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NEW COMPLEXES [CpFe(DPPE)THIOPHENES]PF_6

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Abstract—The reactions of CpFe(dppe)I with thiophenes in the presence of $TlPF_6$ afforded the new complexes [CpFe(dppe)thiophenes]PF_6 (thiophenes = thiophene, 2-methyl-thiophene, 3-methyl-thiophene, 2,5-dimethyl-thiophene, benzothiophene and dibenzothiophene). They were characterized by elemental analysis, IR, ^1H, ^{31}P and ^{13}C NMR as well as by UV–visible spectroscopic methods. Substitution of coordinated thiophenes in [CpFe(dppe)thiophene]PF_6 complexes by neutral ligands occurs in mild conditions. Copyright © 1996 Elsevier Science Ltd

Hydrodesulfurization and hydroliquefaction are two essential steps in the effective utilization of abundant, sulfur-rich coal.[1] These reactions are catalysed by a variety of metal compounds, usually heterogeneously.[2] Several organometallic compounds are effective in the hydrodesulfurization activity with coal and coal model compounds. A point of central importance to the mechanism(s) of thiophenes hydrodesulfurization (HDS) on heterogeneous catalysts is the mode of thiophene adsorption and activation on a metal site. Of the several known modes of thiophene coordination (see Fig. 1) in transition metal complexes, the S- and η^5-bound forms are most often suggested for thiophene adsorption to catalyst surfaces. While there is much evidence to support η^5-coordination and activation of thiophene in organometallic complexes and on catalysts there is little such evidence for the S-bonded form.

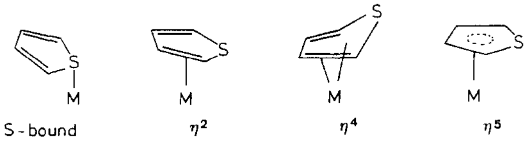

Fig. 1. Most unusual types of thiophene binding in mononuclear transition metal complexes.

Thus, the only known S-bound thiophene complexes are: $Ru(NH_3)_5T^{2+}$[3] (T = thiophenes), [CpFe(CO)$_2$(T)]BF_4,[4,5] CpFe(NCMe)$_2$(2,5-Me$_2$T)$^+$, [6]W(CO$_2$)$_3$(PCy$_3$)(T),[7] [CpRu(PMe$_3$]$_2$ η^1-(S)-BT]PF_6,[8] Cp*MCl$_2$[η^1-(S)-DBT], M = Ir and Rh,[9] Cp*(CO)$_2$Ru(T),[10] Cp(CO)(PPh$_3$)Ru(T)[11] and ($C_5H_4CH_2C_4H_3S$) Ru (PPh$_3$)$_2^+$,[12] in which thiophene is part of a chelate ligand. Other thiophene-containing complexes have been recently reported.[13] The thiophene is very weakly coordinated and easily displaced. This suggests that it would also be weakly coordinated to a site on a catalyst. However, the most stable Cp*(CO)$_2$Re(T) complexes have been prepared.[14] Thus, temperature-programmed desorption studies and vibrational spectroscopy under ultrahigh vacuum have shown that thiophene binds to Mo(100) surfaces in both η^1,S- and η^5-modes.[15] Thiophene also binds to Pt^{III} in both η^1,S- and η^5-manners.[16,17]

Recently, we have reported the preparation of a series of complexes [CpFe(dppe)L]PF_6, dppe = $Ph_2P(CH_2)_2PPh_2$ (L = neutral donor ligand including some sulfur ligands).[18]

Now we report the preparation and characterization of the new thiophene complexes [CpFe(dppe)(thiophenes)]PF_6 and their substitution reactions.

RESULTS AND DISCUSSION

Reaction of CpFe(dppe)I with the thiophene ligands in the presence of $TlPF_6$ as halide abstractor

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and in CH_2Cl_2 as solvent afforded the cationic complexes [CpFe(dppe)(thiophene)]PF_6 according to:

$$\text{CpFe(dppe)I} + \text{thiophene} \xrightarrow[CH_2Cl_2]{TlPF_6} [\text{CpFe(dppe)(thiophene)}]PF_6 + \text{TlI} \quad (1)$$

	Thiophene	Complex
T	thiophene (T)	**1**
2-MeT	2-methylthiophene (2-MeT)	**2**
3-MeT	3-methylthiophene	**3**
2,5-Me_2T	2,5-dimethylthiophene	**4**
BT	benzothiophene	**5**
DBT	dibenzothiophene	**6**

The complexes [CpFe(dppe)(thiophenes)]PF_6 are red–brown to orange solids, moderately stable to the air but in solution decompose slowly. The compounds were characterized by elemental analysis and spectroscopic methods. The IR spectra shows the characteristic bands of the CpFe(dppe)$^+$ moiety,[19] as well as the band centred at 840 cm^{-1}, corresponding to the $\nu(PF_6)$ vibration. However the vibrations of the thiophenes[20] were not observed, because they are masked by the bands of the CpFe(dppe)$^+$ fragment. The ^1H NMR spectra of the complexes show the expected signal of Cp(4,2-4,8 ppm), C_6H_5 and $P(CH_2)_2P$ of the dppe group; these latter, however, mask the signal of thiophene ligands. Data are displayed in Table 1. Unequivocal identification of the sulfur-coordinated thiophenes ligands was achieved by ^{13}C NMR spectroscopy. Table 2 shows the ^{13}C NMR data for complexes **1**–**6**. From the spectra, in addition to the signals of dppe and C_5H_5, the typical signals of sulfur-coordinated thiophene ligands were observed. To aid in the analysis of the spectra as well as for comparison purpose, the ^{13}C NMR spectra of the free thiophene ligands are included in Table 3. Chemical shift data for **1**–**6** are similar to those found for similar η^1(S)-thiophene,[4,10,11] η^1(S) methylthiophenes,[10,11] η^1(S)-benzothiophene[4,8] and η^1-(S)-dibenzothiophene complexes.[4,9]

The ^{31}P NMR spectra of **1**–**6** exhibit the usual doublet in the range 93–90 ppm, typical of η^2-dppe coordinated to a CpFe moiety.[18]

The expected septet corresponding to PF_6^- was observed in the normal range.[19] Data are displayed in Table 1. The visible absorption spectra of the complexes also confirm the sulfur coordination of the thiophene ligands towards the iron fragment. In fact, the spectra of **1**–**6** show one band near 450 nm, which was assigned according to recent UV–vis studies[21] to a *d*–*d* transition.

Substitution of thiophenes

Previous studies[10,12] have shown that thiophenes are very weak ligands and are also easily displaced by other ligands. We found that thiophenes are displaced by CH_3CN or $P(n\text{-}Bu)_3$ under mild conditions from **5** to give the known complexes

Table 1. ^1H and ^{31}P NMR data for the complexes

	^1H-NMR				^{31}P-NMR	
Compound	Cp	$(CH_2)_2P$	C_6H_5	CH_3 (ligand)	dppe	PF_6
1[a]	4.76	2.45 2.65	7–8		92.41	−138.8
2[a]	4.47	2.4 2.70	7–8	2.46	92.50	−138.8
3[b]	4.22		7–7.5	1.34	91.6 (d)	−141.9
4[b]	4.56	1.97 1.62	6–8	1.25	90.3 (d)	−142.2
5[a]	4.47	2.46 2.67	7.1–7.8		92.86 (d)	−139.0
6[b]	4.35	2.30 1.54	7.0–7.7		92.26 (d)	−142.2

[a] Acetone-d_6 solution.

[b] CD_2Cl_2 solution. Other ligand signals are masked by C_6H_5 protons (see text). Multiplet signals at 7.96, 7.89 and 7.37–7.31 corresponding to benzothiophene were also observed Multiplet signals at 8.08, 7.77 and 7.37 p.p. corresponding to dibenzothiophene were observed.

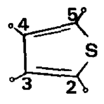
Table 2. ^{13}C NMR for the thiophene complexes **1–6**

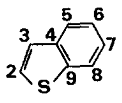
	C_2	C_3	C_4	C_5
1	137.95	137.04	137.04	137.95
2	127.35	125.44	124.89	138.08
3	127.60	125.76	123.69	138.37
4	137.96	125.37	125.37	137.96
	CH_3	C_6H_5	$P(CH_2)_2$	C_5H_5
1		129.2–132.6		80.25
2	15.25	128.8–132.8	26.2	80.36
3	15.38	129.24–133.04	26.46	80.57
4	15.72	128.98–133.42	25.25	80.21
	C_2	C_3	C_4	C_5
5	140.12	126.76	124.58	123.99
	C_6	C_7	C_8	C_9
	124.99	126.76	124.62	140.04
		C_6H_5	$P(CH_2)_2$	C_5H_5
		128.75–134.75	26.25	80.07
	C_1	C_2	C_3	C_4
6	123.24	124.09	127.25	136.01
	C_5	C_6	C_7	C_8
	139.34	136.01	127.27	124.09
	C_9	C_{10}	C_{11}	C_{12}
	123.24	122.08	139.88	139.88
		C_6H_5	$P(CH_2)_2$	C_5H_5
		128.99–132.78	26.2	80.24

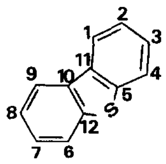
Table 3. ^{13}C NMR for free thiophene ligands[a]

	C_2	C_3	C_4	C_5	CH_3
Thiophene	127.21	125.41	125.41	127.21	—
2-Methylthiophene	126.81	125.05	122.96	139.50	15.0
3-Methylthiophene	129.91	125.94	121.28	138.05	16.0
1,5-Dimethylthiophene	137.68	125.11	125.11	137.68	15.51
	C_2	C_3	C_4	C_5	C_6
Benzothiophene	140.21	126.24	124.56	124.03	123.94
	C_7	C_8	C_9		
	124.25	124.66	140.07		
	C_1	C_2	C_3	C_4	C_5
Dibenzothiophene	122.67	124.22	126.56	124.56	139.34
	C_6	C_7	C_8	C_9	C_{10}
	135.45	126.56	124.22	122.67	121.46
	C_{11}	C_{12}			
	121.46	139.34			

[a] In $CHCl_3$.







$[CpFe(dppe)CH_3CN]PF_6$[22] and $[CpFe(dppe)P(Bu\text{-}n)]_3PF_6$,[18] respectively:

$$[CpFe(dppe)thiophene]PF_6 + L \rightarrow [CpFe(dppe)(L)]PF_6 + thiophene, \quad L = CH_3CN, P(Bu\text{-}n)_3 \quad (2)$$

A detailed substitution study of several reactions:

$$MLn(T) + L' \rightarrow MLn\,L' + T \quad (3)$$

have been recently reported;[10–12] however, we have not made kinetic or quantitative studies on these reactions.

Attempted hydrogenation of thiophenes

Attempts to hydrogenate thiophenes by the fragment $CpFe(dppe)^+$ under mild conditions led to the complex $[CpFe(dppe)thiophene]PF_6$, instead of the expected hydrogenolysis products.[23] Studies of the hydrosulfurization of thiophenes by $CpFe(dppe)^+$ in more drastic conditions are in course.

EXPERIMENTAL

All operations and routine manipulations were performed under nitrogen or argon on a high-vacuum line using modified Schlenk techniques. Solvents were purified by standard methods. CpFe(dppe)I was prepared as previously reported.[22] Thiophenes were obtained from Aldrich Chemical Co. and were used as received.

The ^1H, ^{31}P and ^{13}C NMR spectra were recorded on a Bruker AMX 300 instrument. Chemical shifts are given in δ relative to TMS (^1H or ^{13}C) or 85% H_3PO_4 (^{31}P proton decoupled) downfield positive to the reference. IR spectra were recorded on a Perkin–Elmer 2000 FT-IR spectrophotometer. Visible absorption spectra were measured on a Varian DMS-90 spectrophotometer in 1 cm length cuvettes.

Preparation of the complexes

$[CpFe(dppe)T]PF_6$. The complex CpFe(dppe)I (0.15 g, 0.23 mmol) was placed in a Schlenk with thiophene (1 cm^3 1.05 g, 11.8 mmol) and in the presence of $TlPF_6$ (0.16 g, 0.45 mmol). A total of 20 cm^3 of CH_2Cl_2 was added and the reaction mixture was stirred for 20 h at room temperature. After this, the solution initially black changed to red–brown and the yellow TlI precipitate was formed. The solution was filtered through kielselguhr and concentrated to 5 cm^3 *in vacuo*. A 1 : 10 n-hexane diethylether mixture was slowly added to precipitate an orange–brown solid. The mother liquor was removed *via* cannula and the solid was washed twice with the same n-hexane–ether mixture. The dried orange–brown solid gave 0.11 g product (63% yield). Found: C, 55.7; H, 4.6. Calc. for $C_{36}H_{33}F_6P_3SFe$: C, 56.2; H, 4.4%. IR (KBr): 3050 (w), 2960 (w), 2920 (w), 1480 (m), 1430 (s), 1180 (m), 1092 (m), 1020 (m), 995 (m), 830 (s), 738 (s), 689 (s), 555 (s), 532 (s).

$[CpFe(dppe)2\text{-}MeT]PF_6$. The complex CpFe (dppe)I (0.15 g, 0.23 mmol) and 2-methylthiophene (1 cm^3, 1.01 g, 10.2 mmol) together with $TlPF_6$ (0.16 g, 0.45 mmol) were stirred in a Schlenk flask with CH_2Cl_2 (25 cm^3) at room temperature. After 20 h and with a separation and purification similar to that for complex **1**, an orange solid was obtained (0.09 g, yield 50%). Found: C, 57.2; H, 4.5. Calc. for $C_{36}H_{35}F_6P_3SFe$: C, 56.7; H, 4.6%. IR (KBr) 3058 (w), 2960 (w), 2920 (w) 1482 (m), 1434 (vs), 1300 (w), 1358 (w), 1185 (w), 1095 (vs), 1025 (w), 998 (s) 835 (vs), 746 (vs), 693 (vs), 685 (w), 558 (s), 538 (s).

$[CpFe(dppe)\ 3\text{-}MeT]PF_6$. To a solution of CpFe(dppe)I (1.15 g, 0.23 mmol) and $TlPF_6$ (0.16 g, 0.45 mmol) in CH_2Cl_2 (20 cm^3) was added 3-methylthiophene (1 cm^3, 1.016 g, 10.3 mmol). The reaction was stirred at room temperature for 18 h as the solution gradually turned red–brown. Separation and purification similar to **1** afforded 0.1 g (56%) of an orange–brown solid. Found: C, 57.8; H, 4.6. Calc. for $C_{36}H_{35}F_6P_3SFe$: C, 56.7; H, 4.6%. IR (KBr) 3050 (w) 2960(w), 2930 (w), 1490 (m), 1440 (vs), 1300 (w), 1160 (m), 1180 (w), 1097 (m), 998 (m), 841 (vs), 750 (s), 698 (vs), 560 (vs), 540 (vs).

$[CpFe(dppe)\ (2,5\text{-}Me_2T)PF_6$. To a stirred solution of CpFe(dppe)I (0.15 g, 0.23 mmol) and $TlPF_6$ (0.16 g, 0.45 mmol) in CH_2Cl_2 (20 cm^3) was added 2,5-dimethyl-thiophene (1 cm^3, 0.98 g, 8.7 mmol). After 18 h the solution turned red. Separation and purification procedures similar to that for **1** affords an orange solid, yield 0.12 g, 66%. Found: C, 57.3; H, 4.4. Calc. for $C_{37}H_{37}F_6P_3SFe$: C, 57.2, H, 4.8%. IR (KBr) 3048 (w), 2960 (w) 1480 (m) 1420 (s) 1300 (w) 1250 (w) 1185 (m) 1097 (s) 998 (m) 841 (vs) 760 (s) 698 (vs) 575 (vs) 540 (vs).

$[CpFe(dppe)BT]PF_6$. The compound CpFe (dppe)I (0.15 g, 0.23 mmol) was placed in a Schlenk flask with $TlPF_6$ (0.16 g, 0.45 mmol) and benzothiophene (1 g, 7.45 mmol) in CH_2Cl_2 (15 cm^3). The mixture was stirred for 15 h at room temperature. Then the reaction mixture was filtered through kieselguhr and the solvent was removed *in vacuo*. The red residue was extracted with ether and the solution chromatographed on neutral alumina. The brown eluate was evaporated to dryness to give a pale brown solid which was dried *in vacuo*. Yield 0.15 g (81%). Found: C, 59.7; H, 4.6. Calc. for $C_{39}H_{35}F_6P_3SFe$: C, 58.6; H, 4.4%. IR (KBr) 3055 (w), 2926 (w), 1482 (m) 1457 (s) 1365 (m) 1312 (m) 1179 (w) 1095 (m) 1022 (m) 1000 (m) 838 (vs) 746 (s) 698 (vs) 557 (vs) 524 (vs).

[CpFe(dppe)(DBT)]PF_6. The starting material CpFe(dppe)I (0.15 g, 0.23 mmol) was placed in a Schlenk flask with dibenzothiophene (2 g, 10 mmol) and $TlPF_6$ (0.16 g, 0.45 mmol) in CH_2Cl_2 (25 cm^3). The reaction mixture was stirred for 20 h at room temperature. Separation and purification procedures similar to that for **1** affords a pale brown solid, yield 0.17 g, 86%. Found: C, 60.3; H, 4.3. Calc. for $C_{34}H_{37}F_6P_3SFe$: C, 60.8; H, 4.4%. IR (KBr) 3045 (w) 2920 (w) 1690 (w) 1570 (w) 1460 (m) 1420 (m) 1300 (m) 1220 (s) 1190 (m) 1120 (m) 1097 (s) 998 (m) 841 (vs) 780 (vs) 700 (s) 580 (m) 550 (s).

Attempted catalytic hydrogenation of thiophene

CpFe(dppe)I (0.15 g, 0.23 mmol) and $TlPF_6$ (0.16 g, 0.45 mmol) in CH_2Cl_2 (30 cm^3) were placed in a Schlenk flask and stirred at room temperature for 1 h. The solution changed from black to red. Then thiophene (5 cm^3, 5.25 g, 62 mmol) was added and H_2 was bubbled through the solution for 1 h. The reaction mixture was then filtered through kieselguhr to separate the TlI and H_2 bubbled again through the solution for another 14 h. The solution remained red, so the solvent was evaporated to dryness and the solid washed twice with a n-hexane–ether mixture (1 : 10) and the solid dried under vacuum. The IR spectrum was identical to [CpFe(dppe)thiophene]PF_6.

Reaction of [CpFe(dppe)DBT]PF_6 *with* CH_3CN.

[CpFe(dppe)DBT]PF_6 (0.06 g, 0.07 mmol) was dissolved in CH_3CN and the solution stirred for 5 h at room temperature. After 1 h the solution changed from red–brown to red. The solvent was removed *in vacuo* and the solid washed with diethyl ether and dried *in vacuo*. The compound was identified as [CpFe(dppe)CH_3CN]PF_6 by comparison of their spectroscopic IR, ^1H and ^{31}P NMR data with an authentic sample.[22]

Reaction of [CpFe(dppe)DBT]PF_6 *with* $P(Bu^n)_3$

[CpFe(dppe)DBT]PF_6 (0.08 g, 0.090 mmol) and $P(Bu^n)_3$ (0.5 cm^3, 0.4 g, 2 mmol) in CH_2Cl_2 (20 cm^3) were stirred at room temperature for 3 h. The solution changed from red–brown to red. The solvent was removed *in vacuo* to dryness and the solid residue was twice washed with diethyl ether. The orange–brown compound was identified as [CpFe(dppe)$P(Bu^n)_3$]PF_6 by comparison with an authentic sample.[18]

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