Registry No. (OEP)Fe(C_6F_4H), 96482-32-5; (TPP)Fe(C_6F_4H), 96482-33-6; ((*m*-Me)TPP)Fe(C_6F_4H), 96532-01-3; ((*p*-Me)TPP)Fe(C_6F_4H), 96482-34-7; (OEP)Fe(C_6F_5), 96502-36-2; (TPP)Fe(C_6F_5), 96502-37-3; ((*m*-Me)TPP)Fe(C_6F_5), 96502-38-4; ((*p*-Me)TPP)Fe(C_6F_5), 96532-02-4; ((*p*-Et_2N)TPP)Fe(C_6H_5), 96482-35-8; ((CN)$_4$TPP)Fe(C_6H_5), 96502-39-5; ((*p*-Et_2N)TPP)Fe(Cl), 85529-39-1; ((CN)$_4$TPP)Fe(Cl), 96293-36-6; (OEP)Fe(Cl), 28755-93-3; (TPP)Fe(Cl), 16456-81-8; ((*m*-Me)TPP)Fe(Cl), 52155-49-4; ((*p*-Me)TPP)Fe(Cl), 19496-18-5; C_6H_5Br, 108-86-1; C_6F_4HBr, 1559-88-2; C_6F_5Br, 344-04-7; (*N*-C_6H_5)(*p*-Et_2N)TPPH, 96502-40-8.

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Atropisomerism in Aryl-Substituted Borazines

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The *N,N',N''*-tri-*o*-tolylborazines (*o*-$CH_3C_6H_4NBX)_3$ (X = Cl, Br, Me, Et) were prepared and studied by means of ^1H and ^{13}C NMR. The methyl derivative (X = Me) resulting from the reaction of CH_3MgI on the *B,B',B''*-trichloro-*N,N',N''*-tri-*o*-tolylborazine (X = Cl) in diethyl ether was shown to be a mixture of the cis isomer alone with *B*-hydroxy byproducts that were identified. This methylation reaction fails to provide the expected trans isomer for steric reasons: instead, *B*-hydroxy compounds appear during the hydrolysis step.

Introduction

The fact that aromatic rings of *N,N',N''*-triaryl- (*B,B',B''*-triaryl-) substituted borazines are perpendicular to the plane of the borazine ring is strongly supported by several reports. Such evidence was first derived from ^1H NMR data on *N,N',N''*-triaryl-*B,B',B''*-trimethylborazines $(ArNBMe)_3$;[1] more recently, accurate structural analysis of $(C_6H_5NBCl)_3$ in the solid state led to a value of 77–87° for the angle between the phenyl substitutent and the borazine ring.[2] Furthermore, as a direct consequence of such a conformation for the phenyl group, partial separation of both expected isomers was achieved in the case of (*B*-*o*-Tol-$NEt)_3$, the identification being performed by means of ^1H NMR.[3] In the course of our systematic study of *N,N',N''*-triarylborazines, we were led to investigate from this standpoint the closely related *N,N',N''*-tri-*o*-tolylborazines (*o*-$CH_3C_6H_4NBX)_3$ (with X = Cl, Br, Me, and Et, respectively, for compounds I–IV) (Figure 1), using ^1H as well as ^{13}C and ^{11}B NMR; particular care was brought to the purification of the products by chromatographic methods (TLC and VPC). The results we have so far obtained are somewhat different from the above quoted;[3] in no case was it possible to provide evidence for atropisomerism in such systems.

Experimental Section

General Data. The solvents used were refluxed and distilled from CaH_2. Ethanol-free chloroform was obtained by passing spectrograde material through a short alumina column.[4] All reactions were carried out under a dry nitrogen atmosphere. NMR spectra were recorded on a Varian HT 80 spectrometer. The conditions were as follows: ^1H, 79.542 MHz, solvent $CDCl_3$, Me_4Si as internal standard, 5-mm-diameter tubes; ^{11}B, 25.517 MHz, solvent $CHCl_3$, boric acid as internal reference; ^{13}C, 20.000 MHz, solvent and reference $CHCl_3$ (chemical shifts converted to Me_4Si using $\delta_{Me_4Si} = \delta_{CHCl_3} + 77.2$ ppm). For the last two nuclei, spectra were run in 10-mm-diameter tubes, with a 5-mm coaxial tube containing D_2O for the lock and, eventually, the reference (boric acid). One ^1H NMR spectrum was recorded at 360 MHz on a Bruker WM 360, with $CDCl_3$ as a solvent. The following abbreviations were used to designate the multiplicity of the individual signals: s = singlet, d = doublet, t = triplet, m = multiplet, b = broad, dd = doublet of doublets, td = triplet of doublets. Infrared spectra were obtained as Nujol mulls on a Perkin-Elmer 735 B spectrometer. VPC was obtained on a Varian 1400 apparatus using a 1-m-long column filled with 10% OV 101 on Chromosorb GHP 100/120 mesh. TLC was performed on Merck silica gel 60 F 254 plates, and PLC, on Merck silicagel 60 plates (solvent C_6H_6). Melting points were determined on a Köffler melting point apparatus and are uncorrected.

***B,B',B''*-Trichloro-*N,N',N''*-tri-*o*-tolylborazine (I).** This compound was prepared according to established procedure[5] from BCl_3 and *o*-toluidine in toluene, the chlorobroazine recrystallizing from the solvent on cooling; yield 70%. ^1H NMR: 2.23 (s), 7.2 (m) ppm. ^{13}C NMR: aromatic CH 126.9, 128.1, 128.2, 128.3, 130.7, 131.0 ppm; CN 140 ppm; CCH_3 134 ppm; CCH_3 18.1 ppm.

***B,B',B''*-Trimethyl-*N,N',N''*-tri-*o*-tolylborazine (III).** To a diethyl ether solution of methylmagnesium iodide, prepared from magnesium turnings (1.09 g, 0.045 mol) and a slight excess of methyl iodide, was added *B,B',B''*-trichloro-*N,N',N''*-tri-*o*-tolylborazine (I) (5.68 g, 0.0125 mol) by small fractions, allowing a gentle boiling, and the mixture was refluxed 1 h. After cooling with an ice bath, the mixture was quenched with a solution of NH_4Cl and III was isolated by crystallization from an ether–methanol solution.[5] The yield of crude product was 3.24 g (66% based on I) of white crystals, mp 160–162 °C. TLC of the latter gives rise to three spots (C_6H_6 as eluent.) The same result was obtained by VPC (Figure 2) (oven temperature 280 °C, nitrogen 30 mL/min). Preparative TLC of the crude mixture yields the two main components: 0.080 g of *B,B',B''*-trimethyl-*N,N',N''*-tri-*o*-tolylborazine (III), mp 168–170 °C (lit.[6] mp 158–160 °C), as well as 0.020 g of the *B*-hydroxy derivative V, mp 163–165 °C. ^1H NMR of both compounds is reported (Figure 3). ^{13}C NMR for III: aromatic CH 125.1, 126.6, 128.2, 130.3 ppm; CCH_3 133.9 ppm; CN 147.4 ppm; CCH_3 18.3 ppm; BCH_3 1.4 ppm. ^{13}C NMR for V: aromatic CH 125.1, 125.8, 126.5, 126.6, 126.8, 126.85, 128.3, 128.4, 128.5, 130.3, 130.6 ppm; CCH_3 134.2, 134.7 ppm; CN 143.7, 147.2 ppm; CCH_3 18.1, 18.3 ppm.

***B,B',B''*-Triethyl-*N,N',N''*-tri-*o*-tolylborazine (IV).** To an ether solution of ethylmagnesium iodide (0.045 mol) was added solid *B,B',B''*-trichloro-*N,N',N''*-tri-*o*-tolylborazine I (5.68 g, 0.0125 mol), and the mixture was refluxed for 1 h. After hydrolysis (NH_4Cl method), IV was isolated and then purified by recrystallization from an ether–ethanol solution. The yield of IV was 2.44 g (45% based on I) of white crystals, mp 130–135 °C (lit.[3] mp 130–132 °C). From the ^1H NMR spectrum, it may be concluded that the product is also contaminated by *B*-hydroxy derivatives, but isolation of pure compounds by PLC was unsuccessful. Furthermore, small amounts of unidentified impurities were detected by VPC.

2,4-Dibromo-3-*o*-tolyl-8-methyl-2,4-dibora-1,3-diazanaphthalene (VII). The reaction of boron tribomide BBr_3 (34.43 g, 0.137 mol) with *o*-toluidine (14.85 g, 0.1385 mol) in boiling chlorobenzene, under nitrogen, does not lead to the expected bromoborazine, II, but to the title compound VII in a nearly quantitative yield. After concentration of the solution, 14.25 g of VII (yield 53%) was obtained as yellow crystals most sensitive to moisture. ^1H NMR= CCH_3 2.10 (s), 2.40 (s) ppm; aromatic CH 7.4 (m), 7.92 (d) ppm. ^{13}C NMR: aromatic CH 121.7, 126.7, 126.9, 127.9, 130.5, 134.9, 136.0 ppm; CCH_3 122.8, 133.7 ppm; CN 145.2, 145.3 ppm; CCH_3 16.8, 18.5 ppm. Anal. Calcd for $C_{14}H_{14}N_2$-

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(2) W. Schwarz, D. Lux, and H. Hess, *Cryst. Struct. Commun.*, **6**, 431 (1977).
(3) P. M. Johnson and E. K. Mellon, *Inorg. Chem.*, **13**, 2769 (1974).
(4) "Vogel's Textbook of Practical Organic Chemistry", 4th ed., Longmans, Green and Co., London and New York, 1978, p 268.
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(6) W. Gerrard, E. F. Mooney, and D. E. Pratt, *J. Appl. Chem.*, **13**, 127 (1963).

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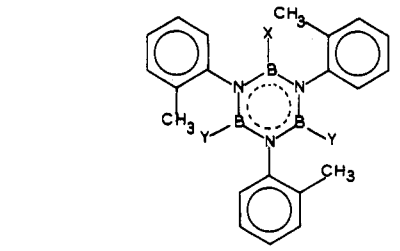
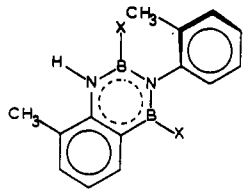


I X = Y = Cl
II X = Y = Br
III X = Y = Me
IV X = Y = Et
V X = OH, Y = Me
VI X = Me, Y = OH



VII X = Br
VIII X = Me

Figure 1.

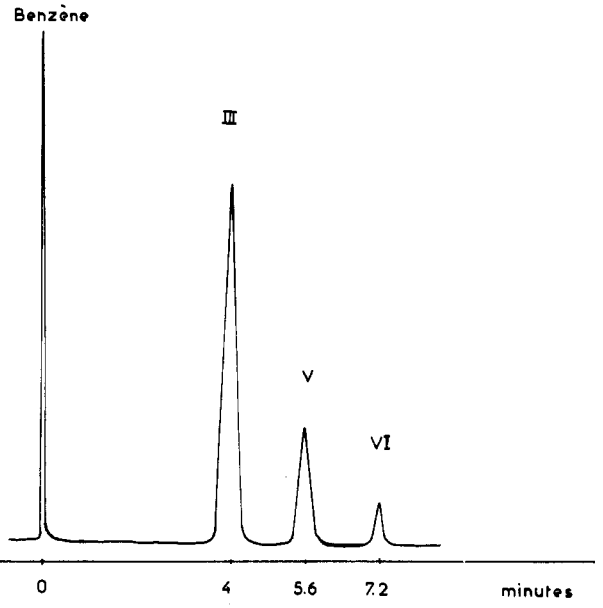


Figure 2. Typical chromatogram (VPC) of the crude material obtained by methylation of *B,B',B''*-trichloro-*N,N',N''*-tri-*o*-tolylborazine (I) after recrystallization (Et_2O–MeOH).

B_2Br_2 (VII): N, 7.15; B, 5.53; Br, 40.85. Found: N, 7.02; B, 5.71; Br, 41.96.

2,4-Dimethyl-3-*o*-tolyl-8-methyl-2,4-dibora-1,3-diazanaphthalene (VIII). To an ether solution of methylmagnesium iodide (0.062 mol) was added solid bromo derivative VII (4.11 g, 0.021 mol); after refluxing for 1 h, the solution was hydrolyzed as before to yield 1.50 g (56% based on VII) of white crystals consisting of a mixture of VIII and III (98% and 2%, respectively, from VPC). On account of the small percentage of III in the mixture, we have only succeeded in enriching it (75% III and 25% VIII) whereas the main component (VIII) was isolated in pure form, by recrystallization from a water–methanol solution. ^1H NMR (360 MHz): aromatic CH 6.96 (dd), 7.10 (t), 7.20 (td), 7.25 (td), 7.31 (dd), 7.39 (dd), 7.90 (dd) ppm; NH 6.51 (b) ppm; CCH_3 2.10 (s), 2.45 (s) ppm; BCH_3 0.32 (s), 0.59 (s) ppm. ^{13}C NMR: aromatic CH 119.6, 125.3, 126.5, 127.6, 130.3, 132.9, 133.8 ppm; CCH_3 122.1, 133.4 ppm; CN 145.0, 147.0 ppm; CCH_3 17.0, 18.3 ppm; BCH_3 0.7 ppm. Mp for VIII: 78–80 °C. Anal. Calcd for $C_{16}H_{20}N_2B_2$ (VIII): N, 10.70; B, 8.27. Found: N, 10.34; B, 8.15.

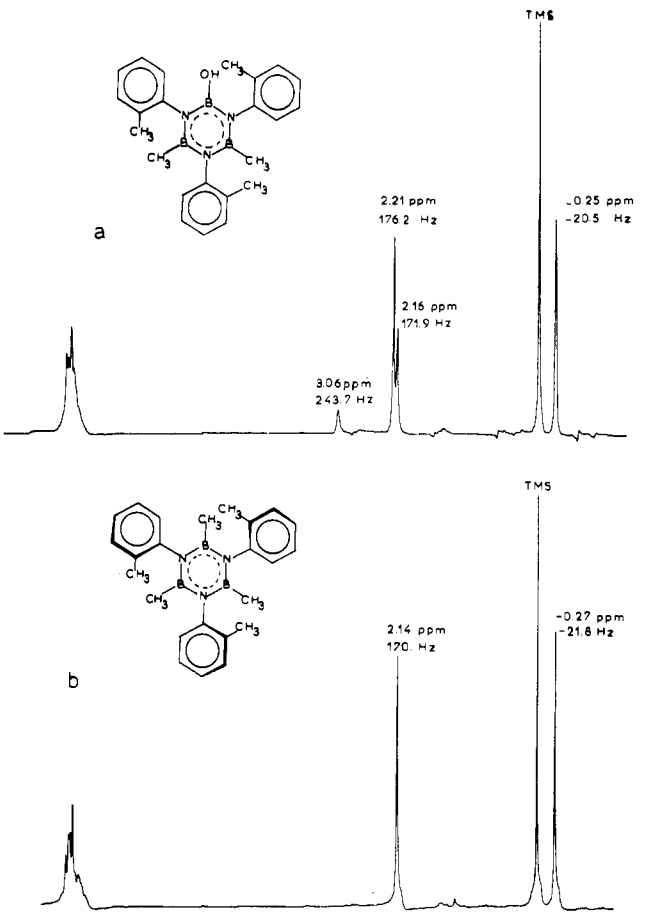
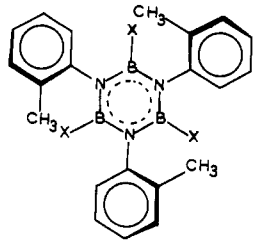


Figure 3. 80-MHz proton NMR spectra: (a) the *B*-hydroxy derivative V; (b) the cis isomer of *B,B',B''*-trimethyl-*N,N',N''*-tri-*o*-tolylborazine (III). Chemical shifts are in ppm and coupling constants in Hz downfield from Me_4Si.

Results and Discussion

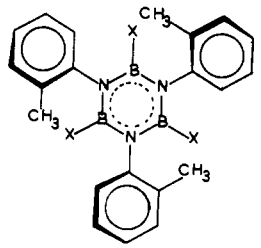
It has been reported[3] that two configurations are to be expected for *N,N',N''*-tri-*o*-tolylborazines bearing identical substituents on the boron atoms (Figure 4). The cis isomer has all three of the tolyl CH_3 groups on one side of the borazine ring plane (C_{3v} symmetry), while the trans isomer has two tolyl CH_3 groups on one side of the borazine ring plane and the third on the opposite side (C_s symmetry). The ^1H NMR spectrum of the *B,B',B''*-trichloro-*N,N',N''*-tri-*o*-tolylborazine (I), prepared from BCl_3 and *o*-toluidine, was reported to present a very sharp tolyl CH_3 singlet, indicating possible equivalence of the three tolyl groups,[3] and we were led to similar results; on the other hand, if the ^{13}C NMR of I shows a single signal for the CCH_3 carbon, the aromatic part of the spectrum is much more complex, probably as a consequence of a partial hydrolysis of I and subsequent polymerization. To prevent such difficulties, I was converted into the *B,B',B''*-trimethyl-*N,N',N''*-tri-*o*-tolylborazine (III), which is much more resistant to hydrolysis. At first glance, the ^1H NMR spectrum of the latter may be interpreted as resulting from a mixture of the two expected isomers. Thus, three signals are observed near 2.2 ppm; the cis isomer of III gives a singlet for the three CCH_3 whereas the trans isomer would lead to two singlets with a resonance line being of twice the intensity of the other for the two different kinds of CCH_3 of the molecule.

Thin-layer chromatography rules out such an interpretation: thus, for the same compound three spots were observed, implying that III (R_f 0.85, C_6H_6 eluent) is in fact contaminated by V (R_f 0.43) and possibly VI (R_f 0.23). The *B*-hydroxy compounds V and VI result from incomplete reaction of CH_3MgI with *B,B',B''*-trichloro-*N,N',N''*-tri-*o*-tolylborazine I and are formed during



CIS

X = Cl ; Br ; Me ; Et.



TRANS

Figure 4. Configurations of cis and trans isomers of *N,N',N''*-tri-*o*-tolylborazines.

the hydrolysis step. VPC of the mixture leads to similar results (Figure 2). Finally, preparative TLC was used to obtain pure samples of III and V,[7] whereas successive recrystallizations and/or sublimations failed to achieve the separation. Both derivatives are crystalline, sharp-melting compounds and were further characterized by means of NMR techniques. Thus, the structure of compound V is clearly demonstrated from its ^1H NMR spectrum (Figure 3a), a careful integration giving the ratios 11.5/0.8/9.7/6.0 for the different protons of the molecule (calculated for V: 12/1/9/6). Furthermore, only consideration of the peak heights leads to the correct number of CH_3 groups. The small signal observed near 3.1 ppm was attributed to the BOH proton. This is substantiated by IR data (ν_{B-OH} = 3600 cm^{-1}). In addition, ^{11}B NMR spectrum of V consists of two broad peaks (integration was too inaccurate) whose chemical shifts are in agreement with the few available data published so far (Table I). The ^1H NMR spectrum of *B,B',B''*-trimethyl-*N,N',N''*-tri-*o*-tolylborazine (III) is also significant (Figure 3b): it displays two sharp singlets for the three CCH_3 and for the three BCH_3 of the molecule. Hence, it may be concluded that either (i) *B,B',B''*-trimethyl-*N,N',N''*-tri-*o*-tolylborazine (III) consists of the pure cis isomer or (ii) III is a mixture of both cis and trans isomers with rapid (on the NMR time scale) rotation about the C–N bond.

In the case of the first hypothesis (i), two possibilities can be envisaged: (a) The reaction of *o*-toluidine with BCl_3 leads to the cis isomer of *B,B',B''*-trichloro-*N,N',N''*-tri-*o*-tolylborazine alone; this is at odds with the fact that formation of *B,B',B''*-trihaloborazines $(ArNBX)_3$ (X = Cl, Br) proceeds through formation of linear intermediates—some of them were isolated in special cases[9,12] —the ring closure being the last step of thee reaction.

(7) It should be noted that if PLC gives pure samples of the *B*-hydroxy compound V (one spot by TLC), in some cases, the samples of III are still contaminated by small amounts of V (two spots by TLC), possibly because of hydrolysis of III catalyzed by the SiO_2 of the plate.

(8) H. Nöth and B. Wrackmeyer in "NMR Basic Principles and Progress", Springer Verlag, New York, 1978.

Table I. ^{11}B Chemical Shifts of *N,N',N''*-Triarylborazines

compd	$\delta(^{11}B)^a$	compd	$\delta(^{11}B)^a$
III	36.1	$(o\text{-}ClC_6H_4NBCH_3)_3$	35.7
V	36.1	$(C_6H_5NBCl)_3$	31.5[c]
	22.7	$(o\text{-}CH_3C_6H_4NBCl)_3$	30.5[b]
$(m\text{-}CH_3C_6H_4NBCH_3)_3$	36.1	$(o\text{-}CH_3C_6H_4NBOH)_3$	20.6[b]
$(C_6H_5NBCH_3)_3$	35.8		

[a] In ppm downfield from $BF_3{\cdot}Et_2O$. Unless otherwise noted, chemical shifts are the results of our own measurements (solvent $CHCl_3$), with boric acid as internal standard, and converted to $BF_3{\cdot}Et_2O$ by the relation[8] $\delta_{B(OH)_3}$ = 18.8 ppm + $\delta_{BF_3\cdot Et_2O}$. [b] From ref 9, with BCl_3 as external standard; converted to $BF_3{\cdot}Et_2O$ by the relation δ_{BCl_3} = 47.4 ppm + $\delta_{BF_3\cdot Et_2}$.[10] [c] From ref 11.

(b) *B,B',B''*-Trichloro-*N,N',N''*-tri-*o*-tolylborazine (I) is a mixture of both cis and trans isomers, but the attack of the Grignard reagent takes place *exclusively* on the less hindered side of the borazine plane opposite to the two tolyl CH_3 groups, thus leading to the *cis isomer* as the sole product.

Such vistas are strongly supported by ^{13}C NMR data, the latter being much more sensitive owing to the broader range of chemical shifts. The ^{13}C NMR spectrum of *B,B',B''*-trimethyl-*N,N',N''*-tri-*o*-tolylborazine (III) and subsequent assignments have been published elsewhere:[13] let us say at this point that the number of lines observed is in complete agreement with the proposed cis configuration. The ^{13}C NMR spectrum of the *B*-hydroxy compound V is much more complex; it is however noteworthy that the number of observed lines precludes the existence of a plane of symmetry in V. Thus, should there be a symmetry plane in V, eight lines would be observed for the aromatic carbons bonded to hydrogen; but, in fact, 11 lines were obtained (out of the 12 expected for a C_s type molecule). In other words, *the boron atom bonded to the hydroxy group of V has for neighbors two o-tolyl groups whose one methyl group lies above the borazine plane and the other group beneath this plane.* This hydroxy compound V is thus obtained from the trans isomer of *B,B',B''*-trichloro-*N,N',N''*-tri-*o*-tolylborazine (I) for which the reaction of CH_3MgI could not be brought to completion in the mild conditions we used (refluxing diethyl ether).

Samples of the cis isomer III were heated above the melting point in evacuated capillaries, but after cooling, no change could be detected either in the melting range or in the ^1H NMR spectra. However, above 350 °C, the initially colorless material turned yellow, giving rise to decomposition byproducts.

Finally, a second component (R_f 0.23, solvent C_6H_6) was formed in a much smaller amount during the course of the methylation of *B,B',B''*-trichloro-*N,N',N''*-tri-*o*-tolylborazine (I) and was tentatively identified as the dihydroxy compound VI. [Careful hydrolysis of V, as suggested by one of the reviewers, leads to larger amounts of VI (as indicated by VPC). Unfortunately, the isolation of a pure compound by preparative TLC has failed. In all cases, this treatment afforded seemingly polymeric materials, insoluble in organic solvents. At this point, therefore, the only evidence for VI rests upon the ^1H NMR spectrum of a mixture of V and VI, which appears to be consistent with the proposed structure.]

In order to answer the question of how much bulk in the substituent X is necessary to prevent free rotation of the aromatic rings in the case of *N,N',N''*-tri-*o*-tolylborazines $(o\text{-}CH_3C_6H_4NBX)_3$, we studied the reaction of boron tribromide with *o*-toluidine, the results obtained with $(o\text{-}CH_3C_6H_4NBCl)_3$ (I) being inconclusive. However, instead of the expected *B,B',B''*-tribromo-*N,N',N''*-tri-*o*-tolylborazine (II), a different heterocycle derived from diboradiazanaphthalene, VII, was obtained as a

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(10) W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959).

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(13) S. Allaoud, H. Bitar, M. El Mouhtadi, and B. Frange, *J. Organomet. Chem.*, **248**, 123 (1983).

major product[14] with a very small amount of II. After methylation of the crude material, a mixture was obtained. It was found to contain 98% of VIII and 2% of III, identical with an authentic sample (cis isomer) as it could be confirmed by VPC and ^{1}H NMR, using a *B,B',B''*-trimethyl-*N,N',N''*-tri-*o*-tolylborazine-enriched sample. *B,B',B''*-Triethyl-*N,N',N''*-tri-*o*-tolylborazine (IV) was also prepared, for the same purpose, but this compound was found more difficult to purify and the ethyl substituent attached to boron led to a complex second-order pattern (A_2B_3 in ^{1}H NMR), rendering difficult accurate identification.

Conclusion

When performed under very mild conditions (refluxing diethyl ether), the reaction of CH_3MgI with *B,B',B''*-trichloro-*N,N',N''*-tri-*o*-tolylborazine (1) leads to the *cis-B,B',B''*-trimethyl-*N,N',N''*-tri-*o*-tolylborazine as the sole isomer. The trans isomer of III could not be obtained, either in the course of the previous reaction or by heating the cis isomer above its melting point. Instead, significant amounts of *B*-hydroxy byproducts, essentially V, are produced, resulting from incomplete methylation of I: they probably originate from unreacted trans isomer of I because of steric reasons. More drastic conditions (refluxing in aromatic solvent for instance) have been used[15,16] for the reaction of Grignard compounds RMgX with such crowded *B,B',B''*-trichloro-*N,N',N''*-triarylborazines: in every case, the yield of *B,B',B''*-trialkyl-*N,N',N''*-triarylborazine was very low, probably because of extensive ring opening. Finally, the reported formation of the trans isomer in those experiments[3] seems somewhat questionable.

Acknowledgment. We are most grateful to the reviewers for a number of valuable comments and suggestions. We are much indebted to Professor J.-L. M. Abboud for helpful discussions.

Registry No. I, 5775-58-6; III, 749-85-9; IV, 52176-11-1; V, 96413-88-6; VII, 96413-89-7; VIII, 42168-28-5; BCl_3, 10294-34-5; MeI, 74-88-4; EtI, 75-03-6; BBr_3, 10294-33-4; *o*-toluidine, 95-53-4.

(14) S. Allaoud, M. El Mouhtadi, and B. Frange, unpublished results.

(15) C. A. Brown and A. W. Laubengayer, *J. Am. Chem. Soc.*, 77, 3699 (1955).

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Reaction of Nickel(II) *N,N'*-Bis(2-aminoethyl)malonamidate(2-) with Triethylenetetramine

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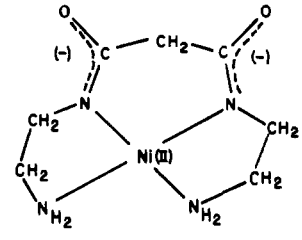
Received November 8, 1984

The reaction of triethylenetetramine with a nickel complex that has an internal six-membered chelate ring and terminal amine donors exhibits rate constants comparable to those observed for reactions with similar nickel-polypeptide complexes. The six-membered chelate ring does increase the rate constants for the reaction with H_3O^+ however. The rate constant values (25.0 °C, I = 0.10 M) are k_{H_2O} = 0.001 s^{-1}, k_{H_3O} = 3.9 × 10^6 M^{-1} s^{-1}, k_T = 0.25 M^{-1} s^{-1}, k_{HT} = 0.73 M^{-1} s^{-1}, and k_{H_3T} = 1.5 × 10^2 M^{-1} s^{-1}.

Introduction

The reactions of nickel(II)-short-chain polypeptide complexes with triethylenetetramine ($Trien_T$) proceed through a variety of different pathways. Complexation of nickel by triglycine[1] establishes the general basic configuration of low-spin square-planar complexes. Nickel transfer from this ligand to trien follows three general pathways: one that is trien and proton independent, one that is trien dependent, and one that is proton dependent. As portions of the peptide ligand are altered, there are dramatic changes in the competitiveness of each pathway.[2-10]

This study utilized a tetradentate ligand *N,N'*-bis(2-aminoethyl)malonamide, BAEM, which forms two five-membered chelate rings and one six-membered chelate ring with Ni(II) (I). The configuration of the six-membered chelate is critical to the kinetic stability. The transfer of Ni(II) from this complex to trien to form $Ni(trien)^{2+}$ proceeds through the three general pathways, and the rate constant values are markedly different from what has been observed for the diglycylethylenediamine complex.[10]



I

Experimental Section

N,N'-Bis(2-aminoethyl)malonamide, BAEM, was synthesized from diethyl malonate and ethylenediamine.[11] A 0.0991 M $Ni(ClO_4)_2$ solution was prepared from the recrystallized salt and standardized by EDTA titration. The complexes were formed by the addition of 50% excess ligand to a $Ni(ClO_4)_2$ solution. The ionic strength was maintained at 0.100 M through the addition of the appropriate amount of 2.0 M $NaClO_4$. The initially acidic solutions were slowly adjusted to the desired pH, which was 9.0 or greater, by adding NaOH. All solutions were bubbled with N_2 in an attempt to eliminate any complex oxidation. Borate buffer, B_T = 0.005 M, was utilized for the reactions in the pH

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