Journal of Organometallic Chemistry, 255 (1983) 143–152
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

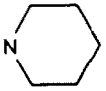
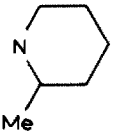
ORGANOBORON COMPOUNDS

XXIV *. AMINOBORATION OF PHENYL ISOCYANATE

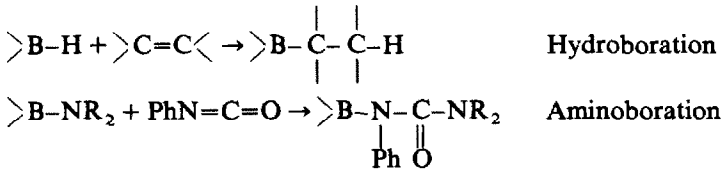
R. HARRY CRAGG and TIM J. MILLER
The Chemical Laboratory, University of Kent at Canterbury, Canterbury, Kent (Great Britain)

(Received May 11th, 1983)

Summary

The reactions between phenyl isocyanate and twenty seven aminoboranes, of the type $PhB(NR_2)X$, (where $X = NR_2$, NHR, OR, SR or halogen), have been studied. The results reveal that the relative migratory aptitudes of the groups attached to boron are in the sequence n-BuNH >  >  > Me_2N > Et_2N > t-BuNH >  > i-Pr_2N and RS > RNH > R_2N > OR, halogen or Ph.

Over the last two decades there has been considerable interest in the hydroboration reaction, whereas the analogous aminoboration has received relatively little attention. Both reactions can be regarded as an insertion or a 1,2-addition reaction to an unsaturated group.

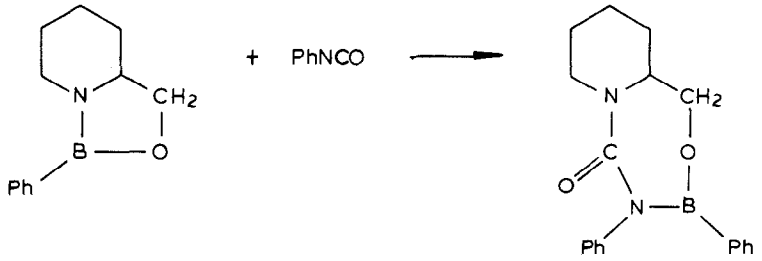


Previous reports [1–18] have been concerned mainly with two aspects of the aminoboration reaction. Firstly if the boron–nitrogen bond is part of a heterocyclic ring the aminoboration reaction provides a novel synthetic route to large ring

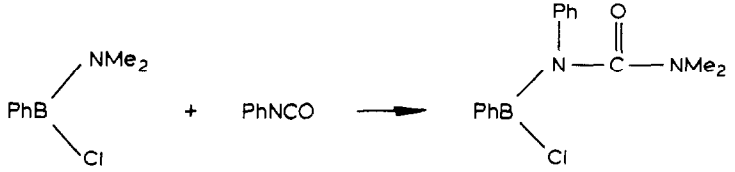
* For part XXIII see J. Organomet. Chem., 241 (1983) 289.

0022-328X/83/$03.00

organoboranes [15].



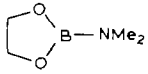
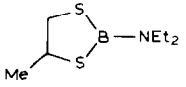
Secondly, in acyclic aminoboranes the aminoboration reaction results in chain elongation [13].



This example demonstrates that the relative migratory aptitudes (RMA) of the groups attached to boron is Me_2N > Cl or Ph. Earlier work concerning the interaction between phenyl isocyanate and dichlorophenylborane demonstrated a RMA order of Ph > Cl [19]. Although there have been several reports concerning the reactions of aminoboranes and organic isocyanates there is little information about the RMA's of groups attached to boron in these reactions, and Table 1 summarises the published data. However there has been no systematic study would give an

TABLE 1

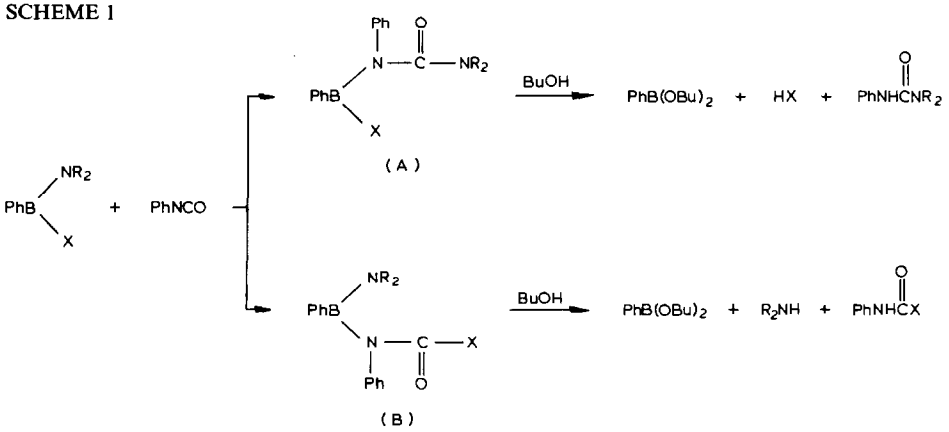
LITERATURE DATA ON RELATIVE MIGRATORY APTITUDES

Isocyanate	Borane	Boration	RMA	Ref.
EtNCO	$PhB(NMe_2)_2$	NMe_2	Me_2N > Ph	6
PhNCO	$PhB(NMe_2)_2$	NMe_2	Me_2N > Ph	6,7,16
PhNCO	$PhB(NH\text{-}t\text{-}Bu)_2$	NH-t-Bu	t-BuNH > Ph	1
PhNCO	$PhB(NMe_2)Cl$	NMe_2	Me_2N > Cl or Ph	13
PhNCO	$n\text{-}Pent_2BNEt_2$	NEt_2	Et_2N > n-Pent	16
PhNCO	$Ph_2BNH\text{-}t\text{-}Bu$	NH-t-Bu	t-BuNH > Ph	1
PhNCO	$(Pr'_2N)_2BNH\text{-}t\text{-}Bu$	NH-t-Bu	t-BuNH > Pr'_2N	1,5
PhNCO		NMe_2	Me_2N > cyclic BO	12
PhNCO		NEt_2	Et_2N > cyclic BS	9
PhNCO	$PhB(OMe)NMe_2$	NMe_2	Me_2N > OMe	24
PhNCO	$PhBCl_2$	Cl	Cl > Ph	19

understanding of the factors controlling the reactivity of different groups attached to boron, although it has been suggested that the RMA is determined by thermodynamic control [1].

In order to evaluate the factors affecting the aminoboration of phenyl isocyanate we have made a systematic study of the reaction of phenyl isocyanate with a comprehensive series of organoboranes of the type $PhBNR_2(X)$ (where $X = NR'_2$, NHR, OR, SR and halogen). It will be recognised that in each case there is the possibility of two reaction products (Scheme 1).

SCHEME 1



Ureidoboranes of the type A have been isolated from the interaction of phenyl isocyanate and t-butylaminodimethylaminophenylborane [20] or chlorodimethylaminophenylborane [13], and have been fully characterised. In the present study the ureidoborane was not isolated but alcoholysed in situ and the resulting urea characterised by infrared, ^1H NMR and mixed melting point determination. Infrared spectroscopy was of value for distinguishing between a 1,1-dialkyl-3-phenylurea or a 1-alkyl-3-phenylurea. Both ureas have a common ν(PhN–H) band at 3300 cm^{-1} and in addition the 1-alkyl-3-phenylureas exhibit a sharp ν(RN–H) band $\sim$ 3400 cm^{-1}, (see Fig. 1). The following example illustrates the technique we used to determine the RMA's.

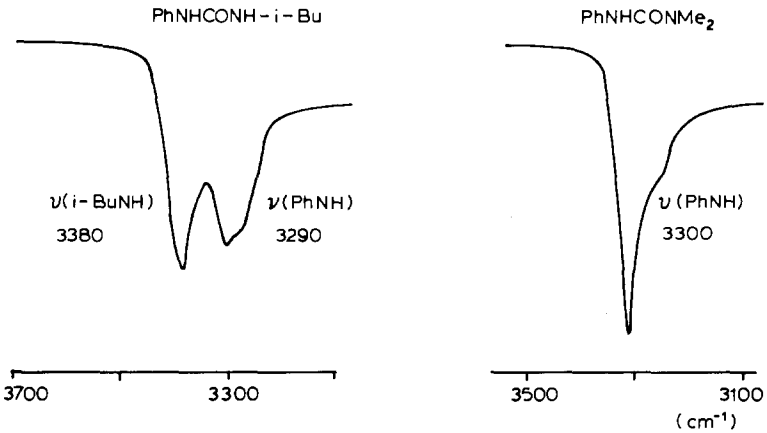
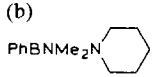
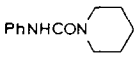
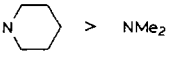
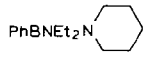
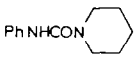
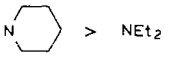
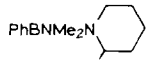
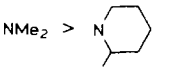
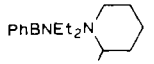
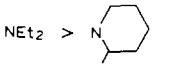
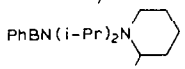
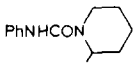
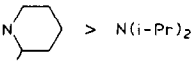
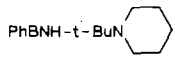
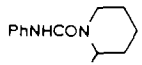
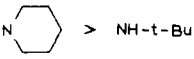
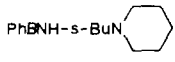
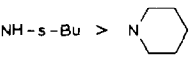
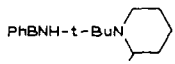
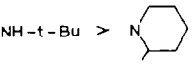
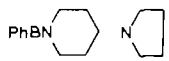
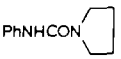
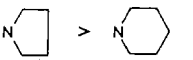


Fig. 1. ν(N–H) stretching bands in ureas.

TABLE 2

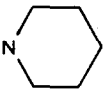
RESULTS OF ISOCYANATE COMPETITION REACTIONS

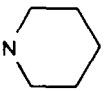
Aminoborane	Urea isolated	M.p. (°C)	Mixed M.p. (°C)	ν(PhNH) (cm^{-1})	ν(RNH) (cm^{-1})	RMA
(a)						
$PhBNMe_2NH$-n-Bu	PhNHCONH-n-Bu	126–128	129–130	3270	3385	NH-n-Bu > NMe_2
$PhBNMe_2NH$-i-Bu	PhNHCONH-i-Bu	153–154	151–152	3290	3380	NH-i-Bu > NMe_2
$PhBNMe_2NH$-s-Bu	PhNHCONH-s-Bu	155–157	154	3300	3350	NH-s-Bu > NMe_2
$PhBNMe_2NH$-t-Bu	$PhNHCONMe_2$	128–129	131–132	3340	–	NMe_2 > NH-t-Bu
$PhBNEt_2NH$-n-Bu	PhNHCONH-n-Bu	127	129–130	3270	3385	NH-n-Bu > NEt_2
$PhBNEt_2NH$-i-Bu	PhNHCONH-i-Bu	154	151–152	3290	3380	NH-i-Bu > NEt_2
$PhBNEt_2NH$-s-Bu	PhNHCONH-s-Bu	155	154	3300	3350	NH-s-Bu > NEt_2
$PhBNEt_2NH$-t-Bu	$PhNHCONEt_2$	80–83	80–82	3300	–	NEt_2 > NH-t-Bu
$PhBN(i\text{-}Pr)_2NH$-t-Bu	PhNHCONH-t-Bu	168	167–168	3320	3380	NH-t-Bu > $N(i\text{-}Pr)_2$
(b)						
		172	172	3280	–	
		172	172	3280	–	
	$PhNHCONMe_2$	129–130	129–130	3340	–	
	$PhNHCONEt_2$	80–83	80–82	3300	–	
		116	117–118	3280	–	
(c)						
		172	172	3280	–	
	PhNHCONH-s-Bu	155–157	154	3300	3350	
	PhNHCONH-t-Bu	168	167–168	3320	3380	
(d)						
$PhBNMe_2NEt_2$	$PhNHCONMe_2$	129–130	129–130	3340	–	NMe_2 > NEt_2
$PhBNMe_2N(s\text{-}Bu)_2$	$PhNHCONMe_2$	129–130	129–130	3340	–	NMe_2 > $N(s\text{-}Bu)_2$
$PhBNEt_2N(n\text{-}Pr)_2$	$PhNHCONEt_2$	80–83	80–82	3300	–	NEt_2 > $N(n\text{-}Pr)_2$
		136	135–137	3300	–	
(e)						
$PhBNMe_2OMe$	$PhNHCONMe_2$	129–130	129–130	3340	–	NMe_2 > OMe
$PhBNMe_2F$	$PhNHCONMe_2$	129–130	129–130	3340	–	NMe_2 > F
$PhBNMe_2Cl$	$PhNHCONMe_2$	129–130	129–130	3340	–	NMe_2 > Cl
$PhBNMe_2Br$	$PhNHCONMe_2$	129–130	129–130	3340	–	NMe_2 > Br
$PhBNMe_2Ph$	$PhNHCONMe_2$	129–130	129–130	3340	–	NMe_2 > Ph
$PhBNMe_2SEt$ [a]						SEt > NMe_2

[a] Characterised by NMR.

Phenyl isocyanate and t-butylaminodimethylaminophenylborane were refluxed together in benzene for 3 h, after which the product of the reaction was alcoholysed in situ to give 1,1-dimethyl-3-phenylurea. The urea had a melting point of 128–129°C and its infrared spectrum contained only one ν(N–H) band at 3300 cm^{-1}. Characterisation of the urea was achieved by a mixed melting point with an authentic sample, chemical analysis and ^1H NMR spectroscopy. It was therefore concluded that the RMA sequence was Me_2N > t-BuNH. Using the same technique RMA sequences for the following classes aminoboranes were established (see Table 2).

(a) $PhB(NR_2)NHR$

(b) $PhB(NR_2)N$ 

(c) $PhB(NHR)N$ 

(d) $PhB(NR_2)NR_2'$

(e) $PhB(NR_2)X$ (where X = OR, SR, halogen or Ph)

The use of ^1H NMR spectroscopy was of value in monitoring the aminoboration reaction. For example when chlorodimethylaminophenylborane reacts with phenyl isocyanate in carbon tetrachloride as solvent, the ^1H NMR spectrum reveals that the doublet normally observed for the dimethylamino group (due to restricted rotation about the boron–nitrogen bond) collapses to a singlet indicating a RMA of the Me_2N > Ph or Cl. However when dimethylaminoethanethiophenylborane reacts with phenyl isocyanate the ^1H NMR spectrum indicates retention of the doublet, demonstrating that the RMA sequence was EtS > Ph or Me_2N.

The aminoboration reaction can also be monitored using infrared spectroscopy. If samples are withdrawn from the reaction mixture at suitable intervals the infrared spectra show the emergence of a ν(CO) band in the 1800–1750 cm^{-1} region with a reduction of the ν(NCO) band at 2225 cm^{-1}. In most cases the reaction is complete after 30 min refluxing in benzene.

Discussion

The aminoboration reaction is envisaged as a nucleophilic attack of the nitrogen lone pair of the amino group on the carbonyl carbon of the isocyanate, and a four centre transition state has been proposed (Fig. 2) and the observed RMA sequences have been interpreted in terms of a transition state which is closer in structure to the products than the reactants [1].

The interaction of an unsymmetrical bis(diamino)phenylborane and phenyl isocyanate can result in the formation of two products.

However phenyl isocyanate will insert into that boron–nitrogen bond which will lead to the more stable product. In the case of bis(dialkylamino)phenylboranes the two possible products differ only in the steric nature of the amino group, since the variation in electronic effects is negligible. Marked changes in the steric nature of an

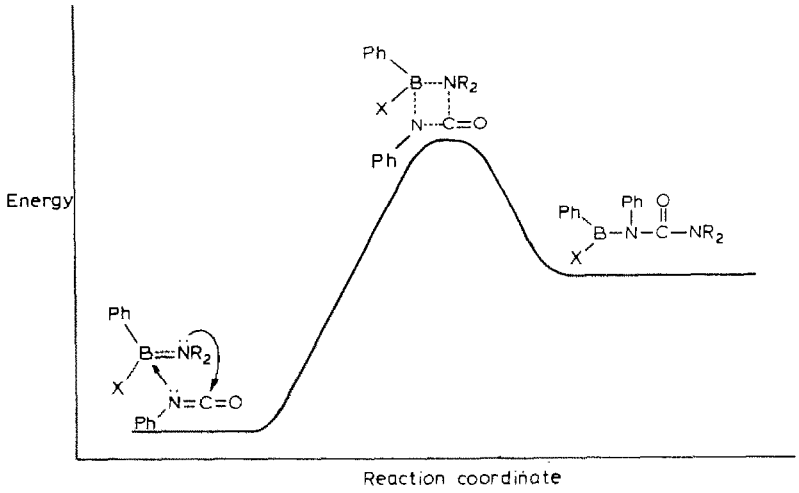
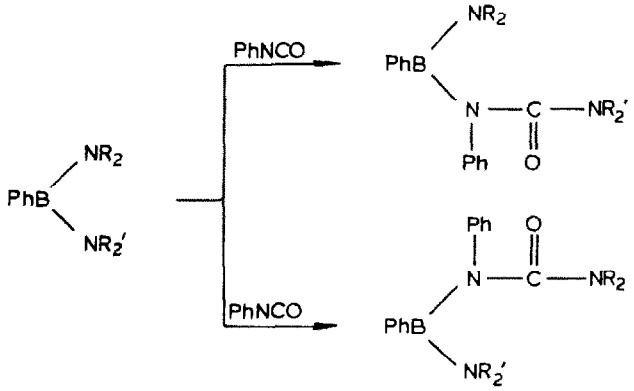


Fig. 2. Energy diagram for the isocyanate insertion reaction.



amino group would therefore be expected to affect the stability of the ureidoborane and hence the RMA.

Interaction of phenyl isocyanate with an alkylaminodialkylaminophenylborane

The results observed (Table 2) show an RMA order

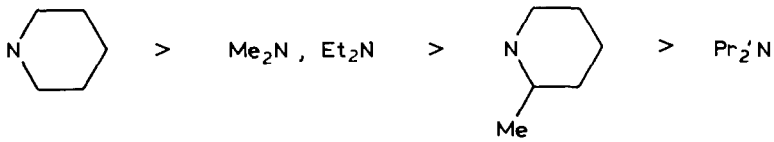
n-BuNH, i-BuNH, s-BuNH > Me_2N, Et_2N > t-BuNH > Pr'_2N.

In general the RMA order RNH > R_2N is observed. However when the primary amino group contains a bulky substituent, for example a t-butyl group, then the RMA order is reversed. On increasing the steric hindrance of the secondary amino group, as in the case of the di-i-propyl group, the RMA order RNH > R_2N pertains. It can therefore be concluded that the crossover points in this series suggest that phenyl isocyanate inserts into the least hindered bond. Further evidence in support of this conclusion comes from the following results which were obtained in investigations of methods of synthesis of alkylaminodialkylaminophenylboranes [21]. The interaction of chlorodiethylaminophenylborane and excess t-butylamine gave t-

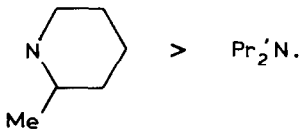
butylaminodialkylaminophenylborane. In contrast, the reaction with excess n-, i- or s-butylamine gave bis(butylamino)phenylborane. It can therefore be concluded that the above reactions proceed to give the least hindered bis(amino)phenylborane, and it is these least hindered amino group which interact with phenyl isocyanate in a competition reaction.

Interaction of dialkylaminopiperidinophenylboranes with phenyl isocyanate

For this class of compound the following RMA is established:



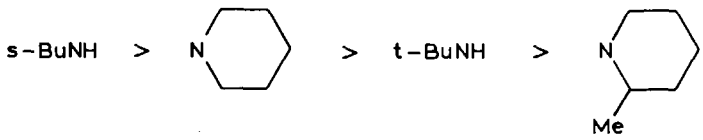
It is observed that the piperidino group is more reactive than an unhindered dialkylamino group. In contrast the 2-methylpiperidino group is less reactive. However when the dialkylamino group is bulky, for example the di-i-propyl group, then the order is reversed, i.e.



These results strongly suggest that the steric hindrance of the amino group is largely responsible for the observed RMA order. This conclusion is again supported by the results obtained in investigations of methods of synthesis for this class of compound [22].

Interaction of phenyl isocyanate and an alkylaminopiperidinophenylborane

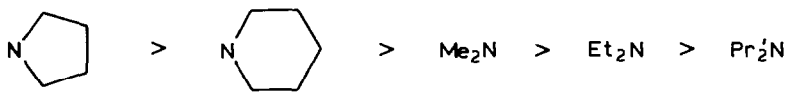
The results obtained establish the following RMA order:



The RMA of the alkylamino group is normally greater than that for the piperidino group except when the primary amino group is bulky. In addition the 2-methylpiperidino group has a lower RMA than the t-butylamino group.

Interaction of unsymmetrical bis(dialkylamino)phenylboranes and phenyl isocyanate

The following RMA order has been established

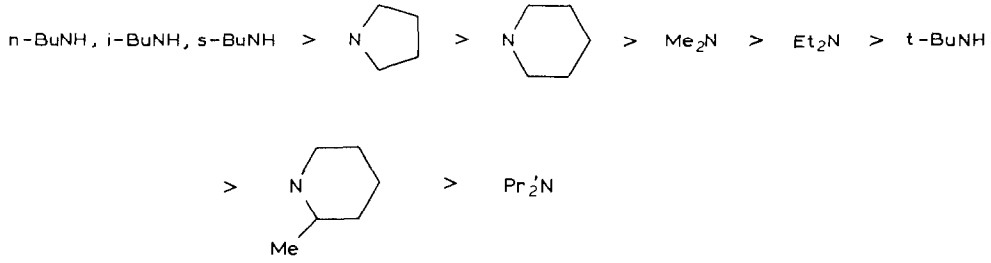


Again the RMA order can be rationalised on steric grounds. It is remarkable that in the reaction of diethylaminodimethylaminophenylborane with phenyl isocyanate, in

a 1/1 mole ratio, the product on alcoholysis was 1,1-dimethyl-3-phenyl urea (90% yield). This observation indicates how small changes in the steric character can affect the RMA, in that if one bond is marginally less hindered then the other insertion occurs almost exclusively into the former bond.

Conclusions

Considering the four classes of unsymmetrical bis(amino)phenylboranes, on the basis of competitive isocyanate insertion reactions, the following order of RMA for the aminoboration of phenyl isocyanate is proposed:



This sequence suggests a good correlation between steric hindrance of the amino group and the RMA. The transition state for the reaction resembles the products more closely than the reactants, and therefore steric changes which increase the stability of the products increase the rate of reaction, i.e. the rate of the reaction should correlate with the equilibrium or thermodynamic stability of the products since the transition state resembles products rather than reactants. Less hindered amino groups give more stable products, and therefore rates of reaction and equilibria should be more favourable for the least hindered amino groups.

Electronic differences between the two boron–nitrogen bonds in bis(amino)phenylboranes have been investigated by ^{13}C NMR [21]. Generally it is found that the bond showing restricted rotation (i.e. p_π–p_π bonding) about the boron–nitrogen bond is the least reactive in the aminoboration reaction.

We therefore conclude that steric arguments provide the best rationalisation of the RMA orders for bis(amino)phenylboranes.

Interaction of phenyl isocyanate and $PhB(NR_2)X$ (where $X = RS$, RO, R_2N, halogen)

The results of the aminoboration reactions (Table 2) show that when R is constant the following RMA order pertains:

RS > RNH > R_2N > RO, halogen or Ph.

The results suggest that steric effects are of secondary importance. The boron–oxygen bond is thermodynamically stronger than the boron–nitrogen bond and is therefore less reactive towards phenyl isocyanate. In addition nitrogen is a better nucleophile than oxygen and since the insertion reaction involves nucleophilic attack on the carbonyl carbon of the isocyanate the amino group will be more reactive than an alkoxy group. The observed order RS > NR_2 is due to the relatively weak boron–sulphur bond compared to the boron–nitrogen bond, p_π–p_π bonding involving nitrogen is better than p_π–p_π bonding involving sulphur [23]. Therefore the formation of a new boron–nitrogen bond will be preferred.

The lack of insertion reactions involving boron–halogen bonds compared with those involving boron–nitrogen bonds might be accounted for by the greater nucleophilicity of an amino group.

Experimental

The aminoboranes used in the aminoboration reactions were prepared by previously published methods; i.e. alkylaminodialkylaminophenylboranes [21], alkylamino- and dialkylamino-phenylpiperidinoboranes [22], bis(dialkylamino)phenylboranes [13], dimethylaminomethoxyphenylborane [24,25], dimethylaminofluorophenylborane [25,26], chlorodimethylaminophenylborane [13,25], bromodimethylaminophenylborane [25], dimethylaminodiphenylborane [27] and dimethylaminoethanethiophenylborane [28]. All solvents were sodium dried and redistilled before use. Necessary precautions were taken to prevent contamination by atmospheric moisture and for melting point determinations the samples were in sealed capillary tubes. Infrared spectra were recorded on Perkin–Elmer 457 and 337 grating spectrometers using potassium bromide optics. ^{1}H NMR spectra were recorded on a Perkin–Elmer R10 spectrometer.

Determination of RMA

Phenyl isocyanate (0.01 mol) and an aminoborane (0.01 mol), were refluxed together in benzene for up to 3 h, after which the product of the reaction was alcoholised in situ to give a urea. The urea was characterised by analysis, infrared spectroscopy, ^{1}H NMR spectroscopy and mixed melting point and hence the RMA established. The results for the aminoboration reactions are given in Table 2.

References

1 R.H. Cragg, M.F. Lappert and B.P. Tilley, J. Chem. Soc., (1964) 2108.
2 U.W. Gerwarth and K.D. Muller, J. Organomet. Chem., 96 (1975) C33.
3 K.D. Muller and U.W. Gerwarth, J. Organomet. Chem., 110 (1976) 15.
4 K.D. Muller and U.W. Gerwarth, Z. Anorg. Allg. Chem., 433 (1977) 268.
5 R.H. Cragg and M.F. Lappert, Adv. Chem. Ser., 42 (1964) 220.
6 H. Beyer, J.W. Dawson, H. Jenne and K. Niedenzu, Adv. Chem. Ser., 42 (1964) 266.
7 T.L. Heying and H.D. Smith, Adv. Chem. Ser., 42 (1964) 201.
8 R.H. Cragg, J. Chem. Soc., (A), (1968) 2962.
9 R.H. Cragg, J.P.N. Husband and A.F. Weston, J. Chem. Soc., Dalton Trans., (1973) 568.
10 B.R. Gragg, R.E. Handshoe and K. Niedenzu, J. Organomet. Chem., 116 (1976) 135.
11 R.H. Cragg, M.F. Lappert, H. Nöth, P. Schweizer and B.P. Tilley, Chem. Ber., 100 (1976) 2377.
12 R.H. Cragg, J. Inorg. Nucl. Chem., 30 (1968) 359.
13 R.H. Cragg and T.J. Miller, J. Organomet. Chem., 232 (1982) 201.
14 R.H. Cragg and T.J. Miller, J. Chem. Soc., Dalton Trans., (1982) 907.
15 R.H. Cragg and T.J. Miller, J. Organomet. Chem., 154 (1978) C3.

16 H. Beyer, J.W. Dawson, H. Jenne and K. Niedenzu, J. Chem. Soc., (1964) 2115.
17 U.W. Gerwarth and K.D. Muller, Z. Anorg. Allg. Chem., 433 (1977) 261.
18 U.W. Gerwarth and K.D. Muller, J. Organomet. Chem., 145 (1978) 1.
19 M.F. Lappert and B. Prokai, J. Chem. Soc., (1963) 4223.
20 R.H. Cragg, PhD., Thesis, University of Manchester, 1964.
21 R.H. Cragg and T.J. Miller, J. Organomet. Chem., 217 (1981) 283.
22 R.H. Cragg and T.J. Miller, J. Organomet. Chem., 235 (1982) 143.
23 R.H. Cragg, J.P.N. Husband and P.R. Mitchell, Org. Magn. Res., 4 (1972) 469.
24 R.H. Cragg and T.J. Miller, J. Organomet. Chem., 235 (1982) 135.
25 P.A. Barfield, M.F. Lappert and J. Lee, J. Chem. Soc., A, (1968) 554.
26 R.H. Cragg and T.J. Miller, J. Organomet. Chem., 217 (1981) 1.
27 C. Brown, R.H. Cragg, T.J. Miller and D.O'N. Smith, J. Organomet. Chem., 217 (1981) 139.
28 R.H. Cragg and T.J. Miller, J. Organomet. Chem., 243 (1983) 387.