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MIXED ARYL-ALKYL-BORON MODEL COMPOUND CONTAINING A $2\text{-}Me_2NCH_2C_6H_4$- BIFUNCTIONAL LIGAND

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Summary

B-($2\text{-}Me_2NCH_2C_6H_4$)-9-BBN has been synthesized by treating borabicyclo[3.3.1.]nonane (9-BBN) with $2\text{-}Me_2CH_2C_6H_4Li$. The structure of the compound is proposed on the basis of ^1H and ^{13}C NMR spectroscopy and also molecular weight measurements.

Introduction

Di- and poly-nuclear species are recently of very wide interest. Their specific catalytic role in organic chemistry stimulated research in this field. In the last decade some characteristic features for $Ar_4Cu_2Li_2$ [1,2], $Ar_4Ag_2Li_2$ [2], $Ar_4Au_2Li_2$ [2,3], $tolyl_4Cu_2Li_2$ [4], $Ar_6Cu_4Ag_2X_2$ [5], $tolyl_6Au_2Zn_2$ [6], $Ph_4Cu_2Mg(Et_2O)$ [8], Me_3Cu_2Li [9], Me_3CuLi_2 [9], $Me_5Cu_3Li_2$ [9], $L_2(CO)MCu(R \doteq N \doteq N \doteq N \doteq R)X$, M = Rh^I, Ir^I [10], were established.

We started to investigate systems containing both Cu and B atoms. Main feature of compounds containing a Cu–C bond is their extremely low thermal stability. The introduction of a 2-(dimethylaminomethyl)phenyl ligand into the molecule results in a significant stabilization of the metal–carbon bond ($2\text{-}Me_2NCH_2C_6H_4$- was first applied by Bahr [11]). Looking for a suitable model boron compound for dimetallic copper-boron species we decided to bond the above mentioned ligand to the boron atom, exchanging with a hydrogen in 9-borabicyclo[3.3.1.]nonane.

Results and discussion

It has already been reported that 9-BBN hydride forms "ate" complexes with lithium compounds, and can be easily hydrolyzed to the appropriate boron compounds [19]. We have established that 2-(dimethylamino-methyl)phenyllithium reacts with 9-BBN according to eq. 1.

An suspension of aryllitium in diethyl ether was added slowly to a solution of

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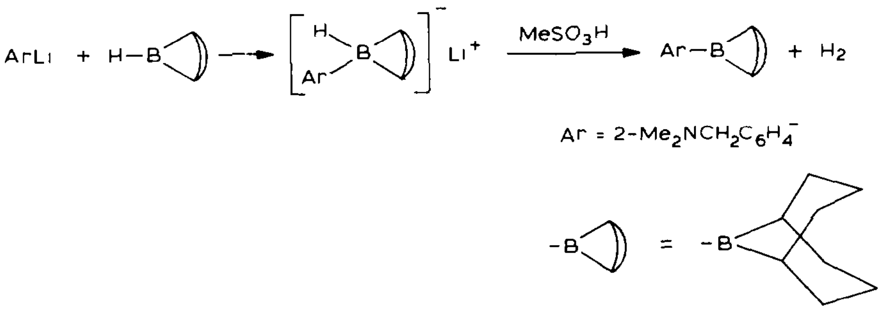


(1)

9-borabicyclo[3.3.1.]nonane in tetrahydrofuran, at room temperature, since at lower temperature ArLi is not reactive enough and the B–H–B bond is still observed in the product. The reaction mixture was then cooled to 0°C and a stoichiometric amount of methanesulfonic acid was added. An almost stoichiometric amount of H_2 evolved.

B-Ar-9-BBN is a white solid, soluble and crystallizable from diethyl ether. Its IR

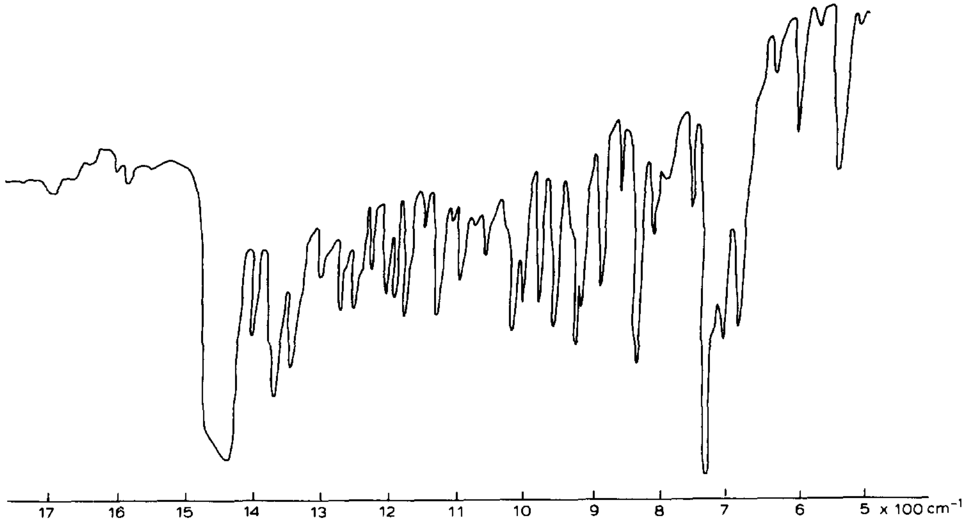


Fig. 1. IR spectrum (Nujol) of B-(2-$Me_2NCH_2C_6H_4$)-9-BBN.

TABLE 1

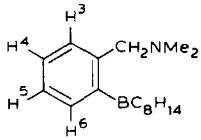
PHYSICAL AND ANALYTICAL DATA FOR B-Ar-9-BBN

Compound	Yield (%)	Colour	m.p. [a] (°C)	Analysis Found(calcd.) (%)				m.w. [c] found (calcd.)	Degree of assoc.
				C	H	N	B [b]		
B-Ar-9-BBN	60	white	118–120	78.40 (80.06)	10.23 (10.20)	5.06 (5.49)	4.02 (4.26)	231.8 (253.8)	0.91

[a] The m.p. was measured in capillary under argon, heating rate 5°C/min. [b] The amount of boron was found after oxidative hydrolysis by titration with NaOH in the presence of mannitol. [c] The m.w. was measured by cryometry in benzene.

TABLE 2

^1H NMR DATA FOR B-Ar-9-BBN



Compound/solvent	δ (ppm) [a]					
	NCH_3	NCH_2	H(3)	H(4,5)	H(6)	C_8H_{14}
B-Ar-9-BBN						
toluene-d_8	2.10s	3.38s	6.98dd $J_{3,4}$ = 7 Hz $J_{3,5}$ = 1 Hz	7.25m	8.00dd $J_{4,6}$ = 7 Hz $J_{5,6}$ = 1 Hz	1.8
$CDCl_3$	2.45s	3.97s	7.16m		7.78dd	1.9
pyridine-d_5	2.25s	3.75s	7.07m		7.67dd	1.8
Ar-H						
$CDCl_3$	2.05s	3.45s	7.14			

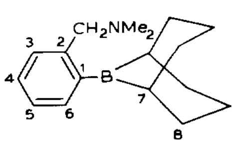
[a] Relative to TMS. [b] Protons from the C_8H_{14} ligand appear as a complicated unresolved broad multiplet with the maxima given here.

spectrum was run to confirm that the strong B–H–B (1560 cm^{-1}) band had disappeared completely in the product.

The ^1H NMR spectrum (Table 2) has the expected pattern characteristic for compounds containing a $2\text{-}Me_2NCH_2C_6H_4$ ligand. NCH_3 and CH_2 protons appear as singlets, shifted downfield (0.4 to 0.52 ppm) in comparison with the parent amine. This fact cannot be a measure of coordination, if the complexation of nitrogen to boron is considered, since both downfield (for Pd, Pt, Hg and Tl [12]) and upfield (Co[13], CuLi[14], Li[14]) shifts have been observed. Signals assigned to protons of the $2\text{-}Me_2NCH_2C_6H_4$- ligand are temperature independent in the range from −70°C to 50°C. A characteristic downfield shift of protons *ortho* to boron, of the aromatic system is observed at about 7.7 ppm. A similar effect has been discussed for aryl-lithium [15], -zinc [15], -magnesium halide [15] and -copper [16] compounds

TABLE 3

^{13}C NMR DATA FOR B-Ar-9-BBN

Compound	δ (ppm) [a]						
	NMe_2	NCH_2	C(1)	C(2)–C(6)	C(7)	C(8)	C(9)
	49.20 [b]	69.90	n.o. [c]	138.1	n.o.	33.98	23.99
	30.68 [b]			133.4			
				126.4			
				124.7			
				121.3			

[a] In $CDCl_3$, ppm relative to TMS. [b] Diastereotopic Me groups. [c] n.o. = not observed, carbon atoms bonded to boron are not observed using the above techniques of measurements because of the quadrupole nature of boron nucleus (^{10}B: $I = 3$: ^{11}B: $I = 3/2$).

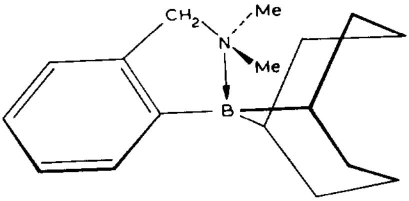


Fig. 2. Structure of B-(2-$Me_2NCH_2C_6H_4$)-9-BBN.

in terms of magnetic anisotropy of C [1]. For arylboron compounds a significant B–C p_π–p_π interaction should be taken into consideration [17].

The ^{13}C NMR spectrum (Table 3) shows the presence of different methyl groups at 30.68 and 49.2 ppm, which usually suggest coordination of nitrogen to the metal atom with the free electron pair. B-Ar-9-BBN does not form higher associates, as it has been indicated by molecular weight measurements. In conclusion we propose the following structure with a four coordinate boron center (Fig. 2).

Experimental

All experiments were carried out under deoxidized and dried argon. Solvents were deoxidized and dried prior to use. 9-BBN was synthesized at the Max Planck Institute in Mülheim (Federal Republic of Germany). 2-$Me_2NCH_2C_6H_4Li$ was synthesized as described by G. van Koten et al. [18].

The elemental analyses for C, H, N were performed using a Perkin-Elmer 240 apparatus. IR spectra were run on a Perkin-Elmer 527 spectrometer in Nujol mull. ^1H NMR spectra were recorded on JNM-100-H (JEOL) and TESLA 80 MHz spectrometers and ^{13}C spectra on a Bruker 0 MHz apparatus.

Preparation of B-Ar-9-BBN

A freshly prepared suspension of 3.2 of ArLi (0.023 mmol) in 80 cm^3 of Et_2O was added slowly (about 40 min) to a solution of 2.76 g of 9-BBN (0.023 mmol) in 40 cm^3 of THF. The reaction mixture was then cooled to 0°C and 1.5 cm^3 of CH_3SO_3H was added by means of a syringe. About 440 cm^3 of H_2 evolved (calcd. 510 cm^3). After the salt had precipitated, the liquid layer was separated, concentrated by LTD to 1/4 of the starting volume. The solid white product was decanted, dried and recrystallized from cold diethyl ether. Yield about 60%.

Acknowledgement

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References

1 G. van Koten and J.G. Noltes, J. Organomet. Chem., 174 (1979) 367.
2 G. van Koten and J.G. Noltes, J. Organomet. Chem., 171 (1979) C39.
3 G. van Koten, C.A. Schaap, J.T.B.H. Jastrzebski and J.G. Noltes, J. Organomet. Chem., 186 (1980) 427.

4 G. van Koten and J.T.B.H. Jastrzebski, J. Organomet. Chem., 140 (1977) C23.
5 G. van Koten and J.G. Noltes, J. Organomet. Chem., 102 (1975) 551.
6 P.W.J. de Graaf, J. Boersma and J.J.M. van der Kerk, J. Organomet. Chem., 78 (1974) C19.
7 G. Costa, A. Camus, L. Gatti and N. Marsich, J. Organomet. Chem., 5 (1966) 568.
8 L.M. Seitz and R. Madl, J. Organomet. Chem., 34 (1972) 415.
9 E.C. Aschby and J.J. Lin, J. Org. Chem., 42 (1977) 2805.
10 J. Kuyper, P.J. van Vliet and K. Vrieze, J. Organomet. Chem., 96 (1975) 289.
11 G. Bähr and H. Zohm, Angew. Chem., 75 (1963) 94.
12 A.F.M. van der Ploeg, doc. thesis 1981, Univ. Amsterdam.
13 A.C. Cope and R.N. Gourley, J. Organomet. Chem., 8 (1967) 527.
14 G. van Koten, doc. thesis 1974, OChI TNO Utrecht.
15 J.A. Ladd, Spectrochim. Acta, 22 (1966) 1157.
16 A. Baici, A. Camus and G. Pellizer, J. Organomet. Chem., 26 (1971) 431.
17 J.D. Odom, T.F. Moore, R. Goetze, H. Nöth and B. Wreckmeyer, J. Organomet. Chem., 173 (1979) 15.
18 G. van Koten, A.J. Leusink and J.G. Noltes, J. Organomet. Chem., 84 (1975) 117: 85 (1975) 105.
19 H.C. Brown, M.M. Rogic and M.W. Rathke, J. Amer. Chem. Soc., 91 (1969) 4304.