

$J = 13.9$ and 3.9 Hz); 3.13 (distort.q, 1 H, H(4)); 3.98–4.13 (m, 3 H, H(6')_A, H(6')_B, H(6)_A); 4.29 (s, 1 H, H(4')); 4.46 (d, 1 H, H(6)_B, $J = 8.3$ Hz); 5.06 (dm, 1 H, H(5')), $J = 4.6$ Hz); 5.24 (m, 1 H, H(5)); 5.83 (s, 1 H, H(1')); 5.96 (d, 1 H, H(1), $J = 1.9$ Hz); 7.50 (br.s, 2 H, NH₂). ¹³C NMR (DMSO-*d*₆), δ : 28.6 (C(3)); 39.2 (C(7)); 40.0 (C(4)); 42.8 (C(2)); 47.3 (C(10)); 47.6 (C(4')); 68.1, 69.0 (C(6), C(6')); 73.4 (C(8)); 71.9, 74.2 (C(5), C(5')); 95.9, 101.4 (C(1), C(1')); 110.3, 110.4, 111.2, 114.0, 114.3, 115.1 (5 CN, C(3')); 130.7 (C(2')); 144.6 (C(9)). IR (KBr), ν/cm^{-1} : 3420, 3340, 3220 (νNH_2); 2260, 2220 (CN); 1640 (δNH_2); 1580 (C=C). UV (MeCN), $\lambda_{\text{max}}/\text{nm}$: 342 (ϵ 9600). MS (EI, 70 eV), m/z (I_{rel} (%)): 414 [M]⁺ (10), 388 (41), 312 (64), 235 (100), 210 (36), 209 (97), 148 (41).

References

1. F. Shafizadeh and D. Pang, *Carbohydr. Res.*, 1982, **102**, 217.
2. A. L. Laikhter, M. E. Niyazymbetov, D. H. Evans, A. V. Samet, and V. V. Semenov, *Tetrahedron Lett.*, 1993, **34**, 4465.
3. A. V. Samet, A. L. Laikhter, V. P. Kislyi, B. I. Ugrak, and V. V. Semenov, *Mendeleev Commun.*, 1994, 134.
4. A. Forsyth, R. Paton, and I. Watt, *Tetrahedron Lett.*, 1989, **30**, 993.
5. A. V. Samet, V. P. Kislyi, N. B. Chernysheva, D. N. Reznikov, B. I. Ugrak, and V. V. Semenov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 409 [*Russ. Chem. Bull.*, 1996, **45**, 393 (Engl. Transl.)].
6. A. V. Samet, A. N. Yamskov, B. I. Ugrak, M. G. Vorontsova, M. G. Kurella, and V. V. Semenov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 415 [*Russ. Chem. Bull.*, 1996, **45**, 399 (Engl. Transl.)].
7. A. V. Samet, A. N. Yamskov, B. I. Ugrak, and V. V. Semenov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 553 [*Russ. Chem. Bull.*, 1997, **46**, 532 (Engl. Transl.)].
8. E. C. Taylor and A. McKillop, *The Chemistry of Cyclic Enaminonitriles and o-Aminonitriles*, in *Advances in Organic Chemistry*, **7**, Interscience Publishers, New York, 1970, 415 pp.
9. A. V. Samet, M. E. Niyazymbetov, V. V. Semenov, A. L. Laikhter, and D. H. Evans, *J. Org. Chem.*, 1996, **61**, 8786.
10. F. S. Babichev, Yu. A. Sharanin, V. P. Litvinov, V. K. Promononkov, and Yu. M. Volovenko, *Vnutrimolekulyarnoe vzaimodeistvie nitril'noi gruppy i C—H, O—H i S—H grupp* [Intramolecular Interactions of the Nitrile Group with the C—H, O—H, and S—H Groups], Naukova Dumka, Kiev, 1985, 199 pp. (in Russian).

Received July 3, 1998

Interaction of ferrocenecarbaldehyde with zinc tetrahydroborate and its derivatives

V. D. Makhaev,^{a*} L. V. Gorobinskii,^b N. S. Kedrova,^b and N. N. Mal'tseva^b

^aInstitute of New Chemical Problems, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.

Fax: +7 (096) 742 0004. E-mail: vim@incp.ac.ru

^bN. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,
31 Leninsky prosp., 117907 Moscow, Russian Federation.

Fax: +7 (095) 954 1279

Ferrocenecarbaldehyde was reduced to methylferrocene upon interaction with zinc tetrahydroborate in THF. The reactions proceeded rapidly (5–10 min) in high yields (ca. 90%). Analogous results were obtained when a mechanically activated mixture of zinc chloride and sodium tetrahydroborate or the complex of zinc tetrahydroborate with dibenzo-18-crown-6, 2Zn(BH₄)₂·DB-18-C-6, was used in the reaction.

Key words: ferrocenecarbaldehyde, methylferrocene, reduction, zinc tetrahydroborate, complex 2Zn(BH₄)₂·DB18C6, mechanochemistry.

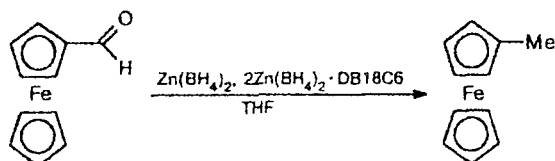
Alkylferrocenes find application as efficient combustion stabilizers, antiknock compounds, and motor oil additives as well as in some other fields.¹ The procedure most generally employed for the preparation of alkylferrocenes involves reduction of acetyl derivatives of ferrocene with lithium aluminum hydride in the

presence of AlCl₃. Recently, it was found that carbonyl derivatives of ferrocene were reduced to form the corresponding alkylferrocenes upon interaction with a mixture of zinc chloride and zinc tetrahydroborate or zinc chloride and sodium tetrahydroborate in THF for 8–10 h.^{2,3}

Zinc tetrahydroborate is used as a selective reducing agent in organic synthesis.^{4,5} Therefore, it was of interest to study the reactions of carbonyl derivatives of ferrocene with $\text{Zn}(\text{BH}_4)_2$ and some its derivatives. In this work, we studied the reactions of ferrocenecarbaldehyde with $\text{Zn}(\text{BH}_4)_2$, a mechanically activated $\text{ZnCl}_2 + 2\text{NaBH}_4$ mixture, and the complex of zinc tetrahydroborate with dibenzo-18-crown-6, $2\text{Zn}(\text{BH}_4)_2 \cdot \text{DB18C6}$.

Results and Discussion

Our data on interactions of ferrocenecarbaldehyde with zinc tetrahydroborate or its complex with crown ether demonstrate that the reactions are completed in 5–10 min to give methylferrocene in high yields.



Ferrocenecarbaldehyde is also efficiently reduced with a $\text{Zn}(\text{BH}_4)_2 + 2\text{NaCl}$ mixture, which is formed as a result of mechanochemical interaction of zinc chloride with sodium tetrahydroborate. This makes it possible to use this mixture as a reducing agent without isolation of $\text{Zn}(\text{BH}_4)_2$.

The use of $\text{Zn}(\text{BH}_4)_2$ in this reaction resulted in a substantial acceleration of the process compared to the reported reactions of ferrocenecarbaldehyde with a mixture of zinc chloride and zinc tetrahydroborate² or with a mixture of zinc chloride and sodium tetrahydroborate,³ which were completed in 8–10 h.

In this connection, the statements^{2,3} that this reaction proceeds according to the ionic mechanism and that it is necessary to use Lewis acids (ZnCl_2) seem to be unjustified. The elucidation of the mechanism of this reaction calls for further investigation.

Unlike the Geisler reagent (a solution prepared by the reaction of ZnCl_2 with NaBH_4 in THF^{2,3} and which is, according to the published data,^{6–8} a mixture of the reagents, namely $\text{Zn}(\text{BH}_4)_2$, $\text{NaZn}(\text{BH}_4)_3$, $\text{NaZnCl}_x(\text{BH}_4)_{3-x}$, etc.), which is used as a reducing agent and which can be stored for no more than 2–3 weeks at 0 °C, zinc tetrahydroborate (a $\text{Zn}(\text{BH}_4)_2 + 2\text{NaCl}$ mixture) prepared mechanochemically and its complex with DB18C6 are stable upon storage under an inert atmosphere at room temperature for one year and more.

Therefore, we demonstrated that zinc tetrahydroborate is an efficient convenient reagent for reducing ferrocenecarbaldehyde to methylferrocene. It is of interest to examine the possibility of the use of $\text{Zn}(\text{BH}_4)_2$ for reducing other carbonyl derivatives of metallocenes.

Experimental

All operations with the use of $\text{Zn}(\text{BH}_4)_2$ were performed under an inert atmosphere. The solvents and reagents were purified and dried according to procedures commonly used in operations with tetrahydroborates. The solvents were distilled over LiAlH_4 before use. Ferrocenecarbaldehyde ($\text{C}_{11}\text{H}_{10}\text{FeO}$) was purchased from Aldrich.

Elemental analyses for the C and H contents in the compounds under study were carried out on a Carlo Erba EA-1108 C,H,N-analyzer (Italy). The Zn and B contents were determined by titration according to standard procedures. The IR spectra were recorded on a UR-20 spectrophotometer in the 400–4000 cm^{-1} region (KBr windows); the samples were prepared as Nujol mulls.

Preparation of zinc tetrahydroborate. A (as a mixture with NaCl). Zinc tetrahydroborate was prepared by the solid-phase reaction of ZnCl_2 with NaBH_4 upon mechanical activation of the initial compounds in a steel reactor with the use of a vibrating mill; 9- or 12-mm steel balls (the total weight was 100 g) were used as an activating packing. The amplitude of vibrations was 11 mm; the frequency was 12 Hz; the molar ratio of the initial compounds $\text{NaBH}_4 : \text{ZnCl}_2 = 2 : 1$; the total weight of the reaction mixture was ~0.6 g (0.39 g (2.86 mmol) of ZnCl_2 and 0.216 g (5.72 mmol) of NaBH_4). The duration of activation was 40 and 10 min in the case of 9- and 12-mm balls, respectively. The course of the reaction was monitored by IR spectroscopy. After completion of the reaction, the $\nu(\text{B}-\text{H})$ band at 2300 cm^{-1} , which is typical of the BH_4^- ion, disappeared and the system of bands in the 2000–2500 cm^{-1} region, which correspond to stretching vibrations of the terminal and bridging B–H bonds, appeared. The mixtures prepared by mechanical activation remained unchanged under an inert atmosphere for a long period (for more than a year).

B (a solution in THF). After mechanical treatment, zinc tetrahydroborate was isolated from a mixture of products by dissolving in THF with stirring at ~20 °C for 2–3 h. The resulting solution contained only traces of chlorine. The solvent was distilled and zinc tetrahydroborate tetrahydrofuranate was isolated in ~75% yield.

In most experiments, $\text{Zn}(\text{BH}_4)_2$ solutions were used without isolation of this compound in the individual state.

C (the complex of $\text{Zn}(\text{BH}_4)_2$ with dibenzo-18-crown-6). Dibenzo-18-crown-6 (1.9 g, 5.2 mmol) was added to a solution of $\text{Zn}(\text{BH}_4)_2$ (1.0 g, 10.4 mmol) in diethyl ether (90 mL). The reaction mixture was stirred using a magnetic stirrer for 10 h. The resulting colorless finely crystalline precipitate was filtered off, washed with diethyl ether, and dried *in vacuo*. The $2\text{Zn}(\text{BH}_4)_2 \cdot \text{DB18C6}$ complex was obtained as a colorless finely crystalline compound insoluble in ether in a yield of 2.7 g (95%). Found (%): C, 43.41; H, 7.47; B, 7.46; Zn, 23.63. $\text{C}_{20}\text{H}_{40}\text{B}_4\text{O}_6\text{Zn}_2$. Calculated (%): C, 43.63; H, 7.32; B, 7.86; Zn, 23.75.

Reduction of ferrocenecarbaldehyde. A (with a $\text{Zn}(\text{BH}_4)_2 + \text{NaCl}$ mixture in THF). A solution of ferrocenecarbaldehyde (0.3091 g, 0.0014 mol) in THF (30 mL) was added to a mixture of $\text{Zn}(\text{BH}_4)_2$ and NaCl (the total weight was 0.3207 g; $\text{NaCl} : \text{Zn}(\text{BH}_4)_2 = 2 : 1$), which was prepared by mechanochemical interaction of ZnCl_2 with NaBH_4 and which contained $\text{Zn}(\text{BH}_4)_2$ (0.1330 g, 0.0014 mol). The reaction mixture was stirred using a magnetic stirrer for 5 min. The color changed from red to yellow. The course of the reaction was monitored by paper chromatography (a 4 : 1 hexane–diethyl ether mixture was used as the eluent; R_f of ferrocenecarbaldehyde was 0.67; R_f of methylferrocene was 0.33).

Chromatography demonstrated that the reaction proceeded to completion (ferrocenecarbaldehyde was absent in the reaction mixture). The solution was filtered. Et₂O (40 mL) and a 25% aqueous solution of NH₄OH (25 mL) were added to the filtrate. When an aqueous ammonia solution was added, vigorous gas evolution was observed. Hexane (15 mL) was added to more completely remove the organic fraction. The organic layer was separated. The aqueous layer was extracted with Et₂O (2×15 mL). The organic layers were combined and concentrated. The resulting yellow finely crystalline precipitate of methylferrocene was recrystallized from hexane. In the IR spectrum of the product, an absorption band at 1690 cm⁻¹, which corresponds to vibrations of the carbonyl group of ferrocenecarbaldehyde, is absent. The yield of methylferrocene was 0.27 g (95% with respect to the theoretical value), m.p. 36 °C (published data:³ m.p. 35.5–36.5 °C). Found (%): C, 65.90; H, 6.52. C₁₁H₁₂Fe. Calculated (%): C, 66.04; H, 6.05.

B (with a solution of Zn(BH₄)₂ in THF). Analogously, when a solution of ferrocenecarbaldehyde (0.135 g, 0.63 mmol) in THF (20 mL) reacted with a solution containing Zn(BH₄)₂ (0.059 g, 0.63 mmol) in THF (20 mL) for 10 min, methylferrocene formed as a yellow crystalline compound in a yield of 0.11 g (90%).

C (with the 2Zn(BH₄)₂·DB18C6 complex in THF). The 2Zn(BH₄)₂·DB18C6 complex (0.275 g, 0.0005 mol) was added to a solution of ferrocenecarbaldehyde (0.21 g, 0.001 mol) in THF (30 mL). The suspension was stirred for 10 min. The color of the solution changed from red to yellow. Paper chromatography demonstrated that the reaction proceeded to completion. Et₂O (40 mL) and a 25% aqueous solution of

NH₄OH (25 mL) were added to the reaction mixture. The solution was filtered off. The organic layer was separated. The inorganic layer was extracted with Et₂O (2×30 mL). The organic layers were combined and concentrated to 2/3 of the initial volume. The white flocculent precipitate of crown ether that formed was filtered off. The solvent was distilled off from the filtrate. Methylferrocene was obtained as a yellow finely crystalline precipitate. The precipitate was recrystallized from hexane. The yield was 0.18 g (90% with respect to the theoretical value).

References

1. E. G. Perevalova, M. D. Reshetova, and K. I. Grandberg, *Metody elementoorganicheskoi khimii. Zhelezgoorganicheskie soedineniya. Ferrotsen [Methods of Organometallic Chemistry. Organoiron Compounds. Ferrocene]*, Nauka, Moscow, 1983, 544 pp. (in Russian).
2. S. Bhattacharyya, *Organometallics*, 1996, **15**, 1065.
3. S. Bhattacharyya, *Synt. Commun.*, 1996, **26**, 4647.
4. N. M. Yoon and I. Kang, *J. Korean Chem. Soc.*, 1975, **19**, 355.
5. H. Kotsuki, Y. Ushio, N. Yoshimura, and M. Oichi, *Tetrahedron Lett.*, 1986, **27**, 4213.
6. E. Wiberg and W. Henle, *Z. Naturforsch.*, 1952, **7b**, 576.
7. H. Noth, E. Wiberg, and R. P. Winter, *Z. anorg. allgem. Chem.*, 1969, **370**, 209.
8. V. I. Mikheeva, N. N. Mal'tseva, and N. S. Kedrova, *Zh. Neorg. Khim.*, 1979, **24**, 408 [*J. Inorg. Chem. USSR*, 1979, **24** (Engl. Transl.)].

Received July 10, 1998;
in revised form September 25, 1998

¹³C NMR study of 2,3,4,5-tetraphenylsilole dilithium salt

S. N. Tandura,* N. A. Troitskii, S. P. Kolesnikov, K. S. Nosov, and M. P. Egorov

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328. E-mail: stas@ioc.ac.ru

The complete assignment of the signals in the ¹³C NMR spectra of 2,3,4,5-tetraphenyl-1-R¹,R²-1-silacyclopenta-2,4-dienes (R¹ = R² = H, Me) and of the dianion of lithium salt [(PhC)₄Si]²⁻·2Li⁺ was carried out by 2D NMR spectroscopy.

Key words: silicon; 2,3,4,5-tetraphenylsiloles; silole dianion; ¹³C NMR spectra.

Recently, we have reported a correct assignment of the signals of carbon atoms in the ¹³C NMR spectra of 2,3,4,5-tetraphenylgermoles **1b** and corresponding dianion **2b** and showed that the values of their chemical shifts differ appreciably from those reported previously.^{1–3}

In this connection it was of interest to analyze the spectral data for the corresponding silole dianion **2a**.

The values of the chemical shifts and conclusions drawn on their basis and reported in the studies of the ¹³C NMR spectra of siloles and their anions^{4–8} are