Journal of Organometallic Chemistry, 378 (1989) 91–98
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20241

Trisferrocenylborane and its amine adducts

T. López and A. Campero *

Departamento de Química, Universidad Autónoma Metropolitana-Iztapalapa, A.P. 55-534, México D.F. 09340 (Mexico)

(Received February 17th, 1989)

Abstract

The synthesis and characterization by infrared, diffuse reflectance, thermogravimetric and Mössbauer techniques of trisferrocenylborane and its adducts with ammonia, methylamine, ethylamine, propylamine, dimethylamine and pyridine, are reported. Bands in the 1250 and 760 cm^{-1} IR regions are assigned to vibration of the B–C and B–N bonds, respectively. In the visible region the spectra show besides the two typical ferrocene bands, shifted to lower frequency, a third one around 15000 cm^{-1} probably due to the splitting of the first excited level of ferrocene, caused by its decrease in symmetry when bonding covalently to boron in trisferrocenylborane. Mössbauer spectroscopy shows that the *s*-electron density around the ^{57}Fe nucleus is higher in trisferrocenylborane than in ferrocene; part of this *s*-electron density is decreased by additional *d*-electron density in the case of the adduct compounds.

Introduction

The well-known synthesis of ferrocenyllithium has been our starting point in obtaining trisferrocenylborane, by reaction of the former with the electrophilic compound boron trifluoride. Subsequent reaction of trisferrocenylborane with various nitrogen-containing compounds, gives several interesting tetrahedral adducts [1–3].

Compounds of this type are not only structurally interesting by themselves, but are useful in the information they can provide about the bonding and the structure of metallocene systems such as the eventual transmission of electronic effects from one ferrocene ligand to the other through the central boron atom.

We would like to describe the synthesis and characterization of trigonal trisferrocenylborane and some of its tetrahedral amine adducts.

Experimental

Synthesis of trisferrocenylborane. An 8.47 g portion (0.03 mol) of bromoferrocene [4], was dissolved in 200 ml of dry ether, and stirred at −70 °C under a nitrogen atmosphere until complete solution had been achieved; then 20 ml (0.03 mol) of n-butyllithium was added dropwise (20 min), and stirring was continued for 30 min more. The temperature was increased to 0 °C for 20 min, whereupon an orange precipitate formed. The temperature was then lowered to −78 °C, and 3 ml (0.024 mol) of redistilled boron trifluoride etherate were added drop by drop. After 1 h the temperature was increased to 50 °C during 30 min, and then lowered to 20 °C overnight. When both the solution and the precipitate were distinctly red, the suspension was evaporated to dryness. The residue was extracted with 350 ml of dry ether. The resulting extract was filtered and then washed with portions of dry ether until the ether was colorless. Concentration of the combined ethereal extracts, followed by addition of methanol, led to the instant precipitation of red crystalline trisferrocenylborane, which was filtered under vacuum and finally purified by recrystallization with benzene. Yield 50%, soluble in ether and benzene. Elementary analysis is reported in Table 1.

Synthesis of adducts. Portions consisting of 100 mg (0.000176 mol) of trisferrocenylborane were placed in a tube kept under a nitrogen atmosphere at −40 °C. The nitrogen-containing compounds were added, in order to form the corresponding adduct compounds in a stoichiometric 1/1 ratio. The solution was stirred at −40 °C during 2.5 h. The color of the solution changed from red to yellow, indicating a reaction. The solid product was filtered at low temperature in order to avoid the dissociation of the adduct. The compounds employed to form the adducts were ammonia, methylamine, ethylamine, propylamine, dimethylamine and pyridine, respectively. All adducts dissociate upon warming. The reactions with primary amines gave a higher yield than those with secondary amines. Even though a weak equilibrium cannot be rejected, no isolable products could be obtained in the reaction with tertiary amines, probably owing to steric hindrance. Final purification of the adducts was done by recrystallization in cold n-heptane. Elementary analysis is reported in Table 1.

Table 1

Elemental analysis data (Found (calcd.) (%))

Compound	Elemental				
	C	H	Fe	B	N
$C_{30}H_{27}Fe_3B$	63.44	4.57	29.9	2.1	
	(63.67)	(4.77)	(29.63)	(1.91)	
$Fc_3B:NH_3$ [a]	61.82	5.15	28.76	1.85	2.4
	(61.45)	(5.0)	(28.43)	(2.0)	(2.65)
$Fc_3B:NH_2CH_3$	62.38	5.36	28.09	1.81	2.34
	(62.1)	(5.5)	(28.2)	(1.90)	(2.5)
$Fc_3B:NH(CH_3)_2$	62.91	5.57	27.44	1.77	2.29
	(62.95)	(5.60)	(27.3)	(1.80)	(2.35)
Fc_3B: Pyridine	65.0	4.58	26.3	1.60	2.25
	(65.18)	(4.96)	(25.99)	(1.67)	(2.17)

[a] Fc_3B = trisferrocenylborane.

IR spectra were obtained on samples in KBr pellets on a Nicolet FT MX-1 spectrometer. As all adducts dissociate on being dissolved in all solvents that were tried, they were studied by diffuse reflectance in the visible region, using a Cary 17-D spectrometer. Thermogravimetric analyses were run under a nitrogen atmosphere on a Dupont 951 instrument. Mössbauer spectra were obtained using a source of ^{57}Co in iron foil.

Results and discussion

The IR bands in the spectra of trisferrocenylborane and ferrocene are reported in Table 2. In comparison with the latter, the bands in trisferrocenylborane are slightly displaced towards higher energy values [5–8]. Aromatic structures can be distinguished by the C–H stretching vibration at 3045 cm^{-1} in ferrocene, and 3080 cm^{-1} in trisferrocenylborane. Various types of bending vibrations can be observed; those out of plane are seen at 1000 cm^{-1} and those in plane in the region between 1360 and 1050 cm^{-1} in both compounds. The C–C ring vibrations (stretching and bending) are clearly seen in ferrocene at 1527 cm^{-1}, whereas in trisferrocenylborane these are observed as a split band at 1653 and 1610 cm^{-1}.

In Table 3 we list the bands observed for the adducts. In general, relatively slight shifts can be observed in all bands of their spectra, in comparison with trisferrocenylborane, as a result of the change in symmetry in going from the latter (C_{3v}) to the tetracoordinated adducts (approximately tetrahedral [9]).

In Table 4 we list the B–C and B–N vibrations of trisferrocenylborane and of the adduct compounds. The first band (B–C) [10] is located between 1244 and 1317 cm^{-1} in these compounds, at higher energies compared to trisferrocenylborane. The second band (B–N) [11–13] shows rather small shifts which can be attributed to the well-known differences in basicities in the various amine compounds forming covalent bonds to boron.

Table 2

IR bands for trisferrocenylborane and ferrocene

Ferrocene (cm^{-1})	Fc_3B [a] (cm^{-1})	Intensity	Assignment
3110	3110	Medium	CH stretching
3045	3080	Weak	CH stretching
1527	1653	Strong	CC deformation
–	1610	Strong	CC stretching
1390	1375	Weak	Ring breathing
1361	1350	Weak	CH deformation (∥)
1188	1189	Weak	CH deformation (⊥)
1104	1106	Medium	CH deformation (⊥)
1054	1053	Strong	CC deformation (∥)
1004	1000	Strong	CH deformation (∥)
818	818	Strong	CH deformation (⊥)
–	590	Weak	–
567	576	Medium	CCC deformation (⊥)
–	489	Strong	Ring tilt
306	470	Strong	Fe–ring stretching

[a] Fc_3B = trisferrocenylborane.

Table 3

IR bands for the adducts

Sample	Bands (cm^{-1})										
$Fc_3B:NH_3$ [a]	3097	3082	1700	1653	1380	1180	1105	1000	816	491	482
$Fc_3B:NH_2CH_3$	3111	3082	1700	1653	1375	1180	1105	1000	816	493	483
$Fc_3B:NH_2CH_2CH_3$	3100	3079	1700	1653	1385	1190	1104	1001	820	479	473
$Fc_3B:NH_2(CH_2)_2CH_3$	3109	3075	–	1653	1380	1187	1104	1002	805	490	478
$Fc_3B:NH(CH_3)_2$	–	3088	1700	1653	1399	1180	1103	1000	816	489	478
Fc_3B : Pyridine	3095	3065	1700	1653	1377	1190	1105	1000	806	480	475

[a] Fc_3B = trisferrocenylborane.

Table 4

IR bands for B–C and B–N bonds

Sample	B–C bond (cm^{-1})	B–N bond (cm^{-1})
Fc_3B [a]	1254	–
$Fc_3B:NH_3$	1317	765
$Fc_3B:NH_2CH_3$	1317	760
$Fc_3B:NH_2CH_2CH_3$	1244	760
$Fc_3B:NH_2(CH_2)_2CH_3$	1230	776
$Fc_3B:NH(CH_3)_2$	1260	790
Fc_3B: Pyridine	1258	755

[a] Fc_3B = trisferrocenylborane.

Concerning the electronic spectra in the visible region, d^6 ferrocene (D_{5d} symmetry in the solid state) has $^1A_{1g}$ $(1e_{2g})^4(2a_{1g})^2$ as its ground state. Its room temperature visible spectrum shows two bands at 22700 and 30800 cm^{-1}, normally assigned to *d–d* transitions [14].

Our room temperature diffuse reflectance spectra in the visible region show for trisferrocenylborane, two distinct bands, at 20000 and 26300 cm^{-1} corresponding to the two bands in ferrocene, shifted to lower frequencies; this is due in all probability to the modification in electronic density induced in the ferrocene molecule as a result of its covalent bonding to the boron central atom, so decreasing the magnitude of the splitting between the ground state and the first and second excited states. A third band is observed at 15500 cm^{-1} probably owing to a splitting of the first excited level of ferrocene, caused by its bonding to boron.

The diffuse reflectance spectra for the amine adducts of trisferrocenylborane show likewise three bands. The two higher energy bands of trisferrocenylborane are located at substantially the same frequencies in the adducts. The third band, located at 15500 cm^{-1} is shifted to lower values in the adducts. In the ammonia adduct, this band appears at 14084 cm^{-1} (Table 5) reflecting a decrease in the splitting giving rise to this transition, due to the symmetry change and probably to some electron density donated to ferrocene via the boron central atom, by the free electron pair in ammonia. In the other adducts, this splitting as compared to that observed for the ammonia adduct, increases a little; in this regard the influence of the steric hindrance of the bulkier amine ligands can be important.

Table 5

Electronic spectra (diffuse reflectance) bands for trisferrocenylborane and its amine adducts

Sample	Bands (cm^{-1})		
Fc_3B [a]	26300	20202	15503
$Fc_3B:NH_3$	27500	20408	14084
$Fc_3B:NH_2CH_3$	27200	20000	14285
$Fc_3B:NH_2CH_2CH_3$	27100	20120	14388
$Fc_3B:NH_2(CH_2)_2CH_3$	27000	20202	14492
$Fc_3B:NH(CH_3)_2$	27200	20000	14492
Fc_3B: Pyridine	27200	20000	14492

[a] Fc_3B = trisferrocenylborane.

Table 6

Thermal decomposition results

Sample	Temperature of first plateau (° C)	Temperature of second plateau (° C)
Fc_3B [a]	-	550
$Fc_3B:NH_3$	157	528
$Fc_3B:NH_2CH_3$	223	445
$Fc_3B:NH_2CH_2CH_3$	225	490
$Fc_3B:NH(CH_3)_2$	220	580
Fc_3B: Pyridine	215	530

[a] Fc_3B = trisferrocenylborane.

The thermogravimetric study in a nitrogen atmosphere of the stability of the compounds shows two distinct plateaus. The first shows the elimination of the amine adduct. It takes place at 157 °C for the ammonia adduct, at 220 °C for the other adducts excepting the pyridine adduct, which is lost at a slightly lower temperature (Table 6). These results give the respective strengths of the B–N bond. In the pyridine adduct, excessive steric hindrance should decrease the strength of the bond [9].

A second plateau, indicating the end of the decomposition of the trisferrocenylborane structure, is observed at about 550 °C for all of the compounds studied in this work.

Mössbauer spectroscopy has been used extensively to investigate the structure of ferrocene and ferricinium-like compounds.

The parent compound, trisferrocenylborane, has an isomer shift (IS) smaller than ferrocene, indicating a larger *s* electron density around the iron atom, possibly as a result of electron density withdrawal from the ferrocenyl ligand to the central boron atom via the e_1 symmetry ligands of ferrocene to corresponding empty orbitals in boron. This would lessen the *d* electron shielding, thus increasing the *s* electron density at the iron nucleus. In the case of trisferrocenylborane adducts higher IS values relative to the parent compound are observed.

A possible explanation of this might be that electron density is fed back to the ferrocenyl ligands through the boron atom, increasing the *d* electron density of these ligands and as a consequence decreasing the *s* electron density around the iron nucleus.

Concerning the quadrupole splitting (QS), the value of 2.18 mm/sec observed for trisferrocenylborane (Table 7) is noticeably smaller than that of ferrocene itself (2.4 mm/s). This fact precludes the following two possibilities concerning the bonding of ferrocenyl rings to the central boron atom:

(a) The ferrocenyls might be thought to be bonded to boron in such a way that the iron atom in the ferrocenyl ligand is displaced from its symmetrical normal position in ferrocene, thus establishing a direct chemical interaction with boron, the so-called "ring slip" [15]. Such bonding should result in a rather large distortion of the electric field gradient on the iron nucleus, and the QS should increase drastically, contrary to our results, where smaller QS values are observed.

(b) There is a different possibility, which might account for an ever larger QS decrease than that obtained, the so-called "ring tilting" phenomenon [16], which

Table 7

Mössbauer spectroscopy data

Sample	Isomeric shift (mm/s)	Quadrupole splitting (mm/s)
Fc_3B [a]	0.4219	2.178
$Fc_3B:NH_3$	0.4520	2.260
$Fc_3B:NH_2CH_3$	0.4650	2.270
$Fc_3B:NH_2CH_2CH_3$	0.4550	2.297
$Fc_3B:NH(CH_3)_2$	0.4550	2.360
Ferrocene (Ref. 20)	0.4750	2.400

[a] Fc_3B = trisferrocenylborane.

consists roughly in the two cyclopentadienyl rings of ferrocene no longer being parallel. This structure has been shown by Extended Hückel methods to provide an energy minimum [17]. However, this ring-tilt formulation should provide simultaneously a direct iron atom chemical interaction with the central boron, thus increasing the QS value as was discussed for case (a).

We have thus to postulate that non-distorted ferrocenyl groups establish σ-type bonds to the central boron atom exclusively through one carbon atom of one of the cyclopentadienyl rings. This is in accordance with the X-ray structure of the pyridine adduct [9]. The low QS value in trisferrocenylborane should come as a result of electron density withdrawal by the electropositive central boron atom from the iron $3d_{xz}$ and $3d_{yz}$ orbitals of e_1 symmetry, producing a distorted electric gradient around the iron nucleus. Such an explanation has been given in the case of ferrocenophanes [18], assuming a release of electron density from e_1 orbitals belonging to the ferrocenyl ligands overlapping with orbitals of appropriate symmetry on the bridging heteroatom.

As a final remark, we observe that the QS values obtained for the amine adducts are larger than those for the parent compound, approaching the value of ferrocene. This is due to the fact that in these compounds the bonds between the ferrocenyl rings and the central boron atom are no longer coplanar. Electron density withdrawal through π-bonds from the ferrocenyl groups to boron is thus less efficient, resulting in higher QS values, as observed [19].

References

1 E.W. Neuse, R.K. Crossland, J. Organomet. Chem., 7 (1967) 344.
2 M.D. Rausch, J. Org. Chem., 28 (1963) 3337.
3 G.E. Coates, K. Wade, Organometal. Comp., 1 (1967) 205.
4 C. LeVanda, D.O. Cowan, K. Bechgaard, J. Am. Chem. Soc., (1974) 6788.
5 E.R. Lippincot, R.D. Nelson, J. Chem. Phys., 21 (1953) 1307.
6 F. Delgado-Pena, D.R. Talham, D.O. Cowan, J. Organomet. Chem., 253 (1983) C43.
7 W.K. Winter, B. Curnutle, S.E. Whitcomb, Spectrochim. Acta, 15 (1959) 10785.
8 E.R. Lippincot, R.D. Nelson, Spectrochim. Acta, 10 (1958) 307.
9 M. Soriano-Garcïa, R.A. Toscano, T. López, A. Campero, J. Crystallographic and Spect. Res., 17 (1987) 719.
10 B. Rice, R.J. Galiano, W.J. Lehmann, J. Chem. Phys., 61 (1957) 1222.
11 R.C. Taylor, Advan. in Chem. Series, 42 (1964) 59.
12 D.R. Schultz, A.R. Emery, J. Am. Chem. Soc., 80 (1958) 27.
13 R.C. Taylor, C.L. Cluff, Nature, 182 (1958) 390.

14 D.R. Scott, R.S. Baker, J. Chem. Phys., 35 (1961) 516.
15 J.J. Denenberg, M.K. Levenberg, J.H. Richards, Tetrahedron, 29 (1973) 1575.
16 M.L. Good, J. Buttons, D. Foyt, Ann. N. Y. Acad. Sci., 239 (1974) 193.
17 R. Gleiter, R. Seeger, Helv. Chim. Acta, 54 (1971) 217.
18 M.C. Clemance, R.M.G. Roberts, J. Silver, J. Am. Chem. Soc., 243 (1983) 461.
19 M.C. Clemance, R.M.G. Roberts, J. Silver, J. Am. Chem. Soc., 247 (1983) 219.
20 C. LeVanda, D.O. Cowan, K. Bechgaard, J. Am. Chem. Soc., 98 (1976) 3181.