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A Convenient Synthesis of Cationic Vinylidene and 1,2-Propadienylidene Iron Complexes by Photoreaction of $[CpFe(CO)(dppe)]^+BF_4^-$ with 1-Alkynes

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Synopsis. Photoreaction of $[CpFe(CO)(dppe)]^+BF_4^-$ with 1-alkynes proceeded to give cationic vinylidene and 1,2-propadienylidene iron complexes in good yields.

There has been considerable interest in the chemistry of unsaturated carbene iron complexes such as vinylidene and 1,2-propadienylidene complexes which are useful intermediates in organic transformations.[1] Several routes for the preparation of the complexes are now available. Among them, CpFe(dppe)X (dppe=1,2-bis(diphenylphosphino)ethane, X=Cl and Br) have been employed as reagents for the preparation of cationic vinylidene iron complexes having diphosphine as a ligand.[2,3] CpFe(dppe)X are, however, air sensitive compounds and can not be obtained in satisfactory yields.[4,5] In contrast to CpFe(dppe)X, $[CpFe(CO)(dppe)]^+BF_4^-$ is air-stable and also can be prepared as pure crystals in good yield. We now report here a convenient synthesis of cationic vinylidene and 1,2-propadienylidene iron complexes by photoreaction of cationic carbonyl iron complex $[CpFe(CO)(dppe)]^+BF_4^-$ **1** with 1-alkynes.

Experimental

Nuclear magnetic resonance spectra were taken on a JEOR JNM-GX 270 FT-NMR spectrometer. IR spectra (KBr tablets) were measured with a JASCO FT-IR 5000 spectrometer.

Materials. $CpFe(CO)_2X$ (X=Cl, Br, I) were synthesized by the usual methods.[6] Other reagents employed were either commercially available or synthesized by the usual methods.

$[CpFe(CO)(dppe)]^+X^-$ (1a—c, 1a; X=Cl, 1b; X=Br, 1c; X=I): A mixture of $CpFe(CO)_2X$ (10 mmol) and dppe (11 mmol) and toluene (50 ml) was heated at 110 °C for 0.5—8 h under argon. Crystalline precipitates were collected by filtration. The yields were 96% for **1a**, 81% for **1b**, and 77% for **1c**. These products were sufficiently pure for most purposes.

$[CpFe(CO)(dppe)]^+BF_4^-$: (1d). To a mixture of **1a**—**c** (8.0 mmol) and methanol (40 ml) was added with vigorous stirring a solution of $NaBF_4$ (40 mmol) in 40 ml of water-methanol (1 : 4, v/v) at room temperature. The solids precipitated were collected by filtration and were rinsed with aqueous methanol and then with diethyl ether. Recrystallization of the solids from dichloromethane-hexane gave **1d** as pale yellow crystals in 71—78% yields.

General Procedure for the Preparation of Vinylidene and 1,2-Propadienylidene Iron Complexes: A solution of **1d** (1.0 mmol) and 1-alkyne (1.2 mmol) in CH_2Cl_2 (40 ml) was irradiated with high-pressure UV-lamp (>280 nm) under argon for 12 h. After evaporation of the solvent in vacuo, recrystallization of the crystalline residue from dichloromethane-diethyl ether afforded iron complexes in pure form.

Properties of the compounds obtained are as follows:

For **2a;** mp 85 °C (decomp), IR (KBr) 1630 cm^{-1} ($\nu_{C=C}$), ^1H NMR $\delta=7.20—8.00$ (20H, m, Ph), 5.02 (5H, s, Cp), 3.97 (2H, t, $J_{HP}=3.1$ Hz, CH_2), 3.04—3.18 (4H, m, PCH_2). ^{13}C NMR$\{^1H\}$ $\delta=354.7$ (t, $J_{CP}=35.2$ Hz, Fe=C), 128.9—136.2 (m, Ph), 107.1 ($\underline{C}$=C=Fe), 89.1 (Cp), 28.7 (t, $J_{CP}=23.3$ Hz, PCH_2). Found: C, 62.16; H, 4.88%. Calcd for $C_{33}H_{31}BF_4P_2Fe$: C, 62.27; H, 4.94%.

For **2b;** mp 121 °C (decomp), IR (KBr) 1660 cm^{-1} ($\nu_{C=C}$), ^1H NMR $\delta=7.14—7.80$ (20H, m, Ph), 5.02 (5H, s, Cp), 4.19—4.31 (1H, m, =CH), 2.97—3.12 (4H, m, PCH_2), 1.15—1.23 (2H, m, CH_2), 0.78—0.96 (2H, m, CH_2), 0.55 (3H, t, $J=7.2$ Hz, CH_3). ^{13}C NMR$\{^1H\}$ $\delta=356.2$ (t, $J_{CP}=33.5$ Hz, Fe=C), 123.2—136.6 (m, Ph, =C), 88.5 (Cp), 28.4 (t, $J_{CP}=23.5$ Hz, PCH_2), 24.2, 22.9, 13.2 (C_3H_7). Found: C, 64.37; H, 5.65%. Calcd for $C_{36}H_{37}BF_4P_2Fe$: C, 64.13; H, 5.53%.

For **2c;** mp 150 °C (decomp), IR (KBr) 1662 cm^{-1} ($\nu_{C=C}$), ^1H NMR $\delta=7.08—7.80$ (25H, m, Ph), 5.28 (1H, s, CH=), 5.02 (5H, s, Cp), 2.75—3.38 (4H, m, PCH_2). ^{13}C NMR$\{^1H\}$ $\delta=364.0$ (t, $J_{CP}=33.3$ Hz, Fe=C), 124.3—136.8 (m, Ph, =C), 89.1 (Cp), 27.6 (t, $J_{CP}=23.4$ Hz, PCH_2). Found: C, 66.37; H, 5.02%. Calcd for $C_{39}H_{35}BF_4P_2Fe$: C, 66.13; H, 4.98%.

For **2d;** mp 140 °C (decomp), IR (KBr) 3052 (ν_{OH}), 1662 cm^{-1} ($\nu_{C=C}$), ^1H NMR $\delta=6.97—7.90$ (20H, m, Ph), 5.08 (5H, s, Cp), 4.62—4.74 (1H, m, =CH), 3.90 (2H, d, $J=7.9$ Hz, CH_2O) 2.89—3.15 (4H, m, PCH_2). ^{13}C NMR$\{^1H\}$ $\delta=355.0$ (t, $J_{CP}=33.3$ Hz, Fe=C), 124.3—136.8 (m, Ph, =C), 89.0 (Cp), 53.5 (CH_2), 28.4 (t, $J_{CP}=23.3$ Hz, PCH_2). Found: C, 61.65; H, 5.25%. Calcd for $C_{34}H_{33}BOF_4P_2Fe$: C, 61.67; H, 5.02%.

For **2e;** mp 140 °C (decomp), IR (KBr) 1652 cm^{-1} ($\nu_{C=C}$), ^1H NMR $\delta=6.64—7.70$ (25H, m, Ph), 5.05 (5H, s, Cp), 4.67—4.70 (1H, m, =CH), 3.97 (2H, d, $J=8.5$ Hz, CH_2O), 2.84—3.18 (4H, m, PCH_2). ^{13}C NMR$\{^1H\}$ $\delta=353.1$ (t, $J_{CP}=33.3$ Hz, Fe=C), 115.4—135.9 (m, Ph, =C), 89.3 (Cp), 59.2 (CH_2), 28.6 (t, $J_{CP}=23.2$ Hz, PCH_2). Found: C, 65.11; H, 5.15%. Calcd for $C_{40}H_{37}BOF_4P_2Fe$: C, 65.07; H, 5.05%.

For **2f;** mp 115 °C (decomp), IR (KBr) 1654 cm^{-1} ($\nu_{C=C}$), ^1H NMR $\delta=7.00—8.00$ (20H, m, Ph), 5.13 (5H, s, Cp), 4.52—4.64 (1H, m, =CH), 3.48 (2H, d, $J=7.3$ Hz, CH_2O), 2.94—3.20 (4H, m, PCH_2), −0.04 (9H, s, $SiCH_3$). ^{13}C NMR$\{^1H\}$ $\delta=353.4$ (t, $J_{CP}=33.3$ Hz, Fe=C), 124.3—136.3 (m, Ph, =C), 88.8 (Cp), 53.0 (CH_2), 28.2 (t, $J_{CP}=22.5$ Hz, PCH_2), −0.62 ($SiCH_3$). Found: C, 60.37; H, 5.65%. Calcd for $C_{37}H_{41}BOF_4SiP_2Fe$: C, 60.51; H, 5.63%.

For **2g;** mp 105 °C (decomp), IR (KBr) 1730 (ν_{CO}), 1634 cm^{-1} ($\nu_{C=C}$), ^1H NMR $\delta=6.85—8.16$ (20H, m, Ph), 5.11 (5H, s, Cp), 4.40—4.54 (1H, m, =CH), 3.77 (2H, d, $J=8.6$ Hz, CH_2O), 2.95—3.20 (4H, m, PCH_2), 1.92 (3H, s, CH_3). ^{13}C NMR$\{^1H\}$ $\delta=353.8$ (t, $J_{CP}=33.5$ Hz, Fe=C), 170.5 (CO), 128.5—137.5 (m, Ph, =C), 89.3 (Cp), 55.5 (CH_2O), 28.4 (t, $J_{CP}=22.5$ Hz, PCH_2), 20.9 (CH_3). Found: C, 61.37; H, 5.35%. Calcd for $C_{36}H_{35}BO_2F_4P_2Fe$: C, 61.40; H, 5.01%.

For **3;** mp 115 °C (decomp), IR (KBr) 1926 cm^{-1} ($\nu_{C=C=C}$), ^1H NMR $\delta=7.02—7.62$ (30H, m, Ph), 5.28 (5H, s, Cp), 2.87—3.00 (4H, m, PCH_2). ^{13}C NMR$\{^1H\}$ $\delta=289.5$ (t, $J_{CP}=37.2$ Hz, Fe=C), 228.4 ($\underline{C}$=C=Fe), 151.6 ($\underline{C}$=C=C=Fe), 123.2—136.6 (m, Ph), 89.8 (Cp), 29.1 (t, $J_{CP}=22.5$ Hz, PCH_2). Found: C, 69.55; H, 4.78%. Calcd for $C_{46}H_{39}BF_4P_2Fe$: C, 69.37; H, 4.94%.

Results and Discussion

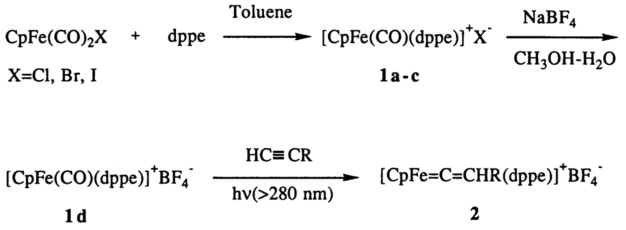
Cationic carbonyl iron complexes **1** have been prepared generally by the reaction of $CpFe(CO)_2X$ with dppe. However, the formation of **1** depends distinctly on the reaction conditions.[4-8] We have found that **1d**

Table 1. Formation of Cationic Vinylidene Carbene Iron Complexes **2**[a)]

Complex **1**	HC≡CR R	Solvent	Yield of **2**/%[b)]	
$[CpFe(CO)(dppe)]^+BF_4^-$	H	CH_2Cl_2	**2a**	40
	C_3H_7	CH_2Cl_2	**2b**	96
	C_3H_7	CH_3OH	**2b**	94
	C_3H_7	CH_3COCH_3	**2b**	84
	C_3H_7	$ClCH_2CH_2Cl$	**2b**	88
	C_3H_7	C_6H_6	**2b**	0
	C_6H_5	CH_2Cl_2	**2c**	90
	CH_2OH	CH_2Cl_2	**2d**	85
	CH_2OPh	CH_2Cl_2	**2e**	90
	$CH_2OSi(CH_3)_3$	CH_2Cl_2	**2f**	80
	CH_2OCOCH_3	CH_2Cl_2	**2g**	70
	$Si(CH_3)_3$	CH_2Cl_2	**2a**[c)]	65
$[CpFe(CO)(dppe)]^+BPh_4^-$	C_3H_7	CH_2Cl_2	**2h**	94
$[CpFe(CO)(dppe)]^+ClO_4^-$	C_3H_7	CH_2Cl_2	**2i**	95
$[CpFe(CO)(dppe)]^+X^-$ X=Cl, Br, I	C_3H_7	CH_2Cl_2	**2b**	0

a) Irradiated for 12 h at room temperature. b) Isolated yields. c) Trimethylsilyl group was replaced by hydrogen (R=H).

was conveniently synthesized in high yields by heating a toluene solution containing $CpFe(CO)_2X$ and dppe, followed by metathesis reaction.



$$CpFe(CO)_2X + dppe \xrightarrow{Toluene} [CpFe(CO)(dppe)]^+X^- \xrightarrow[CH_3OH\text{-}H_2O]{NaBF_4}$$

X=Cl, Br, I; **1a-c**

$$[CpFe(CO)(dppe)]^+BF_4^- \xrightarrow[h\nu(>280\ nm)]{HC\equiv CR} [CpFe{=}C{=}CHR(dppe)]^+BF_4^-$$

1d; **2**

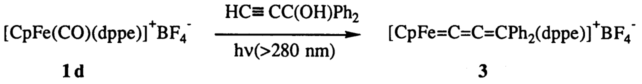
Scheme 1.

Cationic vinylidene iron complexes **2** were prepared in good yields upon irradiation of dichloromethane solution of **1d** and 1-alkynes. The results are summarized in Table 1.

Characteristics of this reaction are as follows: 1) The reaction is applied for 1-alkynes and their aryl derivatives having functional groups such as hydroxyl, siloxyl, carbonyl, and aryloxyl groups. 2) Other solvents such as methanol, acetone, and 1,2-dichloroethane can be employed, but benzene and diethyl ether are not suitable because of the insolubility of **1d**. The reaction did not proceed in acetonitrile solutions, but resulted in replacement of CO with acetonitrile. 3) Complexes **2** were also obtained when tetraphenylborate and perchlorate salts of **1** were used as the starting materials. No complex **2** was formed by use of **1a**—**c**. 4) The reaction of 1-alkyne with $[CpFe(CO)_2(PPh_3)]^+BF^-$ and $[CpFe(CO)(dppf)]^+BF_4^-$ (dppf=1,1′-bis(diphenylphosphino)ferrocene) did not give the corresponding cationic vinylidene iron complexes under the same reaction conditions. 5) UV-irradiation is essential for the reaction.

It is noticed here that the present reaction is a simple and useful method for the preparation of cationic vinylidene iron complexes because **1d** can be easily prepared in a good yield and also is air stable in contrast to CpFe(dppe)X.[2)]

Similar treatment of **1d** with 1,1-diphenyl-2-propyn-1-ol afforded cationic 3,3-diphenyl-1,2-propadienylidene iron complex **3** in 77% yield. However, the reaction of **1d** with 2-methyl-3-butyn-2-ol and 1-ethynylcyclohexanol gave complex products, giving no corresponding 1,2-propadienylidene iron complexes.



$$[CpFe(CO)(dppe)]^+BF_4^- \xrightarrow[h\nu(>280\ nm)]{HC\equiv CC(OH)Ph_2} [CpFe{=}C{=}C{=}CPh_2(dppe)]^+BF_4^-$$

1d; **3**

Scheme 2.

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