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A SIMPLE ROUTE TO FeCpCp'

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Abstract—A new method for the synthesis of the mixed-ligand compound FeCpCp' (where Cp' denotes the pentamethyl cyclopentadienyl group) is described from the reaction of a solution of NaCp' and LiCp with FeCl₂ in THF. The mixture of products includes $FeCp_2$, FeCpCp' and FeCp₂' in approximately a 1:3:1 mole ratio. Partial oxidation of the mixture leads to preferential precipitation of the ferricinium salts of the derivatives with the most negative reduction potentials. Subsequent treatment with a reducing agent regenerates the ferrocenes. Implementation of a couple of redox cycles allows the isolation of other unsymmetrical ferrocenes is straightforward so long as there is a modest spread in the reduction potentials of the components. The development of new synthetic methods is worthwhile because substituted ferrocenes are useful reagents in studies of electron-transfer processes. The method described herein is attractive because it is quite simple and adaptable to large-scale preparations.

Ferrocenes have proven useful in numerous studies of electron-transfer phenomena.^{1–3} One of the most compelling properties of these systems is the fact that the ferricinium–ferrocene reduction potential varies significantly with substitution on the cyclopentadienyl ligand.^{4–6} As a consequence, one can employ a homologous series of ferrocene reagents to characterize the kinetic reactivity of a transient species.^{7.8}

Unsymmetrical, mixed-ring derivatives are kinetically inert, because the exchange of the pentahapto ligand is an extremely slow process at the iron center. The classic example of a mixed-ring derivative is FeCpCp', where Cp denotes the (η^5) cyclopentadienyl ligand and Cp' denotes the pentamethyl analogue. It is possible to make FeCpCp' from FeCp₂ by chemical means, e.g. by the use of the Friedel–Crafts reaction.⁹ Alternatively, one can synthesize the mixed-ring derivative from the preformed ligands. The most obvious approach involves sequential addition of the ligands. However, when Bunel *et al.* treated a THF solution of FeCl₂ with 1 mole equivalent of Cp' anion and then 1 mole equivalent of Cp anion, they found that the product was mainly a mixture of FeCp₂ and $FeCp'_{2}$.¹⁰ On the other hand, when they used Fe (acac)₂ as the iron precursor, they obtained the desired mixed-ring compound.¹⁰ Later, Phillips et al. prepared FeCpCp' by photolyzing Cp'Fe (CO)₂Br in solution in the presence of the cyclopentadienyl anion.¹¹ Here we report a convenient synthesis of FeCpCp' that involves the simultaneous addition of the two ligand anions to a solution of FeCl₂ in THF. To be sure, the reaction yields a mixture of products, but it is easy to separate the components on the basis of the reduction potentials by a batch-processing method. From start to finish the procedure takes only a couple of hours, and it is therefore suitable for incorporation in a student laboratory.

EXPERIMENTAL

Materials

We used reagent-grade materials as received from standard chemical supply houses except as noted. A solution of sodium pentamethylcyclopentadienide (NaCp') in THF as well as the pure solids lithium

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cyclopentadienide (LiCp), sodium ascorbate, and 1,4-benzoquinone came from Aldrich. Strem Chemical Co. supplied anhydrous $FeCl_2$, and Johnson Matthey, Inc. provided HBF_4 as a 48% solution. The CDCl₃ NMR solvent came from Cambridge Isotope Laboratories.

Methods

We purified THF by distillation from benzophenone over sodium metal, and recrystallized the tetrabutylammonium hexafluorophosphate (TBAH) from ethanol. A modification of the method of King and Bisnette¹² produced the original mixture of ferrocenes. First, we took a 1:1 solution of LiCp and NaCp' in THF and added it to 1 equiv. of FeCl₂. After several minutes we passed the resulting solution through a basic-alumina column and eluted with diethyl ether under aerobic conditions. The yellow fractions yielded a mixture of ferrocenes after the solvent evaporated. The ¹H-NMR spectrum and the cyclic voltammogram revealed the distribution of products.

We used a conventional three-electrode cell for the voltammetry studies. The working electrode was a gold disc, and the auxiliary electrode was a Pt wire. For the reference electrode, we used an AgCl-Ag electrode in contact with 3 M Cl(aq). A solution of 0.1 M TBAH in CH₂Cl₂ served as the supporting electrolyte. We purged the solution with nitrogen gas to remove oxygen prior to making the electrochemical measurements at a scan rate of 50 mV s⁻¹.

Isolation of FeCp₂. The first step in the separation involved dissolving the mixture of ferrocenes in diethyl ether containing excess HBF₄. Dropwise addition of an ether solution of 1,4-benzoquinone with stirring induced the formation of solid ferricinium tetrafluoroborate.¹³ We adjusted the stoichiometry so as to oxidize all of the $FeCp'_2$ and nearly all of the FeCpCp' in the original sample and obtained a yellow-orange solution (A) and a green precipitate (B). Evaporation of solution A gave a solid that was mostly FeCp₂ along with some FeCpCp' as shown by the NMR spectrum. We isolated FeCp₂ by dissolving the solid and oxidizing once again to remove the residual FeCpCp' as a ferricinium salt. Evaporation of the mother liquor then yielded pure FeCp₂ [¹H NMR : $\delta = 4.15$ ppm (10 H)].

Isolation of FeCpCp'. We then dissolved solid B in a 1:1 by volume solution of ether and methanol. After the addition of excess sodium ascorbate, the green solution turned yellow. We then extracted with water, collected the organic layer, and finally obtained a mixture of FeCpCp' and FeCp'₂ after removing the solvent. Oxidation of a solution of this mixture removed all the $[FeCp'_2]BF_4$ present as part of a green precipitate (C). We extracted pure FeCpCp' from the remaining solution. Found : C, 70.6; H, 8.1. Calc for FeC₁₅H₂₀: C, 70.3; H, 7.9 [¹H NMR : $\delta = 3.67$ ppm (5 H), $\delta = 1.91$ ppm (15 H)].

Isolation of FeCp'₂. Reduction of a solution of compound C gave a mixture of FeCpCp' and FeCp'₂ after workup and solvent removal as before. As FeCp'₂ is relatively insoluble, we obtained pure decamethyl ferrocene by recrystallization from acetonitrile [¹H NMR : $\delta = 1.67$ ppm (30 H)].

Instrumentation

The NMR instrument was a Gemini 200 MHz FT-NMR. In conjunction with a Hewlett–Packard 7015B X–Y recorder, a BAS CV-27 instrument yielded the cyclic voltammograms.

RESULTS AND DISCUSSION

The cyclic voltammogram in Fig. 1 indicates the mixture of products obtained from the reaction of FeCl₂ with LiCp and NaCp'. A comparison run with an authentic sample showed that one of the signals in Fig. 1 corresponds to ferrocene. Since this is our reference, it occurs at $E^0 = 0$. As reported many years ago by Kuwana et al.,⁴ the addition of electron-donating alkyl substituents shifts the reduction potential to a more negative value. Accordingly, FeCpCp' and FeCp'₂ have E^0 values of -0.30 and -0.59 V, respectively, vs ferrocene. The integration of the ¹H-NMR spectrum of the mixture showed there was a 1:3:1 ratio of FeCp₂, FeCpCp' and FeCp'₂, respectively. The isolated yield of FeCpCp' was about 30% on the basis of total iron, while the initial yield of ferrocenes was about 90%.

The decamethyl ferrocene is relatively easy to oxidize, and solutions of the compound are air sensitive. Also, the reduction of $[FeCp'_2]BF_4$ with ascorbate apparently did not go to completion. Thus, the NMR spectrum of the crude material showed the presence of the ferrinicium ion because the methyl resonance was typically rather broad and shifted upfield from the normal position.¹ To obtain pure FeCp'_2, we sublimed the mixture or recrystallized it from acetonitrile.

In closing, it is appropriate to compare our method for the preparation of FeCpCp' with others that have appeared in the literature. Bunel *et al.* reported a procedure based upon the sequential addition of cyclopentadienide and pentamethyl-cyclopentadiene.¹⁰ Their method is attractive because it has the potential for a high yield.



Fig. 1. Cyclic voltammogram of the ferrocene mixture. The reference is the $FeCp_2^{+:0}$ couple in CH_2Cl_2 containing 0.1 M TBAH at 25°C.

However, there are some practical problems. One is that $Fe(acac)_2$ is very air sensitive. In addition, the procedure requires high-purity reagents because the stoichiometry is so important for the reaction. Phillips et al. reported another route to FeCpCp' that uses Cp'Fe(CO)₂Br as the starting compound.¹¹ But this method is basically a photolytic method; hence one must have access to an appropriate light source. The isolation of FeCpCp' is also a multi-step process. By comparison with either of the above, our method is quite simple as it involves the direct combination of the ligands with FeCl₂. Although the product contains FeCpCp' as part of the mixture, the byproducts are useful compounds and easy to isolate. The separation method we devised depends upon the difference in the redox potentials and is adaptable to other ferrocene mixtures as long as the differences in the reduction potentials of the constituents are reasonable.

REFERENCES

 E. S. Yang, M. S. Chan and A. C. Wahl, J. Phys. Chem. 1980, 84, 3094.

- R. M. Nielson, G. E. McManis, M. N. Golovin and M. E. Weaver, J. Phys. Chem. 1988, 92, 3441.
- 3. S. Wherland, Coord. Chem. Rev. 1993, 123, 169.
- T. Kuwana, D. E. Bublitz and G. Hoh, J. Am. Chem. Soc. 1960, 82, 5811.
- 5. M. M. Sabbatini and E. Cesarotti, *Inorg. Chim. Acta* 1977, **24**, L9.
- J. L. Robbins, N. Edelstein, B. Spencer and J. C. Smart, J. Am. Chem. Soc. 1982, 104, 1882.
- F. R. Lemke, R. M. Granger, D. A. Morgenstern and C. P. Kubiak, J. Am. Chem. Soc. 1990, 112, 4052.
- E. J. Lee and M. S. Wrighton, J. Am. Chem. Soc. 1991, 113, 8562.
- A. N. Nesmeyanov and N. S. Kochetkova, *Izvest.* Akad. Nauk S.S.S.R. Otdel. Khim. Nauk 1958, 242; Chem Abstr. 1958, 52, 12852d.
- 10. E. E. Bunel, L. Valie and J. M. Manriquez. Organometallics 1985, 4, 1680.
- 11. L. Phillips, A. R. Lacey and M. K. Cooper, J. Chem. Soc. Dalton Trans. 1988, 1383.
- R. B. King and M. B. Bisnette, J. Organomet. Chem. 1967, 8, 287.
- D. N. Hendrickson, Y. S. Sohn and H. B. Gray, *Inorg. Chem.* 1971, 10, 1559.