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

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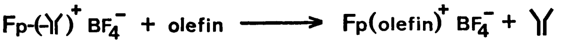
Synopsis. η^5-$C_9H_{11}Fe(CO)_2(isobutylene)^+BF_4^-$ (**6**), [Fpi(isobutylene)]$^+BF_4^-$, was prepared and used as a protecting group of carbon–carbon double bonds. The complex **6** undergoes ligand exchange with a variety of diolefins to give Fpi(diolefin)$^+BF_4^-$ complexes, whose subsequent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

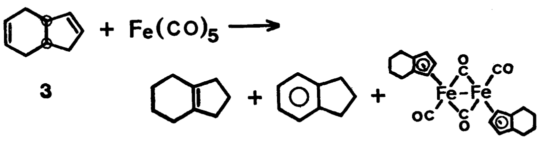
The dicarbonyl η^5-cyclopentadienyliron cation moiety, η^5-$C_5H_5Fe(CO)_2^+$ (Fp$^+$), serves as a good protecting group for the carbon–carbon double bond of olefins.1,2) The Fp(isobutylene)$^+BF_4^-$ complex (**1**), which is readily available from the Fp dimer, undergoes ligand exchange with olefins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



(1)

1 **2**

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(η^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)



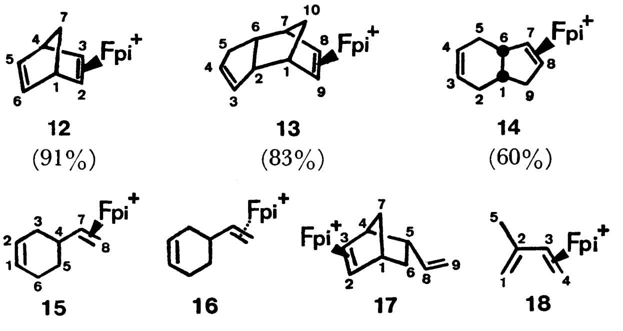
(2)

3 **4** **5**

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 method5) 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 diolefins1) (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 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.



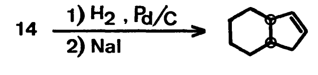
12 (91%) **13** (83%) **14** (60%)

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

Scheme 1.

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).

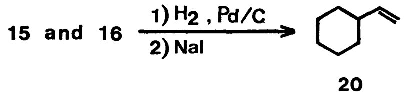


(3)

19

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).



(4)

20

Previously, Nicholas1) 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

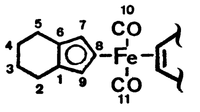
Complex	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
12	47.9	86.3	86.3	47.9	143.8	143.8	56.2			
13	43.4[a]	54.3	129.6	132.5	31.1	41.1	44.5[a]	75.8	81.0	38.6
14	30.0	23.9	124.8[a]	125.1[a]	27.2	38.6	85.5	80.8	35.9	
15 and **16**	126.5	124.8	32.8	39.2	30.7	24.2	94.0	52.0		
	126.5	124.8	32.8	39.2	29.7	24.2	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 ^{1}H 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(η^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; ^{1}H NMR (CD$_3$NO$_2$) δ=1.9 (m, 10H), 2.5 (m, 4H), 3.7 (s, 2H), 5.2 (s, 3H); ^{13}C NMR (CD$_3$NO$_2$) δ=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).