at mass number two was measured.

After several washings a brown solid with the following partial composition was isolated: $NiAl_{4.4}Cl_{10.2}H_{0.1}$. This is a partial composition since Ni, Al, Cl, and H^- were the only moieties analyzed. The brown solid would not redissolve in benzene or any other non-coordinating solvent so its recrystallization was impossible. The brown solid was observed to dissolve to some extent in solvents containing $Et_3Al_2Cl_3$.

Acknowledgements

This research was supported in part by University Research Council Funds, Board of Trustees of Institutions of Higher Learning, State of Mississippi. One of the authors (BTP) held a NDEA Traineeship during the time the research was carried out.

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