# The $\eta^5$-$C_9H_{11}Fe(CO)_2$(isobutylene)$^+BF_4^-$ Complex as a Protecting Group of Carbon-Carbon Double Bonds

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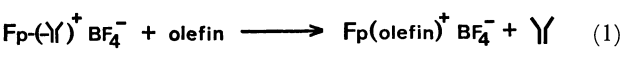
(Received February 12, 1983)

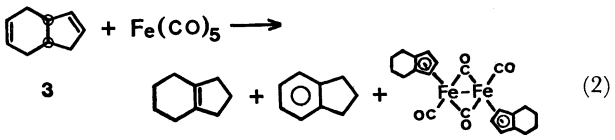
**Synopsis.** $\eta^5$-$C_9H_{11}Fe(CO)_2$(isobutylene)$^+BF_4^-$ (**6**), [Fpi(isobutylene)]$^+BF_4^-$, was prepared and used as a protecting group of carbon–carbon double bonds. The complex **6** undergoes ligand exchange with a variety of diolefins to give Fpi(diolefin)$^+BF_4^-$ complexes, whose subsequent hydrogenations on Pd/C give olefins hydrogenated regioselectively.

The dicarbonyl $\eta^5$-cyclopentadienyliron cation moiety, $\eta^5$-$C_5H_5Fe(CO)_2^+$ ($Fp^+$), serves as a good protecting group for the carbon–carbon double bond of olefins.[1,2] The Fp(isobutylene)$^+BF_4^-$ complex (**1**), which is readily available from the Fp dimer, undergoes ligand exchange with olefins under mild conditions to give Fp(olefin)$^+BF_4^-$ (**2**) (Eq. 1).




1 2 (1)

In a previous paper, we have reported the $Fe(CO)_5$ catalyzed disproportionation of *cis*-bicyclo[4.3.0]nona-3,7-diene (**3**) to bicyclo[4.3.0]non-1(6)-ene (**4**) and indan (Eq. 2).[3] In the course of the reaction, it was found that tetracarbonylbis($\eta^5$-4,5,6,7-tetrahydroindenyl)diiron (**5**) (Fpi dimer), which is structurally analogous to the Fp dimer, was formed. The stoichiometric reaction of **3** and $Fe(CO)_5$ gave **5** in a moderate yield (35—46%).[4]

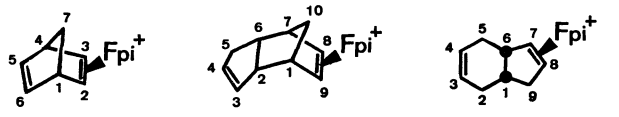



4 5 (2)

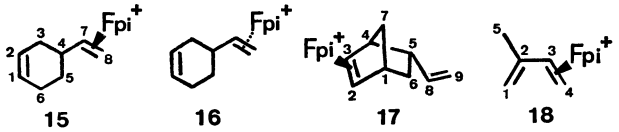
The Fpi moiety, which is more bulky than the Fp moiety, can be expected to provide a method for protecting the carbon–carbon double bonds. Thus, the Fpi(isobutylene)$^+BF_4^-$ complex (**6**) was prepared and used as a protecting group of the double bonds for various diolefins.

The preparation of **6** from **5** was achieved in 60—65% yields by a modification of the Rosenblum method[5] for the synthesis of **1**. Complex **6** reacted with a variety of diolefin **3**, **7**—**11** in 1,2-dichloroethane to afford Fpi(diolefin)$^+BF_4^-$ complexes **12**—**18** (Scheme 1). The yields of the Fpi(diolefin)$^+BF_4^-$ complexes were preferable to those of the ligand exchange between Fp(isobutylene)$^+BF_4^-$ and diolefins[1] (Scheme 1). The $^{13}C$ NMR chemical shifts of these complexes are listed in Tables 1 and 2.

The ligand exchange of **6** with bicyclo[2.2.1]hepta-2,5-diene **7** gave **12** in a 91% yield. In the $^{13}C$ NMR spectrum of **12**, the signal of the α-carbons (C-2 and C-3) shifted about 55 ppm upfield compared with those of **7**.[6] The *exo*-configuration of the $Fpi^+$ moiety in **12** was confirmed on the basis of the upfield shift (*ca.* 18 ppm) of the bridge carbon (C-7) attributable to the steric compression effect. The exchange of **6** with *endo*-tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene **8** proceeded




12 (91%) 13 (83%) 14 (60%)



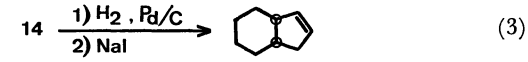

15 (31%) 16 (31%) 17 (60%) 18 (95%)

Scheme 1.

regio- and stereoselectively, affording **13** in an 83% yield. A similar steric effect by the $Fpi^+$ moiety was observed at the bridge carbon (C-10) of **13**. This shows that the configuration of the $Fpi^+$ group in **13** has the *exo*-orientation.

The reaction of **6** with **3** gave exclusively complex **14**, in which the $Fpi^+$ group is probably located in an anti-direction. If the $Fpi^+$ moiety in **14** is situated in a sterically more crowded *syn*-geometry, obvious upfield shifts due to the steric compression effect must be observed in $^{13}C$ resonances of the fused cyclohexene ring.

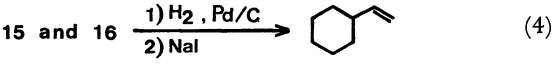
The hydrogenation of **14** on Pd/C, followed by treatment with NaI, gave olefin (**19**) (Eq. 3).




19 (3)

The regiospecific formation of **14** is noteworthy, since the reactivities of the two double bonds in **3** closely resemble each other.

In the exchange of **6** with 4-vinyl-1-cyclohexene (**9**), the $^{13}C$ NMR spectra of resulting $Fpi^+$ complexes showed two pairs of signals having approximately equal intensities. Although the complexes could not be separated into components, from a consideration of their NMR spectra it was found that the exchange occurred regioselectively, but not stereoselectively, at the vinyl-double bond to give a stereoisomeric mixture of **15** and **16** whose subsequent hydrogenations led to the same olefin (**20**) (Eq. 4).




20 (4)

Previously, Nicholas[1] has reported that the exchange of **1** with 5-vinylbicyclo[2.2.1]hept-2-ene (**10**)[8] affords two regioisomers in which the $Fp^+$ group is coordinated to the vinyl- and bicyclo[2.2.1]heptenyl double bonds in a ratio of 65:35. However, the ligand exchange of **6** with **10** occurred preferentially at the bicyclo-[2.2.1]heptenyl double bond to give the Fpi complex **17**.[9]

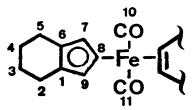
Table 1. $^{13}C$ NMR chemical shifts of Fpi(diolefin)$^+BF_4^-$ complexes

| Complex | C-1 | C-2 | C-3 | C-4 | C-5 | C-6 | C-7 | C-8 | C-9 | C-10 |
|---|---|---|---|---|---|---|---|---|---|---|
| **12** | 47.9 | 86.3 | 86.3 | 47.9 | 143.8 | 143.8 | 56.2 | | | |
| **13** | 43.4[a] | 54.3 | 129.6 | 132.5 | 31.1 | 41.1 | 44.5[a] | 75.8 | 81.0 | 38.6 |
| **14** | 30.0 | 23.9 | 124.8[a] | 125.1[a] | 27.2 | 38.6 | 85.5 | 80.8 | 35.9 | |
| **15** and **16** | 126.5 | 124.8 | 32.8 | 39.2 | 30.7 | 24.2 | 94.0 | 52.0 | | |
| | 126.5 | 124.8 | 32.8 | 39.2 | 29.7 | 24.2 | 93.4 | 52.0 | | |
| **17** | 46.2 | 75.8 | 79.0 | 40.9 | 31.5 | 42.8 | 37.1 | 139.0 | 114.8 | |
| **18** | 123.1 | 140.9 | 89.1 | 49.2 | 15.5 | | | | | |

a) An alternative assignment is also possible in each line.

Table 2. $^{13}C$ NMR chemical shifts of the Fpi-moiety[a]

| Complex | C-1 | C-2 | C-3 | C-4 | C-5 | C-6 | C-7 | C-8 | C-9 | C-10 or C-11 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **12** | 108.0 | 21.2[b] | 20.8[b] | 20.8[b] | 21.2[b] | 108.0 | 84.4 | 90.6 | 84.4 | 211.7 | 211.7 |
| **13** | 108.0 | 21.1[b] | 20.7[b] | 20.7[b] | 21.1[b] | 108.0 | 83.9[c] | 90.4 | 84.3[c] | 212.0 | 211.7 |
| **14** | 108.1 | 21.3[b] | 20.9[b] | 20.9[b] | 21.3[b] | 108.1 | 83.8[c] | 91.1 | 84.1[c] | 212.0 | 211.8 |
| **15** and **16** | 108.7 | 21.6[b] | 20.7[b] | 20.7[b] | 21.6[b] | 108.7 | 85.3 | 90.1 | 85.3 | 211.5 | 209.2 |
| | 107.4 | 20.7 | 20.7 | 20.7 | 20.7 | 107.4 | 81.6[b] | 90.1 | 82.3[b] | 211.5 | 209.2 |
| **17** | 107.9 | 21.2[b] | 20.8[b] | 20.8[b] | 21.2[b] | 107.9 | 84.2[c] | 90.9 | 84.2[c] | 211.7 | 211.6 |
| **18** | 108.2 | 21.3[b] | 20.7[b] | 20.7[b] | 21.3[b] | 107.8 | 83.6[c] | 90.4 | 84.0[c] | 210.9 | 210.6 |

a) 

b, c) An alternative assignment is also possible in each line.

The reaction of **6** with acyclic diene, isoprene **11**, took place regioselectively at the less hindered double bond to form Complex **18** in a 95% yield.

These results suggest that Complex **6**, which was readily prepared from the Fpi-dimer, serves as a good protecting group of carbon-carbon double bonds, especially toward the diolefins with a closely analogous reactivity. Furthermore, **6** shows a higher regioselectivity than Complex **1** in the exchange with certain diolefins.

## Experimental

The IR spectra were taken with a JASCO-A202 spectrometer. The $^1H$ and $^{13}C$ NMR spectra were recorded with a JEOL PMX-60 and a JNM-PS-100 FT-NMR spectrometer respectively. The chemical shifts were obtained in a nitromethane-$d_3$ solution, containing TMS as the internal standard.

*Materials.* The Fpi dimer (**5**) was obtained in a manner similar to that described above.[3]

Fpi(isobutylene)$^+BF_4^-$ (**6**) was prepared by a modification of Rosenblum procedure.[5] To a solution of Fpi($\eta^1$-2-methyl-2-propenyl) (33 mmol), which has been prepared from FpiNa and 2-methyl-2-propenyl chloride,[10] we added, drop by drop, 1 equiv of 42% $HBF_4$ in acetone (1:1) at 0 °C. Stirring was continued at 0 °C for 1 h. At the end of this time, 20 cm$^3$ of acetone was added, and then the solution was poured to a large amount of ether (500 cm$^3$). The orange crystals thus precipitated were collected and recrystallized from dichloromethane to give pure **6** in 60—65% overall yields; $^1H$ NMR ($CD_3NO_2$) $\delta$=1.9 (m, 10H), 2.5 (m, 4H), 3.7 (s, 2H), 5.2 (s, 3H); $^{13}C$ NMR ($CD_3NO_2$) $\delta$=21.4(t), 21.9(t), 27.7(q), 55.1(t), 84.0(d), 91.3(d), 110.1 (s), 122.7(s), 211.0(s); IR(Nujol) 3400, 2050, 1990, 1060, 1010 cm$^{-1}$.

*Ligand Exchange of **6** with Diolefins.* To a solution of diolefin (60 mmol) in 1,2-dichloroethane (200 cm$^3$) we added **6** (6 mmol) in 1,2-dichloroethane (80 cm$^3$). Stirring was continued at 65—70 °C for 10—15 min. After the subsequent removal of the solvent and unreacted diolefin *in vacuo*, the residue was dissolved in a minimum amount of acetone and filtered off. The filtrate was poured into 500 cm$^3$ of ether to precipitate Fpi(diolefin)$^+BF_4^-$ complexes in 60—95% yields.

*Hydrogenation of Fpi(diolefin)$^+BF_4^-$ Complexes and Liberation of the Fpi Moiety from Complexes.* The hydrogenations of **14**—**16** were accomplished according to the Nicholas procedure.[2] The hydrogenated complexes (0.8 mmol) were dissolved in nitromethane-$d_3$ (2 cm$^3$) containing sodium iodide (1.0 mmol), after with the mixture was refluxed for 3 h. After centrifugation, the supernatant was subjected to NMR measurements.

### References

1) P. R. Boyle and K. M. Nicholas, *J. Org. Chem.*, **40**, 2682 (1975).
2) K. M. Nicholas, *J. Am. Chem. Soc.*, **97**, 3254 (1975).
3) T. Kagayama, S. Okabayashi, Y. Amaike, Y. Matsukawa, Y. Ishii, and M. Ogawa, *Bull. Chem. Soc. Jpn.*, **55**, 2297 (1982).
4) Complex **5** was synthesized from spirononadiene and $Fe(CO)_5$ in a 30% yield: B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, **1958**, 646.
5) W. P. Giering and M. Rosenblum, *J. Chem. Soc., Chem. Commun.*, **1971**, 441.
6) A similar upfield shift was observed in the ethylene-ligand carbons of Fp(ethylene)$^+BF_4^-$: J. M. Fallor and B. Y. Johnson, *J. Organomet. Chem.*, **88**, 101 (1975).
7) The ligand exchange of **1** with **9** has been attempted by Nicholas,[1] but the formation of stereoisomeric Fp-(diolefin)$^+BF_4^-$ complexes has not been described.
8) Compound **10** was a mixture of *endo* and *exo* vinyl derivatives (75:25).
9) A small amount of some other Fpi(diolefin)$^+BF_4^-$ complexes were produced together with **17**, but no components other than **17** could be identified.
10) W. P. Giering and M. Rosenblum, *J. Organomet. Chem.*, **25**, C71 (1970).