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PREPARATION AND REACTIONS OF THE (DICARBONYL)(η^5-CYCLOPENTADIENYL)(TETRAHYDROFURAN)IRON CATION: A CONVENIENT ROUTE TO (DICARBONYL)(η^5-CYCLOPENTADIENYL)(η^2-OLEFIN)IRON CATIONS AND RELATED COMPLEXES

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Abstract

The versatile reagent [(η^5-C_5H_5)Fe(CO)$_2$(THF)]BF$_4$ has been isolated from the reaction of (η^5-C_5H_5)Fe(CO)$_2$I and AgBF$_4$ in THF and shown to react in CH_2Cl_2 with olefins to yield [(η^5-C_5H_5)Fe(CO)$_2$(η^2-olefin)]BF$_4$ complexes. For most olefins the yields are high. The yield in these reactions can be increased by treating the CH_2Cl_2 solution of [(η^5-C_5H_5)Fe(CO)$_2$(THF)]BF$_4$ and olefin with gaseous BF_3 in order to complex the THF as the BF_3-THF adduct. Most striking is the increase in yield for the cyclohexene complex from 17% to 92%.

Introduction

One of the most widely studied classes of transition metal organometallic complexes is that of the derivatives of (η^5-C_5H_5)Fe(CO)$_2$ [1] (hereafter designated by the symbol Fp). There are two major reasons for this. First, straightforward and inexpensive routes are available for the synthesis of Fp complexes. Second, most derivatives that have been reported are quite stable.

Because of our interests in converting organometallic metal-halide complexes into metal alkyls and cationic metal-L(L=neutral 2-electron donating ligand) complexes, we have investigated substitution reactions of FpI using $AgBF_4$ as a Lewis acid to remove the iodide to generate the reactive Fp^+ intermediate. Reported here is the isolation of the complex $[Fp\text{-}(THF)]^+$ (1) produced from this reaction when carried out in THF. It is shown to be a convenient reagent for the preparation of $[Fp\text{-}L]^+$ complexes. This complex was mentioned briefly in 1971 [2] and the analogous acetone adduct in 1973 [3].

Experimental Section

General Data. All operations on complexes in solution were carried out under an atmosphere of prepurified nitrogen using solvents that were purified and degassed before use. Carbon-13 NMR spectra were recorded on a Varian CFT-20 spectrometer using CH_2Cl_2 as the solvent and internal standard. Chemical shifts are reported vs. TMS assigning the CH_2Cl_2 resonance to be at 54.00 ppm and all spectra were run with ^1H decoupling. The $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ [4] was recrystallized from a hot mixture of heptane-toluene (4:1, v/v, 20 ml/g). The $AgBF_4$ was purchased from Ozark-Mahoning. The η^2-olefin complexes prepared below are known [1b], were shown to be pure by ^1H and ^{13}C NMR, and were further characterized by IR. The aniline [5], PPh_3 [6], and nitrate [7] complexes are also known and were characterized as above. Melting and decomposition points were determined in sealed evacuated capillaries and are uncorrected.

(Dicarbonyl)(η^5-cyclopentadienyl)(tetrahydrofuran)iron(II)Tetrafluoroborate. A mixture of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ (15.0 g, 49.3 mmol) and $AgBF_4$ (9.75 g, 50.0 mmol) was stirred in THF (250 ml) for 3 h. The solvent was evaporated, the residue extracted with CH_2Cl_2 (four 75 ml portions), and these solutions filtered using large quantities of filter aid. The filtrate was concentrated to 125 ml and hexane (150 ml) added to precipitate red flocculent crystals. After cooling the solution at -20° for 3 h, the crystals were collected, washed with hexane (two 25 ml portions), and dried *in vacuo* (16.05 g, 97%), dec 103° (Found: C, 39.09; H, 3.90; F, 22.68. $C_{11}H_{13}BF_4FeO_3$ calcd: C, 39.28; H, 3.87; F, 22.62). ^1H NMR spectrum (δ (ppm) in acetone-d_6): 5.71 (5, singlet, η^5-C_5H_5), 3.63 (4, multiplet, OCH_2), 1.82 (4, multiplet, CH_2). IR spectrum (cm^{-1} in CH_2Cl_2): ν (CO) 2019, 2065. ^{13}C NMR spectrum (in ppm): 208.94 (CO), 85.77 (η^5-C_5H_5), 81.89 (OCH_2), 23.67 (CH_2).

(Dicarbonyl)(η^5-cyclopentadienyl)(triphenylphosphine)iron(II)Tetrafluoroborate. To a solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(THF)]BF_4$ (1.0 g, 2.97 mmol) in CH_2Cl_2 (25 ml) was added PPh_3 (0.85 g; 3.24 mmol). This solution was stirred for 0.5 h. Hexane (20 ml) was added, and the yellow powder which formed collected, washed with hexane (10 ml), and dried *in vacuo* (1.51 g, 97%), mp 259-260°.

(Aniline)(dicarbonyl)(η^5-cyclopentadienyl)iron(II)Tetrafluoroborate. Aniline (0.55g, 5.94 mmol) was added to a solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(THF)]BF_4$ (1.0 g, 2.97 mmol) in CH_2Cl_2 (50 ml). After 6 h of stirring, this solution was concentrated to 15 ml and hexane (15 ml) added slowly. Orange crystals formed which were collected, washed with hexane (two 5 ml portions) and dried *in vacuo* (1.04 g, 98%), mp 174-175°.

(Dicarbonyl)(η^2-1,5-cyclooctadiene)(η^5-cyclopentadienyl)iron(II)Tetrafluoroborate. A mixture of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(THF)]BF_4$ (1.50 g, 4.46 mmol) and 1,5-cyclooctadiene (1.45 g, 13.4 mmol) was stirred in CH_2Cl_2 (100 ml) for 8 h. This solution was filtered, the filtrate concentrated to 15 ml, and hexane (15 ml) was added slowly. The yellow crystals which formed were collected, washed with hexane (10 ml) and dried *in vacuo* (1.29 g, 78%), dec 130-132°. The filtration step before crystallization is essential in order to remove small amounts of the metal-olefin 2:1 complex which is very insoluble.

(Dicarbonyl)(η^2-1,4-cyclohexadiene)(η^5-cyclopentadienyl)iron(II)Tetrafluoroborate. A mixture of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(THF)]BF_4$ (1.5 g, 4.46 mmol) and 1,4-cyclohexadiene (1.01 g, 13.40 mmol) was heated in refluxing CH_2Cl_2 (100 ml) for 3.5 h. This solution was filtered, concentrated to 15 ml, and hexane (15 ml) added. The yellow crystals which formed were collected, washed with hexane (10 ml), and dried *in vacuo* (1.23 g, 80%), mp 92-93°.

(Dicarbonyl)(n^5-cyclopentadienyl)(n^2-norbornadiene)iron(II)Tetrafluoroborate. A mixture of $[(n^5\text{-}C_5H_5)Fe(CO)_2(THF)]BF_4$ (1.50g, 4.46 mmol) and norbornadiene (1.23 g, 13.40 mmol) was heated in refluxing CH_2Cl_2 (100 ml) for 2.5 h. This solution was filtered and the resulting filtrate concentrated to 15 ml. Hexane (15 ml) was then added and the yellow powder which formed was collected, washed with hexane (two 5 ml portions), and dried *in vacuo* (1.41g, 89%), dec 170-175°.

(n^6-Cyclooctatetraene)(n^5-cyclopentadienyl)iron(II)Tetrafluoroborate. A mixture of $[(n^5\text{-}C_5H_5)Fe(CO)_2(THF)]BF_4$ (1.5 g, 4.46 mmol) and cyclooctatetraene (1.39 g, 13.40 mmol) was heated in refluxing CH_2Cl_2 (100 ml) for 13 h. The solution was then filtered and diethyl ether (120 ml) added slowly. The solution was cooled at -20° for 3 h, the orange crystals which formed were collected, washed with diethyl ether (10 ml), and dried *in vacuo* (0.24 g, 17%), dec 188° (Found: C, 50.23; H, 4.25. $C_{13}H_{13}BF_4Fe$ calcd: C, 50.06; H, 4.17). ^1H NMR spectrum (δ (ppm) in acetone-d_6): 7.26 (2, multiplet, free CH=CH), 6.55 (4, multiplet, complexed CH=CH), 5.42 (5, singlet, $n^5\text{-}C_5H_5$), 4.85 (2, singlet, complexed CH=CH). ^{13}C NMR spectrum: 133.17 (free CH=CH), 103.10, 96.70, 91.12 (complexed CH=CH), 82.59 ($n^5\text{-}C_5H_5$).

(Dicarbonyl)(n^2-cycloheptene)(n^5-cyclopentadienyl)iron(II)Tetrafluoroborate. A mixture of $[(n^5\text{-}C_5H_5)Fe(CO)_2(THF)]BF_4$ (1.50 g, 4.46 mmol) and cycloheptene (1.29 g, 13.40 mmol) was heated in refluxing CH_2Cl_2 (100 ml) for 5 h. This solution was filtered, the filtrate concentrated to 15 ml, and hexane (15 ml) was added. The yellow crystals which formed were collected, washed with hexane (10 ml), and dried *in vacuo* (1.19 g, 75%), dec 151-153°.

(Dicarbonyl)(n^2-cyclohexene)(n^5-cyclopentadienyl)iron(II)Tetrafluoroborate. A mixture of $[(n^5\text{-}C_5H_5)Fe(CO)_2(THF)]BF_4$ (1.00 g, 2.98 mmol) and cyclohexene (3.00 g, 36.5 mmol) was heated in refluxing CH_2Cl_2 (50 ml) for 8 h. This solution was concentrated to 20 ml and filtered. The filtrate was slowly further concentrated until yellow crystals began to precipitate. Hexane (1 ml) was added, and this solution cooled at -20°

for 24 h. The yellow crystals were collected, washed with hexane (10 ml), and dried in vacuo (0.18 g, 17%), dec 108-111°.

(Dicarbonyl)(η^5-cyclopentadienyl)(η^2-ethene)iron(II)Tetrafluoroborate. Ethene was bubbled into a solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(THF)]BF_4$ (1.0 g, 2.98 mmol) in CH_2Cl_2 (75 ml) for 0.5 h. After 0.5 h the ethene addition was stopped and the solution stirred for 8 h. This solution was concentrated to 15 ml and hexane (15 ml) added slowly. The orange powder which formed was collected, washed with hexane (10 ml), and dried in vacuo (0.78 g, 92%), dec 108-112°.

(Dicarbonyl)(η^5-cyclopentadienyl)(nitrato)iron(II). A mixture of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ (2.5 g, 8.22 mmol) and $AgNO_3$ (1.50 g, 8.82 mmol) was stirred in CH_2Cl_2 (75 ml) for 6 h. The solution was filtered using large quantities of filter aid. The filtrate was concentrated to 15 ml and hexane (15 ml) added slowly. The red-orange needles which formed were collected, washed with 10 ml of hexane, and dried in vacuo (1.96 g, 64%), mp 97-98°. (Found: C, 35.38; H, 2.11; N, 5.86. $C_7H_5FeNO_5$ calcd: C, 35.14; H, 2.09; N, 5.85).

Preparation of Olefin Complexes Using Boron Trifluoride. Boron trifluoride was bubbled into a methylene chloride solution (70 ml) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(THF)]BF_4$ (1.5 g, 4.46 mmol) and a three-fold excess of the olefin. The addition of boron trifluoride was stopped after the color of the solution changed from the red color of the starting material to the yellow color of the olefin complexes (ca. 4-5 min). The solvent was then evaporated, the residue extracted with CH_2Cl_2 (80 ml), and this solution filtered. The filtrate was concentrated to 20 ml and hexane (30 ml) added. The yellow crystals which formed were collected, washed with hexane (10 ml) and dried in vacuo. Yields are given in the Table. Characterization of these complexes was the same as outlined above for the thermal reactions. This reaction is not successful for norbornadiene because the BF_3 causes the olefin to polymerize.

(Carbonyl)(η^5-cyclopentadienyl)(tetrahydrofuran)(triphenylphosphine)-iron(II)Tetrafluoroborate. A mixture of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(I)$ (2.0 g, 3.71 mmol) and $AgBF_4$ (0.80 g, 4.10 mmol) was stirred in THF (25 ml) for 10 min. The solvent was evaporated, the residue extracted with chloroform (50 ml), and this solution filtered using filter aid. The filtrate was concentrated to 25 ml and hexane (40 ml) added to precipitate green crystals. The crystals then were collected, washed with hexane (15 ml), and dried in vacuo (1.70 g, 80%), dec starts 105° followed by melting at 108°. (Found: C, 58.73; H, 4.87. $C_{28}H_{28}BF_4FeO_2P$ calcd: C, 58.94; H, 4.91). ^1H NMR spectrum (δ (ppm) in acetone-d_6): 7.60 (15, multiplet, $P(C_6H_5)_3$), 5.06 (5, singlet, η^5-C_5H_5), 3.64 (4, multiplet, OCH_2), 1.80 (4, multiplet, CH_2). IR spectrum (cm^{-1} in $CHCl_3$): ν (CO) 1987.

Results

The complex [Fp-(THF)]BF_4 (1) is prepared from Fp-I and $AgBF_4$ in THF and can be crystallized in over 90% yield from CH_2Cl_2-hexane This red solid can be handled for short period in air, but must be stored with the exclusion of water as it is hygroscopic.

Good Lewis bases such as triphenylphosphine and aniline react nearly quantitatively with 1 in either THF or CH_2Cl_2 to yield [Fp-L]BF_4 derivatives. Because these Lewis bases react with 1 in THF, isolation of 1 is not necessary for the preparation of these complexes. The ligand can be added directly to the THF solution of 1 prepared in situ from Fp-I and $AgBF_4$ and the products isolated in ca. 80% yields.

In contrast, the key to isolation of η^2-olefin adducts is to carry out reactions in CH_2Cl_2. Thus, reactions of 1 with two or three equivalents of fairly strongly coordinating olefins in CH_2Cl_2 yields [Fp-(η^2-olefin)]BF_4 complexes in high yield (see the Table). For 1,5-cyclooctadiene and ethene, the reaction proceeds in a few hours at room temperature. For the preparation of 1,4-cyclohexadiene, cycloheptene and norbornadiene complexes, the CH_2Cl_2 solution is refluxed for a few hours. Cyclohexene does not react well with 1 and even using 14 equivalents of the olefin only the 17% yield shown in the Table was realized of pure material. The cyclohexene complex can be isolated in 60% yield with a contamination of

Table. Yields and ^{13}C NMR Spectra of $[Fp(\eta^2\text{-olefin})]BF_4$

Olefin	Yields from Thermal reaction(%)	Yields from BF_3 reaction(%)	^{13}C NMR resonances of olefin[a] η^2-alkene	free alkene	other
cycloheptene	75	99	80.0	--	32.4,30.5,26.4
ethene	92	--	56.9[b]	--	--
cyclohexene	17	92	82.7	--	26.1,20.3
1,4-cyclohexadiene	80	98	80.2	123.9	26.6
1,5-cyclooctadiene	78	86	82.3	129.6	31.1,30.5
norbornadiene	89	--	86.9	144.2	57.2,48.6

[a] proton decoupled in CH_2Cl_2 reported in ppm from TMS

[b] published value in nitromethane d^3 [8].

15% of starting material. None of these olefin ligands will displace the THF from 1 in THF solution. The olefin complexes can be prepared without isolation of 1 by mixing Fp-I and $AgBF_4$ in THF for a few minutes followed by evaporation of the THF to yield a residue containing 1. This residue can then be redissolved in CH_2Cl_2 and treated with the olefin to produce yields analogous to the two step procedure of first isolating 1 followed by reaction with olefin. The known complex $[Fp\text{-}(NO_3)]$ [7] was prepared and was shown to react with triphenylphosphine but would not react with olefins.

The yields of these reactions can be improved if the initial mixture of 1 and the olefin in CH_2Cl_2 is treated with gaseous BF_3. In this case, the reactions are immediate at room temperature. The products can be worked up as in the thermal reactions after evaporation of the solvent. Yields are shown in the Table. Particularly striking is the improvement of the yield for the cyclohexene complex from 17% to 92%.

Reaction of 1 with cyclooctatetraene in refluxing CH_2Cl_2 yields $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_8H_8)]BF_4$. The $[Fp\text{-}(\eta^2\text{-}C_8H_8)]^+$ complex has recently been prepared and was reported to be unstable above 0°C in nitromethane [1b].

As with the η^2-C_8H_8 complex, this new cyclooctatetraene complex is not fluxional at 35°C. Decomposition in solutions much above 50°C prevented a high temperature NMR experiment.

All of the Fp adducts are known and their complete characterization has recently been reported [1b]. We have observed, in addition, that cyclohexene is displaced by an acetone molecule from the [Fp-(η^2-cyclohexene)]BF_4 complex in acetone in 1.5 hours at 35°C. The THF is also displaced rapidly from 1 by acetone.

The complex [(η^5-C_5H_5)Fe(CO)(PPh_3)(THF)]BF_4 was prepared from the reaction of (η^5-C_5H_5)Fe(CO)(PPh_3)I and $AgBF_4$ in THF. This complex will react with ethene in CH_2Cl_2 to produce the known complex [(η^5-C_5H_5)Fe(CO)(PPh_3)(η^2-C_2H_4)]BF_4, but does not yield stable olefin complexes with the other olefins used here.

Discussion

The thermal reaction of [Fp-(THF)]BF_4(1) with olefins in CH_2Cl_2 is a very good preparative route to [Fp-(η^2-olefin)]BF_4 complexes and is thus complementary to the other known routes of preparing these complexes [1b,f,5]. Yields are high for all but one of the olefins listed in the Table, the reactions are straightforward to run, and the reaction conditions are mild. The one exception is the cyclohexene complex which does not form in high yield even if excess cyclohexene is used in the reaction.

A possible explanation for the low yield with cyclohexene is that the THF which is displaced from 1 by the olefin can react with the [Fp-(η^2-cyclohexene)]$^+$ complex which forms to convert it back into starting material. NMR experiments demonstrate that both THF and cyclohexene are displaced by acetone rapidly when dissolved in acetone. To alleviate this problem, gaseous BF_3 was bubbled into the CH_2Cl_2 solution containing 1 and cyclohexene in order to complex the THF as the well known BF_3-THF adduct. Under these conditions, the reaction is immediate and the yield of the cyclohexene complex was improved from 17% to 92%. Although already high, the yields in reactions with the other olefins are also improved using these reaction conditions (see the Table). This modification of the reaction conditions is not useful for norbornadiene because BF_3 polymerizes the olefin. All of the reactions in the presence of BF_3 are much more rapid than the thermal reactions, so it is probable that the BF_3 influences the reaction to a greater extent than simply to complex the THF produced in the reaction of 1 with olefin. The success of this set of reaction conditions makes 1 a very attractive reagent for the preparation of $[Fp-(\eta^2\text{-ligand})]^+$ complexes where the η^2-ligand is not a particularly good ligand for this system and will not react itself with BF_3. Efforts are underway at present to make new complexes with ligands of this type.

The $[Fp-(\eta^2\text{-olefin})]BF_4$ complexes reported here have been characterized by previous workers [1b, 5]. The reaction of 1 with cyclooctatetraene in refluxing CH_2Cl_2 did not yield the known, unstable [1b] η^2-complex, but instead yielded $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_8H_8)]BF_4$. This molecule was shown not to be fluxional at 35° and decomposed at higher temperatures. Although not previously reported, proton decoupled ^{13}C NMR spectroscopy has proven to be very useful in the characterization of these complexes (see Table). The ^1H NMR spectra are generally not well defined, especially in the olefin region. On the other hand, identification of these complexes from ^{13}C spectra is straightforward. A good example is the new $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_8H_8)]BF_4$ complex. The ^{13}C NMR spectrum of this complex has three resonances around 100 ppm deshielded from TMS for the six metal-coordinated olefin carbons and a resonance at 133.2 for the uncoordinated olefin carbons. A clear interpretation of this type was not possible from the ^1H NMR.

The complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(THF)]BF_4$ was prepared analogously to 1, but was not a useful reagent for the preparation of η^2-olefin complexes other than for ethene. The explanation for this is apparently that the other η^2-olefin complexes are not stable. This THF adduct is, however, useful in reactions with weak nucleophiles such as CH_2PPh_3 as is compound 1 [9].

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