2098 Russian Chemical Bulletin, International Edition, Vol. 59, No. 11, pp. 2098—2101, November, 2010

Alkylation of nitrogen heterocycles with 1,3-bis(hydroxymethyl)ferrocene. Generation of the ferrocene dicarbocation $[\{1,3\text{-}(CH_2)_2C_5H_3\}Fe(C_5H_5)]^{2+}$

D. M. Panov,[a] A. V. Polezhaev,[a] A. V. Polukeev,[a] P. V. Petrovskii,[a] and A. A. Koridze[a,b]★

[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (499) 135 5085. E-mail: koridze@ineos.ac.ru
[b]*Institute of Metalloorganic Chemistry, I. Javakhishvili Tbilisi State University,*
3 Chavchavadze Avenue, 0128 Tbilisi, Georgia.
Fax: (995 32) 22 5107

The alkylation of imidazole and 5-benzyloxycarbonyl-3,4-diethylpyrrole with 1,3-bis(hydroxymethyl)ferrocene (**1**) afforded bis-imidazole (**4**) and bis-pyrrole (**7**) derivatives of ferrocene, respectively. The reaction of diol **1** with trifluoroacetic acid gave the dicarbocationic complex $[\{1,3\text{-}(CH_2)_2C_5H_3\}Fe(C_5H_5)]^{2+}$ (**2**) characterized by ^{1}H NMR spectroscopy.

Key words: ferrocene, (ferrocene-1,3-diyl)dimethylium, imidazole, pyrrole, ferrocenylmethylation.

Previously,[1] we have reported on the phosphorylation of 1,3-bis(hydroxymethyl)ferrocene (**1**) giving ferrocene diphosphines $\{1,3\text{-}(R_2PCH_2)_2C_5H_3\}Fe(C_5H_5)$ (R = Pr^i, Bu^t). The latter were used as the starting compounds for the synthesis of P,C,P pincer complexes with the ferrocene backbone. Rhodium,[1] palladium,[2,3] iridium,[4] and ruthenium[5] bis(phosphine) pincer complexes with the ferrocene or ruthenocene backbone are presently known. These complexes have attracted interest due to their ability to activate small molecules and hydrocarbon substrates and catalyze a variety of reactions, among which of great importance is the homogeneous dehydrogenation. Recently,[4] it has been shown that the iridium complex $IrH_2[\{2,5\text{-}(Bu^t{}_2CH_2)_2C_5H_2\}Fe(C_5H_5)]$ is the most active catalyst for alkane dehydrogenation among all known homogeneous systems.

The chemistry of metallocene-based pincer complexes is in its infancy. In the future, it is necessary to use in a greater extent the potential of these systems conditioned by the sandwich geometry of metallocenes and the ability to vary the metallocene central atom and its oxidation state in the case of the iron atom in ferrocene. It would expect that pincer complexes having the metallocene backbone would be used for the creation of new generation polymetallic catalysts and materials having useful photophysical and sensor properties. The progress in this area is related to the development of convenient methods for the synthesis of functionalized 1,3-disubstituted metallocenes,[3—9] which are nowadays much more difficult to synthesize compared to 1,1´- and 1,2-disubstituted analogs. It is also necessary to design pincer ligands containing donor atoms other than phosphorus, for example, carbon atoms of N-heterocyclic carbenes and nitrogen atoms of N-heterocycles.

In the present study, we describe the first results on the synthesis of precursors of new types of pincer ligands based on ferrocene. The alkylation of imidazole and substituted pyrrole with diol **1** afforded the diimidazole and dipyrrole derivatives of ferrocene, respectively.

Results and Discussion

The ferrocenylmethylation can be performed with the use of ferrocenylmethyl halides (rather unstable compounds), ferrocenylcarbinols, or ferrocenylmethylammonium salts.[10] These reactions proceed through the formation of α-ferrocenyl carbocations, whose enhanced stability is well known.[11] The ferrocene carbocations were characterized by ^{1}H, ^{13}C, and ^{57}Fe NMR spectroscopy. The most stable of them, as well as their ruthenium and osmium analogs, were isolated as crystalline salts and were studied by X-ray diffraction.[11,12] Unlike ferrocene monocarbocations, ferrocene 1,1´- and 1,2-dicarbocations are substantially less stable.[13,14] The latter ions are generated from the corresponding carbinols at low temperatures with the use of superacids, such as $FSO_3H—SbF_5$ or CF_3SO_3H—oleum. It should be noted that ferrocene 1,3-dicarbocations have not been observed previously.

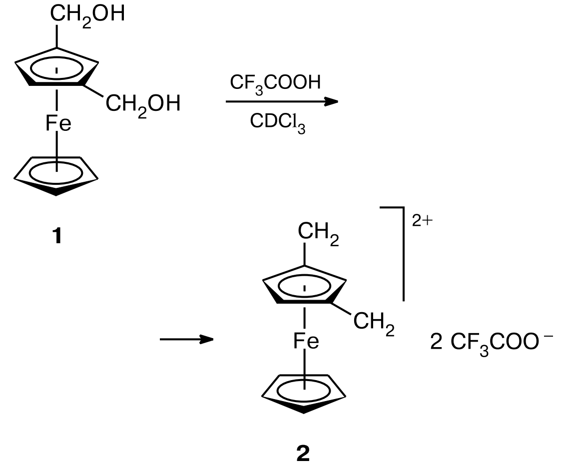
In the present study, diol **1** was used as the alkylating agent in the reactions with heterocycles and it was of in-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2045—2047, November, 2010.

terest to characterize the corresponding dicarbocationic complex $[\{1,3\text{-}(CH_2)_2C_5H_3\}Fe(C_5H_5)]^{2+}$ (**2**).

We found that complex **2** is generated in the reaction of diol **1** with trifluoroacetic acid at room temperature (Scheme 1).

Scheme 1



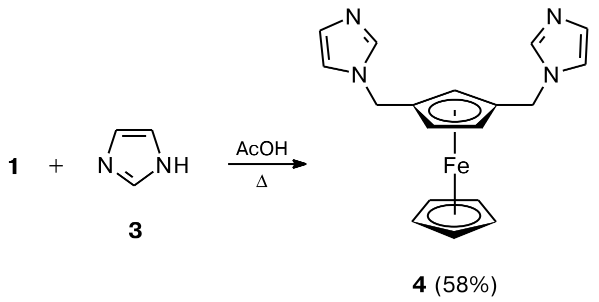
The reaction was carried out directly in an NMR tube by adding the acid to a solution of the diol in $CDCl_3$. The ^1H NMR spectrum, which was recorded immediately after the addition of the acid, unambiguously indicates that complex **2** was formed in quantitative yield. The ^1H NMR spectrum shows singlets for the cyclopentadienyl protons at δ 4.22 (5 H, C_5H_5), 4.40 (2 H, H(3), H(4)), and 4.47 (1 H, H(2)) and for four methylene protons at δ 5.13 (4 H, CH_2). All signals are rather narrow, without evidence of the broadening, except for the signal for the methylene protons, which is slightly broadened at the base of the peak due apparently to the unresolved spin-spin coupling. Dicarbocation **2** appeared to be not quite stable. At room temperature, it quite rapidly decomposes in the above-mentioned solution. It should be noted that the metallocene dicarbocations observed previously belong to either tertiary ions[13] or polyalkylmetallocene ions.[14] Unlike these ions, primary dicarbocation **2** does not contain substituents stabilizing the positive charge at the carbocationic center or in the cyclopentadienyl rings.

The alkylation of imidazole **3** with diol **1** was carried out by refluxing in acetic acid. Diimidazole derivative **4** was obtained in 58% yield (Scheme 2) and was isolated as yellow needles.

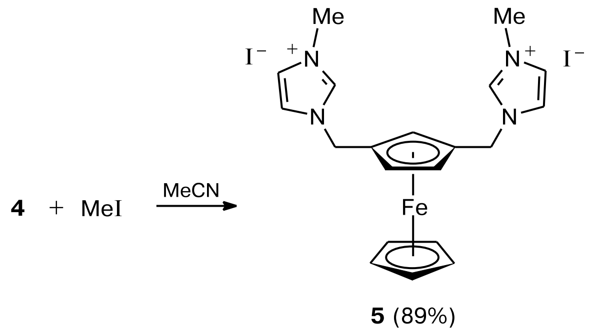
The quaternization of compound **4** with methyl iodide afforded salt **5** in 89% yield (Scheme 3).

Complexes **4** and **5** were characterized by ^1H NMR spectroscopy and elemental analysis. Salt **5** is the starting compound for the preparation of the C,C,C-bis(N-heterocyclic) carbene pincer ligand.

Scheme 2

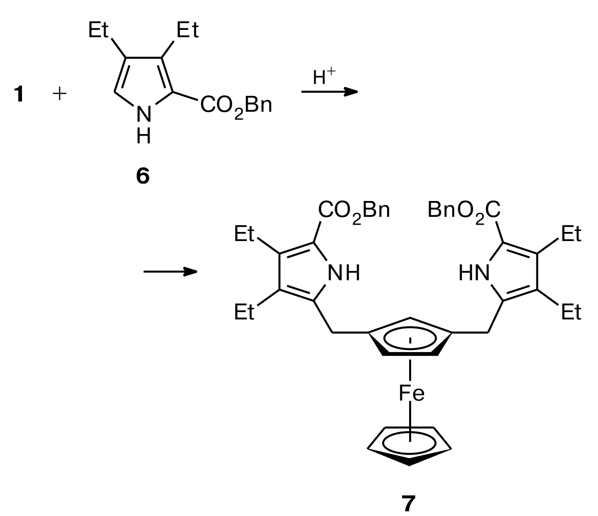


Scheme 3



The ferrocenylmethylation of the pyrrole moiety with diol **1** was performed by an example of the reaction of compound **6**. We chose pyrrole **6** because we intended to use product **7** formed in this reaction (Scheme 4) for the design of porphyrinoid system containing the ferrocene unit included in the macrocycle. Under mild conditions, the benzyl protecting group can be removed from dipyrrole derivative **7**, and the aromatic diacid thus obtained can be

Scheme 4



decarboxylated and involved in the "3+1" condensation with dicarbonyl derivatives of various aromatic or heterocyclic systems. Previously,[15] it has been noted that pyrrole derivatives related to compound **7** offer wide possibilities for the synthesis of various carbaporphyrinoid systems according to the 3+1 condensation, which is a versatile approach providing high yields of carbaporphyrins.

p-Toluenesulfonic acid and Bentonite K-10 were used as catalysts in the synthesis of compound **7**. The product was obtained in a yield of the 51 and 81%, respectively, as a yellow crystalline compound. Compound **7** was characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis.

In summary, we characterized for the first time the ferrocene dicarbocation generated from 1,3-bis(hydroxymethyl)ferrocene **1**. The reactions of diol **1** with imidazole **3** and pyrrole **6** in an acidic medium afforded diimidazole derivative **4** and dipyrrole derivative **7**, respectively.

Experimental

All starting compounds and solvents were dried and purified before use according to standard procedures. Diol **1** (see Ref. 1) and substituted pyrrole **6** (see Ref. 16) were synthesized according to known procedures. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer (400.13 MHz for ^{1}H and 100.25 MHz for ^{13}C). Elemental analysis was carried out in the Laboratory of Microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences.

1,3-Bis[(1*H*-imidazol-1-yl)methyl]ferrocene (4). A solution of diol **1** (0.23 g, 0.94 mmol) and imidazole **3** (0.38 g, 5.56 mmol) in glacial AcOH (5 mL) was refluxed under argon for 4 h. The reaction mixture was evaporated to dryness, and the residue was dissolved in methanol (5 mL). Then potassium carbonate (0.5 g) was added. The reaction mixture was stirred for ~14 h, poured into water (20 mL), and extracted with dichloromethane (2×50 mL). The combined extracts were dried over $MgSO_4$, the solution was concentrated to ~10 mL, and diethyl ether (~50 mL) was added. The precipitate that formed was filtered off and washed with hexane. Compound **4** was obtained as small yellow needle-like crystals in a yield of 0.19 g (58%), m.p. 145—148 °C. ^{1}H NMR ($CDCl_3$), δ: 4.09 (s, 5 H, Cp); 4.17 (m, 3 H, subst. Cp); 4.77 (s, 4 H, CH_2); 6.85 (s, 2 H, imidazole); 6.99 (s, 2 H, imidazole); 7.43 (s, 2 H, imidazole). Found (%): C, 60.96; H, 4.93; N, 15.03. $C_{18}H_{18}FeN_4 \cdot CH_3OH$. Calculated (%): C, 60.33; H, 5.86; N, 14.81.

1,1´-[Ferrocene-1,3-diylbis(methylene)]bis(3-methyl-1*H*-imidazolium) diiodide (5). Methyl iodide (1 mL) was added to a solution of compound **4** (0.19 g, 0.55 mmol) in MeCN (10 mL). The reaction mixture was stirred at ~20 °C in the dark under argon for 3 days. The solution was evaporated to dryness. The residue was recrystallized from a methanol—diethyl ether mixture. Salt **5** was obtained as a yellow powder in a yield of 0.31 g (89%), m.p. 160 °C. ^{1}H NMR (DMSO-d_6), δ: 3.84 (s, 6 H, CH_3); 4.31 (s, 5 H, Cp); 4.54 (d, 2 H, subst. Cp, J = 1.5 Hz); 4.70 (t, 1 H, subst. Cp, J = 1.5 Hz); 7.68—7.69 (m, 2 H, imidazole); 7.77—7.78 (m, 2 H, imidazole); 9.14 (s, 2 H, imidazole). Found (%): C, 36.99; H, 4.15; N, 8.11. $C_{20}H_{24}FeI_2N_4 \cdot H_2O$. Calculated (%): C, 37.06; H, 4.04; N, 8.64.

1,3-Bis[5-(benzyloxycarbonyl)-3,4-diethylpyrrol-2-yl)methyl]-ferrocene (7). ***A.*** A solution of diol **1** (0.125 g, 0.51 mmol), pyrrole **6** (0.250 g, 0.97 mmol), and TsOH (0.050 g) in anhydrous ethanol was refluxed under argon for 3 h. The reaction mixture was evaporated to dryness. The residue was chromatographed on an aluminum oxide column with the use of dichloromethane as the eluent. After the recrystallization, dipyrrole **3** was obtained as a yellow powder in a yield of 0.19 g (51%).

B. Bentonite K-10 (1.33 g) was added to a solution of diol **1** (0.125 g, 0.51 mmol) and pyrrole **6** (0.250 g, 0.97 mmol) in dichloromethane (30 mL). The suspension was stirred under argon at ~20 °C for 3 h. The reaction mixture was filtered, the filtrate was evaporated to dryness, and dipyrrole **7** was obtained in a yield of 0.296 g (81%), m.p. 125—127 °C. ^{1}H NMR ($CDCl_3$), δ: 1.07 (t, 6 H, $C\underline{H}_3CH_2$, J = 7.4 Hz); 1.14 (t, 6 H, $CH_2C\underline{H}_3$, J = 7.4 Hz); 2.40 (q, 4 H, $C\underline{H}_2CH_3$, J = 7.4 Hz); 2.73 (q, 4 H, $C\underline{H}_2CH_3$, J = 7.4 Hz); 3.55 (s, 4 H, pyrrole-$C\underline{H}_2$); 4.10 (s, 3 H, subst. Cp); 4.17 (s, 5 H, Cp); 5.28 (s, 4 H, $PhC\underline{H}_2$); 7.29—7.41 (br.m, 10 H, H arom.); 8.88 (br.s, 2 H, NH). ^{13}C NMR ($CDCl_3$), δ: 15.8, 16.1 ($\underline{C}H_3CH_2$); 16.9, 18.2 ($CH_3\underline{C}H_2$); 25.7 (pyrrole-$\underline{C}H_2$); 65.4 ($Ph\underline{C}H_2$); 68.1, 68.9, 69.7, 85.1 (Cp, subst. Cp); 115.9, 122.8, 131.9, 133.7 (pyrrole); 127.8, 128.0, 128.4, 136.4 (Ph); 160.9 (CO_2). Found (%): C, 72.68; H, 6.33; N, 3.83. $C_{44}H_{48}FeN_2O_4$. Calculated (%): C, 72.93; H, 6.08; N, 3.87.

References

1. A. A. Koridze, A. M. Sheloumov, S. A. Kuklin, V. Yu. Lagunova, I. I. Petukhova, F. M. Dolgushin, M. E. Ezernitskaya, P. V. Petrovskii, A. A. Macharashvili, R. V. Chedia, *Izv. Akad. Nauk*, *Ser. Khim.*, 2002, 988 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 1077].
2. A. A. Koridze, S. A. Kuklin, A. M. Sheloumov, F. M. Dolgushin, V. Yu. Lagunova, I. I. Petukhova, M. G. Ezernitskaya, A. S. Peregudov, P. V. Petrovskii, E. V. Vorontsov, M. Baya, R. Poli, *Organometallics*, 2004, **23**, 4585.
3. S. A. Kuklin, F. M. Dolgushin, P. V. Petrovskii, A. A. Koridze, *Izv. Akad. Nauk, Ser. Khim.*, 2006, 1879 [*Russ. Chem. Bull.*, *Int. Ed.*, 2006, **55**, 1950].
4. S. A. Kuklin, A. M. Sheloumov, F. M. Dolgushin, M. G. Ezernitskaya, A. S. Peregudov, P. V. Petrovskii, A. A. Koridze, *Organometallics*, 2006, **25**, 5466.
5. A. M. Sheloumov, F. M. Dolgushin, M. V. Kondrashev, P. V. Petrovskii, Kh. A. Barbakadze, O. I. Lekashvili, A. A. Koridze, *Izv. Akad. Nauk*, *Ser. Khim.*, 2007, 1695 [*Russ. Chem. Bull., Int. Ed.*, 2007, **56**, 1757].
6. R. Butler, B. Woldt, M.-Z. Oh, D. J. Williams, *Inorg. Chem. Commun.*, 2006, **9**, 1255.
7. M. Steurer, Y. Wang, K. Mereiter, W. Weissensteiner, *Organometallics*, 2007, **26**, 3850.
8. C. Pichon, B. Odell, J. M. Brown, *Chem. Commun.*, 2004, 598.
9. S. V. Safronov, A. M. Sheloumov, A. Z. Kreindlin, A. A. Kamyshova, F. M. Dolgushin, A. F. Smol´yakov, P. V. Petrovskii, M. E. Ezernitskaya, A. A. Koridze, *Izv. Akad. Nauk*,

Ser. Khim., 2010, 1694 [*Russ. Chem. Bull., Int. Ed.*, 2010, **59**, No. 9].

10. *Ferrocenes. Homogeneous Catalysis. Organic Synthesis. Materials Science*, Eds A. Togni, T. Hayashi, Wiley-VCH, Weinheim, 1995.
11. A. A. Koridze, *Usp. Khim.*, 1986, **55**, 277 [*Russ. Chem. Rev.* (*Engl. Transl.*), 1986, **55**, 113].
12. S. Barlow, A. Cowley, J.-C. Green, T.-J. Brunker, T. Hascall, *Organometallics*, 2001, **20**, 5351.
13. C. U. Pittman, *Tetrahedron Lett.*, 1967, 3619.
14. M. I. Rybinskaya, A. Z. Kreindlin, P. V. Petrovskii, R. M. Minyaev, R. Hoffmann, *Organometallics*, 1994, **13**, 3903.
15. T. D. Lash, *Eur. J. Org. Chem.*, 2007, 5461.
16. T. D. Lash, J. R. Belletini, J. A. Bandian, K. B. Couch, *Synthesis*, 1994, **2,** 170.

Received June 7, 2010;
in revised form September 6, 2010