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Reactions of Lithium Dimethylamide with Some Borane Derivatives. Evidence for the Displacement of Lithium Hydride

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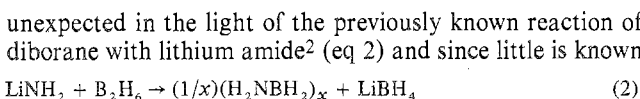
Received June 21, 1974

AIC40404E

The reactions of $\text{LiN}(\text{CH}_3)_2$ with $\text{HB}[\text{N}(\text{CH}_3)_2]_2$, $\text{Li}(\text{CH}_3)_2\text{N}\cdot\text{BH}_3$, $[(\text{CH}_3)_2\text{NBH}_2]_2$, $\text{K}(\text{CH}_3)_2\text{NBH}_2\text{N}(\text{CH}_3)_2\cdot\text{BH}_3$, $(\text{CH}_3)_3\text{N}\cdot\text{BH}_3$, and $\mu\text{-(CH}_3)_2\text{NB}_2\text{H}_5$ in diethyl ether have been studied. The first three compounds are converted to $\text{B}[\text{N}(\text{CH}_3)_2]_3$ and LiH at rates decreasing in the order given. $\text{K}(\text{CH}_3)_2\text{NBH}_2\text{N}(\text{CH}_3)_2\cdot\text{BH}_3$ rapidly forms $\text{B}[\text{N}(\text{CH}_3)_2]_3$, LiH , and $\text{K}(\text{CH}_3)_2\text{N}\cdot\text{BH}_3$, the last being insoluble in diethyl ether. $(\text{CH}_3)_3\text{N}\cdot\text{BH}_3$ is converted to $\text{B}[\text{N}(\text{CH}_3)_2]_3$, $\text{N}(\text{CH}_3)_3$, and LiBH_4 , while $\mu\text{-(CH}_3)_2\text{NB}_2\text{H}_5$ gives $\text{B}[\text{N}(\text{CH}_3)_2]_3$ and $\text{Li}(\text{CH}_3)_2\text{N}\cdot 2\text{BH}_3$. Possible mechanisms are proposed to account for these results and also for the reaction of B_2H_6 with $\text{LiN}(\text{CH}_3)_2$.¹

Introduction

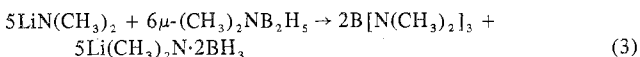
In 1972 we described a study of the action of diborane on a number of lithium mono- and di-*N*-alkylamides.¹ The initial products in most of these reactions were tris(amino)boranes and lithium borohydride (eq 1). Since this result was



of the behavior of bases like $\text{LiN}(\text{CH}_3)_2$ with boron compounds, we have extended our investigations to the reactions of this base with a series of simple borane derivatives. The results throw more light on the way bases like $\text{LiN}(\text{CH}_3)_2$ react with boranes and in particular on the course of the $\text{LiN}(\text{CH}_3)_2\text{-B}_2\text{H}_6$ reaction.

Results

Reaction of $\text{LiN}(\text{CH}_3)_2$ with $\mu\text{-(CH}_3)_2\text{NB}_2\text{H}_5$. We first tried this reaction in an attempt to prepare the NBNB chain anion $(\text{CH}_3)_2\text{N-BH}_2\text{-N}(\text{CH}_3)_2\text{-BH}_3^-$ by adduct formation. Contrary to expectation we found that $\mu\text{-(CH}_3)_2\text{NB}_2\text{H}_5$ reacts with a diethyl ether slurry of $\text{LiN}(\text{CH}_3)_2$ according to eq 3.



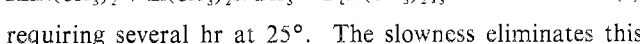
The reaction is complete within a few minutes at 25°. An nmr-monitored experiment using a large excess of $\text{LiN}(\text{CH}_3)_2$ gave the same products and showed no indication of either attack on $\text{Li}(\text{CH}_3)_2\text{N}\cdot 2\text{BH}_3$ or complex formation with $\text{B}[\text{N}(\text{CH}_3)_2]_3$. In a few instances of not quite complete reaction, probably because of the heterogeneity of the system and inadequate mixing, small quantities of $\text{HB}[\text{N}(\text{CH}_3)_2]_2$ and $\text{Li}(\text{CH}_3)_2\text{N}\cdot\text{BH}_3$ were detected by boron-11 nmr. This suggested that these compounds might be intermediates in eq 3, possibly forming *via* the originally sought adduct $\text{Li}(\text{C-H}_3)_2\text{NBH}_2\text{N}(\text{CH}_3)_2\cdot\text{BH}_3$. Accordingly, we investigated the action of $\text{LiN}(\text{CH}_3)_2$ on $\text{HB}[\text{N}(\text{CH}_3)_2]_2$, $\text{Li}(\text{CH}_3)_2\text{N}\cdot\text{BH}_3$, and $(\text{CH}_3)_2\text{N-BH}_2\text{-N}(\text{CH}_3)_2\text{-BH}_3^-$.

Reaction of $\text{LiN}(\text{CH}_3)_2$ with $\text{HB}[\text{N}(\text{CH}_3)_2]_2$. A diethyl ether solution of $\text{HB}[\text{N}(\text{CH}_3)_2]_2$ reacts rapidly with $\text{LiN}(\text{CH}_3)_2$ according to eq 4. The lithium hydride appears as a suspension



of very fine gray-white solid. Boron-11 nmr gave no evidence for a $\text{LiH-B}[\text{N}(\text{CH}_3)_2]_3$ complex.

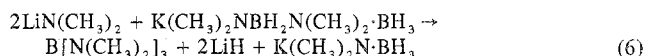
Reaction of $\text{LiN}(\text{CH}_3)_2$ with $\text{Li}(\text{CH}_3)_2\text{N}\cdot\text{BH}_3$. A diethyl ether solution of $\text{Li}(\text{CH}_3)_2\text{N}\cdot\text{BH}_3$ reacts with $\text{LiN}(\text{CH}_3)_2$ according to eq 5. This process is slower than eq 3 and 4,



requiring several hr at 25°. The slowness eliminates this

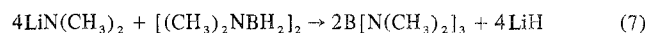
reaction as a significant step in the overall $\text{LiN}(\text{CH}_3)_2\text{-}\mu\text{-(CH}_3)_2\text{NB}_2\text{H}_5$ system. This point is discussed further below.

Reaction of $\text{LiN}(\text{CH}_3)_2$ with $\text{K}(\text{CH}_3)_2\text{NBH}_2\text{N}(\text{CH}_3)_2\cdot\text{BH}_3$. This experiment was performed to test the possibility that $(\text{CH}_3)_2\text{N-BH}_2\text{-N}(\text{CH}_3)_2\text{-BH}_3^-$ may be an intermediate in eq 3. The potassium salt was generated by reduction of $(\text{CH}_3)_2\text{NHBH}_2\text{N}(\text{CH}_3)_2\cdot\text{BH}_3$ with potassium metal in monoglyme.³ Since we found that monoglyme is cleaved easily in $\text{LiN}(\text{CH}_3)_2$ reactions, the solvent was evaporated and replaced by diethyl ether after the potassium reduction. This solution of $\text{K}(\text{CH}_3)_2\text{NBH}_2\text{N}(\text{CH}_3)_2\cdot\text{BH}_3$ reacts rapidly with $\text{LiN}(\text{CH}_3)_2$ in agreement with eq 6. The $\text{B}[\text{N}(\text{CH}_3)_2]_3$ was



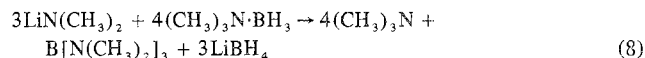
identified immediately by its boron-11 nmr spectrum. Since $\text{K}(\text{CH}_3)_2\text{N}\cdot\text{BH}_3$ is insoluble in diethyl ether, the solvent had to be evaporated and replaced by monoglyme before nmr identification could be realized.

Reaction of $\text{LiN}(\text{CH}_3)_2$ with $[(\text{CH}_3)_2\text{NBH}_2]_2$. The reaction of a diethyl ether solution of dimeric dimethylaminoborane with $\text{LiN}(\text{CH}_3)_2$ occurs in agreement with eq 7. The reaction



is very slow at 25°, requiring weeks to complete. No evidence for intermediates was obtained by periodic monitoring of the system by boron-11 nmr.

Reaction of $\text{LiN}(\text{CH}_3)_2$ with $(\text{CH}_3)_3\text{N}\cdot\text{BH}_3$. A diethyl ether solution of $(\text{CH}_3)_3\text{N}\cdot\text{BH}_3$ reacts with $\text{LiN}(\text{CH}_3)_2$ over a period of weeks according to eq 8. No intermediates or by-products



were detected by periodic nmr monitoring. The free $(\text{CH}_3)_3\text{N}$ was determined by titration with standard acid after separation from $\text{B}[\text{N}(\text{CH}_3)_2]_3$.

Discussion

The Nature of $\text{LiN}(\text{CH}_3)_2$. The base $\text{LiN}(\text{CH}_3)_2$ is capable of displacing hydride ion from simple borane derivatives like $\text{HB}[\text{N}(\text{CH}_3)_2]_2$, $[(\text{CH}_3)_2\text{NBH}_2]_2$, and $\text{Li}(\text{CH}_3)_2\text{N}\cdot\text{BH}_3$, as evidenced by actual precipitation of lithium hydride. With compounds like $\mu\text{-(CH}_3)_2\text{NB}_2\text{H}_5$ and $(\text{CH}_3)_3\text{N}\cdot\text{BH}_3$ the probable generation of lithium hydride is reflected in the appearance of products known to form when lithium hydride reacts with these substances, namely, $\text{Li}(\text{CH}_3)_2\text{N}\cdot 2\text{BH}_3$ ⁴ and LiBH_4 .⁵

The Course of the $\text{LiN}(\text{CH}_3)_2\text{-}\mu\text{-(CH}_3)_2\text{NB}_2\text{H}_5$ Reaction. Several of the reactions described above may function as intermediate steps in this system. The logical first reaction is simple adduct formation (eq 9). The NBNB chain anion

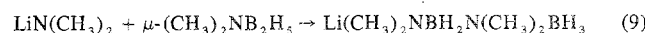
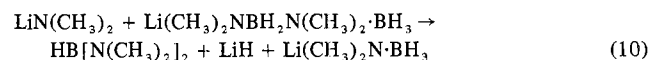


Table I. Summary of Reactions of R_nE⁻ Donors with B₂H₆

Group V		Group VI	
Donor	Products	Donor	Products
N(CH ₃) ₂ ^{-a}	B[N(CH ₃) ₂] ₃ + BH ₄ ⁻	OCH ₃ ^{-b}	B(OCH ₃) ₃ + BH ₄ ⁻
P(CH ₃) ₂ ^{-c}	(CH ₃) ₂ P(BH ₃) ₂ ⁻	SCH ₃ ^{-d}	CH ₃ S(BH ₃) ₂ ⁻
As(CH ₃) ₂ ^{-e}	(CH ₃) ₂ As(BH ₃) ₂ ⁻	SeCH ₃ ^{-f}	CH ₃ Se(BH ₃) ₂ ⁻

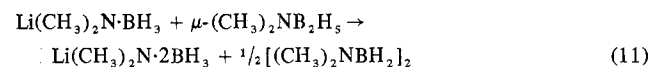
^a This work. ^b H. I. Schlesinger, H. C. Brown, H. R. Hoekstra, and L. R. Ropp, *J. Amer. Chem. Soc.*, **75**, 199 (1953). ^c L. D. Schwartz and P. C. Keller, *Inorg. Chem.*, **10**, 645 (1971). ^d J. J. Mielcarek and P. C. Keller, *J. Chem. Soc., Chem. Commun.*, 1090 (1972). ^e L. D. Schwartz and P. C. Keller, *Inorg. Chem.*, **12**, 947 (1973). ^f J. J. Mielcarek and P. C. Keller, to be submitted for publication.

is attacked rapidly by LiN(CH₃)₂ and the most likely first products are shown by eq 10. These substances have been

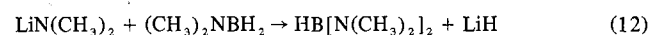


detected in small quantity in poorly mixed reactions. Since the reaction of LiN(CH₃)₂ with HB[N(CH₃)₂]₂ is also rapid (eq 4), the latter would not be observed under ordinary conditions and the reaction would continue on to give the products of eq 6.

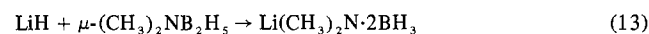
The products formed by LiN(CH₃)₂ and Li(CH₃)₂N·BH₃ (eq 5) are consistent with the general scheme, but the reaction is too slow to be an important intermediate step. An alternative route is the known rapid reaction of Li(CH₃)₂N·BH₃ with μ -(CH₃)₂NB₂H₅ (eq 11).⁶ The reaction of LiN(CH₃)₂ with dimeric dimethylaminoborane (eq 7) is very slow. However, it is possible that reaction 11 initially generates monomeric



dimethylaminoborane as a (p → p)π stabilized product which may only dimerize slowly. The monomer would probably react rapidly with LiN(CH₃)₂ according to eq 12.



Finally, the lithium hydride produced in eq 4, 10, and 12 would be taken up by μ -(CH₃)₂NB₂H₅ according to eq 13.⁴



The LiN(CH₃)₂-(CH₃)₃N·BH₃ Reaction. Reaction 8 may proceed by initial displacement of (CH₃)₃N according to eq 14 or 15. This would be followed by a sequence of lithium



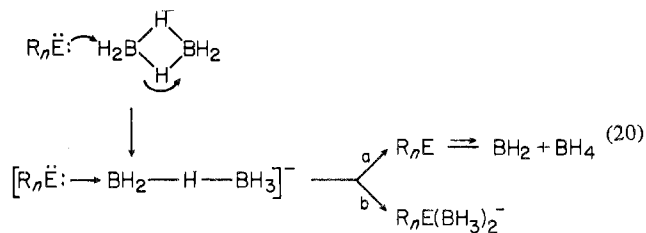
hydride displacements by LiN(CH₃)₂. The formation of LiBH₄ follows from the action of lithium hydride on (CH₃)₃N·BH₃.⁵

The LiN(CH₃)₂-B₂H₆ Reaction. On the basis of the reactions observed and postulated above we suggest the following sequence to account for the action of LiN(CH₃)₂ on B₂H₆.¹



General Comments. The strong base LiN(CH₃)₂ has two chemically active lone electron pairs and can be classed with other bases like (CH₃)₂P⁻, (CH₃)₂As⁻, CH₃O⁻, CH₃S⁻, and CH₃Se⁻. The reactions of these double donors with diborane are compared in Table I. The table shows a clear distinction in product type between first- and second-row donors which

can be rationalized in terms of relative ability to form (p → p)π bonds. We suggest a scheme like eq 20 to account for



the observed reactions. In the intermediate⁷ the second lone pair on oxygen or nitrogen can form a moderately strong dative π bond with boron to generate π-stabilized R_nE→BH₂ and a borohydride ion following path a. Further reaction of R_nEBH₂ with more base would occur rapidly as suggested above. With second- and third-row donors dative π bonding to boron is weak and rearrangement to a dative σ-bonded bis(borane) adduct R_nE(BH₃)₂⁻ should occur by path b.

Experimental Section

General Data. Standard high-vacuum and inert-atmosphere techniques⁸ were employed for all routine manipulations. Boron-11 nmr spectra were obtained using a Varian HA-100 spectrometer operating at 32.1 MHz. Infrared spectra were obtained with a Perkin-Elmer 337 spectrophotometer. X-Ray powder data were obtained with a 57.3-mm radius camera and Cu Kα radiation. Powder samples were contained in 0.5-mm thin-wall quartz capillaries.

Reagents. Lithium dimethylamide was prepared by the reaction of lithium metal containing 1% sodium with dimethylamine in benzene.⁹ The synthesis was carried out in an all-Pyrex vessel with a filter arm to separate insoluble materials from the LiN(CH₃)₂ solution prior to solvent evaporation. μ -Dimethylaminodiborane¹⁰ and (CH₃)₂NHBH₂N(CH₃)₂·BH₃¹¹ were prepared by literature methods. Solutions of K(CH₃)₂NB₂H₅ were generated by reaction of potassium with (CH₃)₂NHBH₂N(CH₃)₂·BH₃ in monoglyme.³ Bis(dimethylamino)borane was prepared by heating diborane and excess tris(dimethylamino)borane (Alfred Bader) at 185° for 24 hr. Dimeric dimethylaminoborane was generated by the pyrolysis of (CH₃)₂NH·BH₃¹² (Research Organic/Inorganic Chemical Corp.). Solutions of Li(CH₃)₂N·BH₃ were generated by the reaction of (CH₃)₂NH·BH₃ with excess lithium hydride in diethyl ether. The synthesis was carried out in an all-Pyrex vessel with a filter arm to remove unreacted lithium hydride. Trimethylamine-borane was purchased from Research Organic/Inorganic Chemical Corp. The solvents diethyl ether and monoglyme (1,2-dimethoxyethane) were stored in evacuated bulbs over LiAlH₄ and when needed were condensed directly into reaction vessels.

General Procedure. Reactions were carried out on a 1–2-mmol scale in vessels designed so that the experiment could be monitored by boron-11 nmr.¹³ Spectra showed that reactions were quantitative. Product identification was accomplished by boron-11 nmr followed up by isolation and characterization by ir. In most experiments recovery of B[N(CH₃)₂]₃ by vacuum-line methods was 85–90% of theoretical.

For the isolation and identification of lithium hydride an all-Pyrex vessel with a filter arm was used. After completion of the reaction, volatile products were removed and dry dimethylamine was condensed into the vessel to dissolve residual LiN(CH₃)₂ and the resulting slurry was filtered. After removal of dimethylamine, the lithium hydride was collected from the filter disk and was identified either by treatment with ethanol to generate hydrogen or by X-ray powder methods.

Acknowledgment. Support of this research by a grant from the National Science Foundation is gratefully acknowledged.

Registry No. LiN(CH₃)₂, 3585-33-9; μ -(CH₃)₂NB₂H₅, 23273-02-1; HB[N(CH₃)₂]₂, 2386-98-3; Li(CH₃)₂N·BH₃, 53042-33-4; K(CH₃)₂NB₂H₅, 53042-34-5; [(CH₃)₂NB₂H₅]₂, 23884-11-9; (CH₃)₃N·BH₃, 75-22-9.

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 (12) A. B. Burg and C. L. Randolph, *J. Amer. Chem. Soc.*, **71**, 3451 (1949).
 (13) P. C. Keller, *Inorg. Chem.*, **11**, 256 (1972).

Notes

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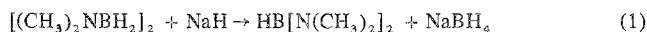
Slow Solution Reaction of Dimeric Dimethylaminoborane with Lithium Hydride

Philip C. Keller

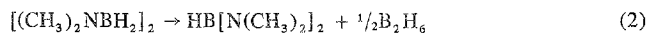
Received July 16, 1974

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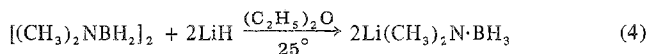
There are no literature reports on the interaction of an alkali metal hydride with $[(\text{CH}_3)_2\text{NBH}_2]_2$ under mild conditions. Burg and Randolph¹ showed that $[(\text{CH}_3)_2\text{NBH}_2]_2$ reacted with NaH (but not LiH) at elevated temperature in the absence of solvent according to



This reaction probably results from a thermally induced disproportionation of $[(\text{CH}_3)_2\text{NBH}_2]_2$

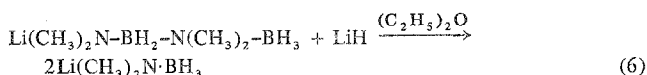
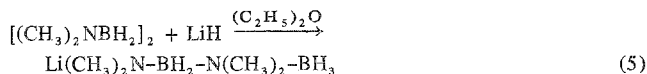


As part of another project, we have had the opportunity to observe the action of LiH on $[(\text{CH}_3)_2\text{NBH}_2]_2$ at room temperature in diethyl ether over periods of several months. We find that under these conditions the sole final product is $\text{Li}(\text{CH}_3)_2\text{N}\cdot\text{BH}_3$.



A typical reaction was 90% complete after 2 months at ambient temperature.

If the system is monitored periodically by boron-11 nmr, weak signals due to an intermediate product can be detected (Figure 1). The nmr parameters compare favorably with those of the ion $(\text{CH}_3)_2\text{NBH}_2\text{N}(\text{CH}_3)_2\text{BH}_3^{-2}$ (triplet -2.4 ppm, $J_{\text{BH}} = 92$ Hz; quartet 13.1 ppm, $J_{\text{BH}} = 81$ Hz; data for potassium salt in 1,2-dimethoxyethane). The presence of this ion strongly suggests that the main pathway for eq 4 involves ring opening by reaction of LiH with dimethylaminoborane dimer followed in a subsequent step by cleavage of the NBNE chain by LiH.



The cleavage reaction (eq 6) has been demonstrated elsewhere.²

Experimental Section

Standard vacuum techniques were used in this work. Lithium hydride (Alfa Inorganics) was used without further purification; $[(\text{CH}_3)_2\text{NBH}_2]_2$ was prepared by the pyrolysis of $(\text{CH}_3)_2\text{NH}\cdot\text{BH}_3$ (Research Organic/Inorganic Chemical Corp.).³ Diethyl ether was stored in an evacuated bulb over LiAlH_4 and when needed was

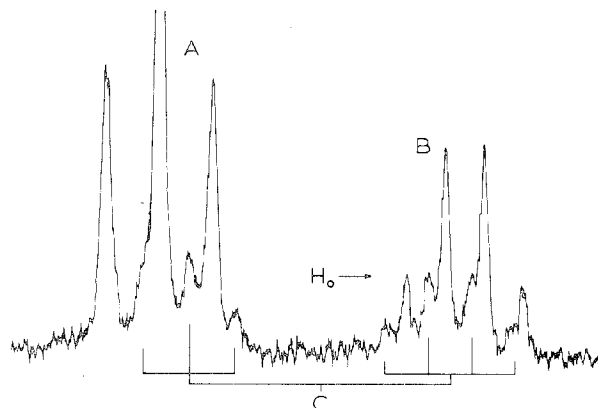


Figure 1. Boron-11 nmr spectrum of the partially complete reaction of $[(\text{CH}_3)_2\text{NBH}_2]_2$ with LiH after 2.5 weeks: A, triplet, $[(\text{CH}_3)_2\text{-NBH}_2]_2$, -5.1 ppm, $J = 113$ Hz; B, quartet, $(\text{CH}_3)_2\text{NBH}_3^-$, 15.0 ppm, $J = 83$ Hz; C, $(\text{CH}_3)_2\text{N}\cdot\text{BH}_2\text{-N}(\text{CH}_3)_2\text{-BH}_3^-$, triplet, -2.7 ppm, $J = 100$ Hz; quartet, 14.1 ppm, $J = 88$ Hz. Chemical shifts are relative to $(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{BF}_3$.

condensed directly into the reaction vessel. Boron-11 nmr spectra were obtained with a Varian HA-100 spectrometer operating at 32.1 MHz. Chemical shifts and coupling constants were measured by the substitution side band method.

In a typical experiment an all-Pyrex nmr reaction vessel was charged with 8-10 mmol of LiH, 1-2 mmol of $[(\text{CH}_3)_2\text{NBH}_2]_2$ and 1 ml of diethyl ether were condensed in, and the vessel was sealed. The mixture was allowed to stand at room temperature for 2-3 months with occasional shaking and periodic monitoring by nmr. Products were identified by their nmr parameters.

Acknowledgment. This research was supported by a grant from the National Science Foundation.

Registry No. $[(\text{CH}_3)_2\text{NBH}_2]_2$, 23884-11-9; LiH, 7580-67-8; ^{11}B , 14798-13-1.

References and Notes

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 (2) P. C. Keller, *J. Amer. Chem. Soc.*, **96**, 3078 (1974).
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Reactions of Coordinated Nickel(II) Complexes Containing Imine and Amine Groups¹

Russell Cheney, Laurel E. Heyman, and Elliott L. Blinn*

Received March 1, 1974

AIC40142G

Nickel(II) complexes (I, II) containing a Schiff base ligand derived from pyrrole-2-carboxaldehyde and dipropylene-triamine (bis(2-pyrrolyl)-2,6,10-triaza-1,10-undecadiene