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Ferrocenyl-derived Electrophilic Phosphonium Cations (EPCs) as Lewis Acid Catalysts

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Oxidation of diphenylphosphinoferrocene and 1,1'-*bis*(diphenylphosphino)ferrocene with XeF_2, resulted in the formation of $CpFe(\eta^{5}\text{-}C_5H_4PF_2Ph_2)$ **1** and $Fe(\eta^{5}\text{-}C_5H_4PF_2Ph_2)_2$ **2** respectively. Subsequent reactions with $[SiEt_3][B(C_6F_5)_4]$ yielded $[CpFe(\eta^5\text{–}C_5H_4PFPh_2)][B(C_6F_5)_4]$ **3** and $[Fe(\eta^5\text{-}C_5H_4PFPh_2)_2]$ $[B(C_6F_5)_4]_2$ **4**. $PhP(\eta^5\text{-}C_5H_4)_2Fe$ **5** was prepared, converted to $[PhMeP(\eta^5\text{-}C_5H_4)_2Fe][O_3SCF_3]$ **6** and then to $[PhMeP(\eta^5\text{-}C_5H_4)_2Fe][B(C_6F_5)_4]$ **7**. The ability of the salts **3**, **4** and **7** to catalyze Friedel-Crafts dimerization of 1,1-diphenylethylene, dehydrocoupling of phenol and triethylsilane, and deoxygenation of acetophenone iand hydrodefluorination of 1-fluoropentane were probed. While compound **7** proved to be ineffective, compounds **3** and **4** were useful Lewis acid catalysts. Compounds **3** and **4** were shown to catalyze the deoxygenation of a series of ketones.

Introduction

Main group catalysts have emerged as potentially green alternatives to precious metals species.[1] Indeed main group Lewis acids have been widely used as initiators and catalysts in organic transformations.[2-7] In addition, the advent of the concept of frustrated Lewis pairs (FLPs) from the discovery that such species can activate H_2[8-9] among other small molecules has spurred main group catalyst development over the last 10 years.[10-14] While a variety of main group Lewis acids have been exploited for FLP chemistry and catalysis, the majority of systems studied to date have been based on group 13 (B, Al) or 14 (C, Si) sites.

In seeking to broaden the range of Lewis acids,[15] we noted the interesting findings from several research groups that have explored the Lewis acidity of electron-deficient phosphorus compounds.[16] For example, dicoordinate P(III) phosphenium cations have been shown to exhibit Lewis acid behavior, forming adducts with N-donors.[17-18] Similarly, phosphoranes form Lewis adducts with N-trimethylsilyl imidazole and pyrazole derivatives.[19] In addition phosphenium cations have been shown to activate C-C/H and P-P bonds,[20-22] In our own efforts, we have described the reactions of a triphosphabenzene derivative with H_2 via an intramolecular FLP-type mechanism. Intriguingly the computational studies reveal that this results from the action of a carbanion as the base and a P(III) centre as a Lewis acid.[23] Gabbai and coworkers have exploited the synergistic action of tetracoordinate P(V) phosphonium cations with a B-Lewis acid to capture fluoride ions in sensor applications.[24] Moreover, phosphonium cations have been used to mediate addition to polar unsaturates. [25] Indeed, the classic Wittig reactions in which P-based ylides react with ketones are driven by the electrophilic nature of the P centre.[26-27]

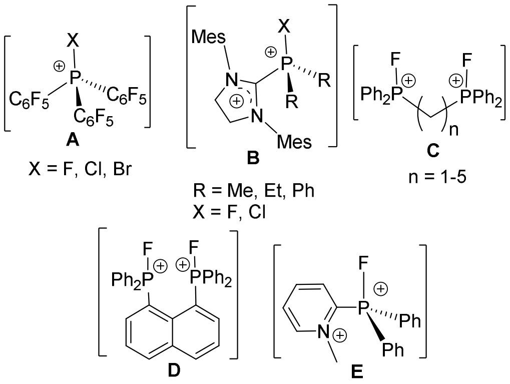

Figure 1. Electrophilic phosphonium cation scaffold types

Our group has recently demonstrated that electrophilic phosphonium cations (EPCs) are strong Lewis acids and can catalyze transformations such as hydrodefluorination of fluoroalkanes,[28-31] hydrosilylation of olefins,[32-33] ketones and imines,[34] transfer hydrogenation[33] and direct hydrogenation of alkenes[35] and deoxygenation of ketones.[36] In these catalysts, the Lewis acidity resides in the σ* orbital and is significantly enhanced by the inclusion of electron-withdrawing substitutents such as C_6F_5 on the phosphorus atom (Figure 1,

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Electronic Supplementary Information (ESI) available: Preparative details and X-ray data are deposited and CCDC 1440505-1440508. See DOI: 10.1039/x0xx00000x

A).[28] Alternatively, incorporation of a neutral donor such as a carbene generates dications that offer Lewis acidity with a diminished need for strongly electron-withdrawing groups (Figure 1, B).[31] In an effort to develop alternative strategies to new P-based Lewis acids, we have explored simple design concepts that exploit commercially-available Lewis bases and apply our protocols for conversion to Lewis acids. These protocols involve formal oxidative addition of X_2 (X = F, Cl, Br) to the P(III) centre followed by abstraction of X^- to yield the phosphonium cation. A complementary strategy to generate diphosphonium dications involves the incorporation of proximal phosphonium centers linked by an organic moiety (Figure 1 C,D).[29-31] In this case ,the enhanced Lewis acidity is thought to result from the inductive effect of a proximal positive charge rather than by a cooperative effect on the substrate.[5] In a similar effort, we have most recently described the utility of pyridinium-phosphonium dications (Figure 1, E)[37] as Lewis acid catalysts for a variety of reactions.

We have noted the previous work of Oestreich who described the synthesis of ferrocenylsilylium cations which are active Lewis acid catalysts in a range of acid-catalyzed transformations.[38-40] Prompted by this precedent, in the present manuscript we describe the preparation of Lewis acidic ferrocenylphosphonium cations. The utility of these species in Friedel-Crafts dimerization, dehydrocoupling, hydrodefluorination and ketone deoxygenation is reported.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen using standard schlenk techniques or a nitrogen-filled glove box (MBRAUN). All solvents (including deuterated solvents) were dried and stored over molecular sieves under a nitrogen atmosphere before use. $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$, XeF_2, $HSiEt_3$, 1,1-diphenylethylene, PhOH, MeO_3SCF_3, and all ketones were commercially available and used as received. $[SiEt_3][B(C_6F_5)_4]$[41] and $Fe(\eta^5\text{–}C_5H_4)_2PPh$ **5**[42] were prepared according to literature known methods. ^1H, ^{13}C, ^{11}B and ^{31}P NMR spectra were recorded on a Bruker Avance III or a Bruker Avance 500 spectrometer. A Perkin-Elmer analyser was used for carbon, hydrogen and nitrogen elemental analyses. ^1H NMR data, referenced to external Me_4Si, are reported as follows: chemical shift (δ/ppm), coupling constant (Hz), normalized integrals. $^{13}C\{^1H\}$ NMR chemical shifts (δ/ppm) are referenced to external Me_4Si. Assignments of individual resonances were done using 2D NMR techniques (HMBC, HSQC, HH-COSY) when necessary. High-resolution mass spectra (HRMS) were obtained on an Agilent 6538 Q-TOF (ESI) or a JEOL AccuTOF (DART) mass spectrometer. Elemental analyses were performed at the University of Toronto employing a Perkin Elmer 2400 Series II CHNS Analyser. Catalytic trial were performed in 5 mm NMR tubes using 0.75 mL of CD_2Cl_2.

Synthesis of $CpFe(\eta^5\text{-}C_5H_4PF_2Ph_2)$ 1 A solution of XeF_2 (34 mg, 0.20 mmol) in CH_2Cl_2 (1 mL) was added dropwise to a solution of phenylphosphinoferrocene (74 mg, 0.20 mmol) in CH_2Cl_2 (1 mL). Effervescence was immediately observed. After stirring 2 h volatiles were removed *in vacuo* resulting in an orange solid in quantitative yield (81 mg, Yield >99 %). X-ray quality crystals were obtained by cooling a saturated solution of the product in CH_2Cl_2 to -35°C. ^1H NMR (CD_2Cl_2, [ppm]): 3.94 (s, 5H, Cp), 4.50 (s, 2H, Cp CH_{β}), 4.83 (2H, s, Cp CH_{α}), 7.44-7.50 (m, 6H, *p*-Ph, *m*-Ph), 7.96-8.08 (m. 4H, *o*-Ph) $^{13}C\{^1H\}$ NMR (CD_2Cl_2, [ppm]): 70.2 (Cp C_{β}), 72.8 (d, Cp C_{α}, $^2J_{PC}$ = 15 Hz), 76.0 (br m, Cp C_{ipso}), 128.9 (d, Ph, C_{α}, $^2J_{PC}$ = 17 Hz), 131.8 (s, Ph, C_{β}) 134.2 (m). Resonances for *ipso*-carbon atoms on phenyl, Cp moieties were not observed. $^{19}F\{^1H\}$ NMR (CD_2Cl_2, [ppm]): -42.7 (d, $^1J_{PF}$ = 656 Hz) $^{31}P\{^1H\}$ NMR (CD_2Cl_2, [ppm]): -50.1 (t, $^1J_{PF}$ = 656 Hz); Elemental Analysis for $C_{22}H_{19}F_2P$: calcd.: C: 64.7, H 4.7, found: C: 63.1, H: 4.9;[43] HRMS (ESI-QTOF$^+$): m/z 387.0596 ($[CpFe(\eta^5\text{-}C_5H_4POPh_2)]$ (calc.: 387.0601).

Synthesis of $Fe(\eta^5\text{–}C_5H_4PF_2Ph_2)_2$ 2 A solution of XeF_2 (68 mg, 0.40 mmol) in CH_2Cl_2 (1 mL) was added dropwise to a solution of 1,1'-bis(diphenylphosphino)ferrocene (111 mg, 0.20 mmol) in CH_2Cl_2 (1 mL) Effervescence was immediately observed. After stirring for 1-2 min. a yellow solid precipitated from the solution. This was filtered and washed with pentane (2 x 1 mL) and dried *in vacuo* to give 118 mg of product (94% yield). ^1H NMR (CD_2Cl_2, [ppm]): 4.10 (m, 4H, Cp, H_{α}), 4.62 (m, 4H, Cp CH_{β}), 7.47 (m, 12H, *p*-Ph, *m*-Ph), 8.00 (m, 8H, *o*-Ph) $^{13}C\{^1H\}$ NMR (CD_2Cl_2, [ppm]): 74.6 (dt, Cp C_{β}, $^3J_{PC}$ = 15 Hz, $^4J_{FC}$ = 2 Hz), 77.2 (dt, Cp C_{α}, $^2J_{PC}$ = 18 Hz, $^3J_{FC}$ = 10 Hz), 129.0 (td, *i*-Ph, $^2J_{PC}$ = 17 Hz, $^4J_{FC}$ = 2 Hz), 132.1 (s, *i*-Ph) 134.6 (dt, *m*-Ph, $^2J_{CP}$ = 13 Hz, $^2J_{CF}$ = 10 Hz), 138.5 (td, *i*-Ph $^1J_{PC}$ = 182 Hz, $^2J_{FC}$ = 28 Hz) Resonances for *ipso* carbon atoms on Cp moieties were not observed. $^{19}F\{^1H\}$ NMR (CD_2Cl_2, [ppm]): − 42.8 (d, $^1J_{PF}$ = 662 Hz) $^{31}P\{^1H\}$ NMR (CD_2Cl_2, [ppm]): -51.5 (t, $^1J_{PF}$ = 662 Hz); Elemental Analysis for $C_{34}H_{28}F_4P_2$: calcd.: C 64.8, H 4.5, found: C: 64.9, H: 4.8; HRMS (ESI-QTOF$^+$): m/z 587.0987 ($[Fe(\eta^5\text{-}C_5H_4P(OH)Ph_2)$ $(\eta^5\text{-}C_5H_4POPh_2)]$) (calc.: 587.0992)

Synthesis of $[CpFe(\eta^5\text{-}C_5H_4PFPh_2)][B(C_6F_5)_4]$ 3 To a solution of 41mg (0.10 mmol) **1** in toluene was added 93 mg freshly prepared $[Et_3Si][B(C_6F_5)_4]2(C_7H_8)$ (0.095 mmol). Stirring for 3 h resulted in precipitation of a dark yellow oil. Washing with toluene (1 x 0.5 mL) and pentane (3 x 0.5 mL) and drying *in vacuo* resulted in 90 mg of **3** as a dull orange solid (84% yield). X-ray quality crystals were obtained by slow diffusion of n-pentane into a saturated solution of **4** in dichloromethane at -35° C, ^1H NMR (CD_2Cl_2, [ppm]): 4.50 (s, 5H,Cp), 4.64 (m, 2H, Cp, H_{α}), 5.07 (m, 2H, Cp, H_{β}), 7.79-7.85 (m, 8H, *o*-Ph, *m*-Ph), 7.99 (t, 2H, *p*-Ph, , $^3J_{HH}$ = 7 Hz) ^{11}B NMR (CD_2Cl_2, [ppm]): -16.7 $^{13}C\{^1H\}$ NMR (CD_2Cl_2, [ppm]): 72.3 (s, Cp), 75.2 (d, Cp C_{α}, $^2J_{PC}$ = 17 Hz), 77.9 (d, Cp C_{β}, $^3J_{PC}$ = 13 Hz), 131.3 (d, Ph, J_{PC} = 14 Hz), 133.5 (d, Ph, J_{PC} = 13 Hz), 138.5 (s, Ph) signals for *ipso*-carbon atom not observed. $^{19}F\{^1H\}$ NMR (CD_2Cl_2, [ppm]): − 112.5 (d, $^1J_{PF}$ = 998 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, [ppm]): 102.9 (d, $^1J_{PF}$ = 998 Hz) Elemental Analysis for $C_{46}H_{19}BF_{21}PFe$: calcd.: C: 51.5, H: 1.8, found: C: 51.0, H: 1.5; HRMS (ESI-QTOF$^+$): m/z 387.0596 ($[CpFe(\eta^5\text{-}C_5H_4POPh_2)]$ (calc.: 387.0601)

Synthesis of $[Fe(\eta^5\text{-}C_5H_4PFPh_2)_2][B(C_6F_5)_4]_2$ 4 To a solution of 63mg (0.10 mmol) **2** in toluene was added 186 mg freshly prepared $[Et_3Si][B(C_6F_5)_4]2(C_7H_8)$ (0.19 mmol). Stirring for 3 h resulted in precipitation of a dark yellow oil. Washing with toluene (1 x 0.5 mL) and pentane (3 x 0.5 mL) and drying *in vacuo* resulted in 156 mg of **4** as a dull orange solid (80% yield). X-ray quality crystals were obtained by slow diffusion of n-pentane into a saturated solution of

4 in dichloromethane at -35° C, ^{1}H NMR (CD_2Cl_2, [ppm]): 4.51 (m, 4H, Cp CH_{α}), 5.19 (m, 4H, Cp $CH_{\beta,}$), 7.47 (m, 12H, p-Ph, m-Ph), 7.72 (m, 4H, Ph), 7.79 (m, 4H, Ph), 8.04 (m, 2H, *p*-Ph) ^{11}B NMR (CD_2Cl_2, [ppm]): - 16.7 $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, [ppm]): 74.6 (dt, Cp C_{β}, $^{3}J_{PC}$ = 15 Hz, $^{4}J_{FC}$ = 2 Hz), 77.2 (dt, Cp C_{α}, $^{2}J_{PC}$ = 18 Hz, $^{3}J_{FC}$ = 10 Hz), 129.0 (td, i-Ph, $^{2}J_{PC}$ = 17 Hz, $^{4}J_{FC}$ = 2 Hz), 132.1 (s, i-Ph) 134.6 (dt, m-Ph, $^{2}J_{CP}$ = 13 Hz, $^{2}J_{CF}$ = 10 Hz), 139.2 (s, o-Ph) $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2, [ppm]): -42.8 (d, $^{1}J_{PF}$ = 662 Hz). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, [ppm]): -51.5 (t, $^{1}J_{PF}$ = 662 Hz); Elemental Analysis for $C_{82}H_{28}B_2F_{42}P_2Fe$: calcd.: C: 50.5, H: 1.5, found: C: 51.0, H: 1.5; HRMS (ESI-QTOF^{+}): m/z 587.0987 ([Fe(η^5-$C_5H_4P(OH)Ph_2$) (η^5-$C_5H_4POPh_2$)]) (calc.: 587.0992)

Synthesis of [PhMeP(η^5-$C_5H_4)_2$Fe][B($C_6F_5)_4$] 7 To a solution of Fe(η–$C_5H_4)_2$PPh in toluene was added a solution of MeO_3SCF_3 in toluene. Successive precipitations yielded .050 g of the product (80% yield). ^{1}H NMR (CD_2Cl_2, [ppm]): 2.39 (d, 3H, CH_3, $^{2}J_{PH}$ = 14 Hz), 4.50 (m, 2H, Cp), 4.80 (m, 2H, Cp), 5.06 (m, 2H, Cp), 5.11 (m, 2H, Cp), 7.79-7.85 (m, 4H, *o*-Ph, *m*-Ph), 7.99 (t, 1H, *p*-Ph, , $^{3}J_{HH}$ = 7 Hz) $^{11}B\{^{1}H\}$: -16.7 ^{13}C $\{^{1}H\}$ NMR (CD_2Cl_2, [ppm]): 12.1 (d, Me, $^{1}J_{CP}$ = 221 Hz), 72.3 (s, Cp), 75.2 (d, Cp, $^{2}J_{PC}$ = 17 Hz), 77.9 (d, Cp, $^{3}J_{PC}$ = 13 Hz), 131.3 (d, Ph, J_{PC} = 14 Hz), 133.5 (d, Ph, J_{PC} = 13 Hz), 138.5 (s, Ph) signals for ipso carbon atom not observed. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, [ppm]): 35.6. Elemental Analysis for $C_{41}H_{16}BF_{20}P$: calcd.: C: 49.9 H: 1.6 found: C: 50.2, H: 1.9; HRMS (ESI-QTOF^{+}): m/z 307.0343 (Ph(O)P(η^5-$C_5H_4)_2$Fe) (calc.: 307.0339)

X-ray Diffraction Studies: Crystals were coated in paratone oil and mounted in a cryo-loop. Data were collected on a Bruker APEX2 X-ray diffractometer using graphite monochromated Mo-Kα radiation (0.71073 Å). The temperature was maintained at 150(2) K using an Oxford cryo-stream cooler for both, initial indexing and full data collection. Data were collected using Bruker APEX-2 software and processed using SHELX and Olex2 an absorption correction applied using multi-scan within the APEX-2 program. All structures were solved by direct methods within the SHELXTL package[42] and refined with Olex2.[44-45]

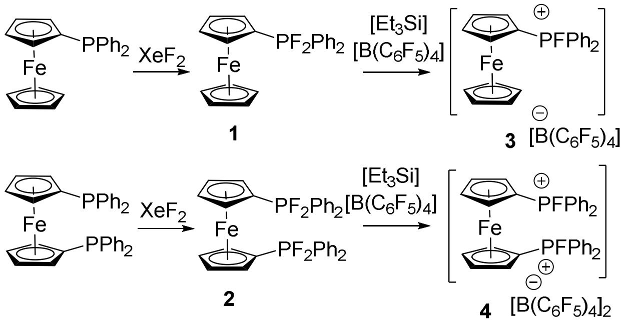
Results and Discussion

Oxidation of diphenylphosphinoferrocene and 1,1'-*bis*(diphenylphosphino)ferrocene (dppf)[46-47] using one or two equivalents of xenon difluoride, respectively, resulted in selective oxidation of the P(III) centres in the ferrocene derivatives, yielding quantitative conversion to ferrocenyl mono- and *bis*-diphenyldifluorphosphoranes, CpFe(η^5-$C_5H_4PF_2Ph_2$) **1** and Fe(η^5-$C_5H_4PF_2Ph_2)_2$ **2** respectively (Scheme 1). The $^{31}P\{^{1}H\}$ NMR spectrum for **1** exhibited a triplet at -50.1 ppm, while the associated doublet resonance in the ^{19}F NMR spectrum appeared at -42.7 ppm. ($^{1}J_{PF}$ = 656 Hz). The corresponding $^{31}P\{^{1}H\}$ and ^{19}F NMR spectra for **2** were very similar, showing a triplet at – 51.5ppm and a doublet at -42.8 ppm, respectively ($^{1}J_{PF}$ = 662 Hz). Interestingly, the P-F couplings in **1** and **2** are significantly smaller than those seen in Fe(η^5-$C_5H_4PF_4)_2$ (817 Hz, 977 Hz).[48]

Clear differences between the two compounds were only observed in the ^{1}H NMR spectra, where the higher symmetry of **2** results in only two distinct resonances for the Cp protons, in a 1:1 ratio at 4.10 ppm and 4.62 ppm, while **1** exhibits three resonances in the proton spectrum due to the inequivalence of the Cp rings, with the five protons of the unsubstituted Cp moiety appearing at 3.94 ppm, and the two resonances assigned to the β and α protons of the substituted Cp ring at 4.50 ppm and 4.83 ppm.

A solid-state structural X-ray diffraction analysis of crystals of **1** (Figure 2) confirmed a pseudo-trigonal bipyramidal geometry at phosphorus with the two fluorine atoms occupying the axial positions with a F–P–F: 177.0(1) ° and P-F bond lengths averaging 1.677(5) Å, typical of aryl fluorophosphoranes.[28]

Subsequent reaction of **1** and **2** using one or two equivalents of $[SiEt_3][B(C_6F_5)_4]$, respectively, resulted in abstraction of fluoride ion from the difluorophosphoranes yielding the $B(C_6F_5)_4$ salts of the ferrocenyldiphenylfluorophosphonium cation, [CpFe(η^5–$C_5H_4PFPh_2$)][B($C_6F_5)_4$] **3** and ferrocenyl*bis*-(diphenylfluorophosphonium) dication, [Fe(η^5-$C_5H_4PFPh_2)_2$] [B($C_6F_5)_4]_2$ **4**, respectively (Scheme 1). The ^{31}P and ^{19}F NMR spectra of **3** and **4** are very similar, with ^{31}P doublet resonances appearing at 102.8 and 102.9 ppm and doublets in the ^{19}F NMR spectra at -112.4ppm for **3** and at -119.6 ppm for **4.** $^{1}J_{PF}$ coupling constants were characteristic of fluorophosphonium cations at 998 Hz for **3** and 1002 Hz for **4**. Signals In the ^{1}H NMR spectra of **3** and **4** were shifted downfield compared to those of the phosphorane precursors.



Scheme 1. Syntheses of ferrocenyl-phosphonium cation salts **3** and **4.**

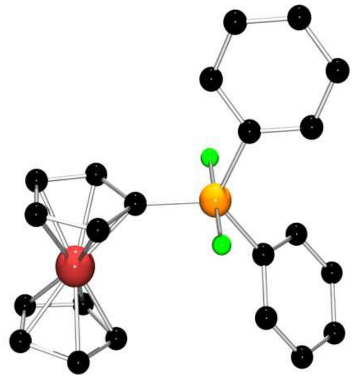


Figure 2 POV-ray depiction of **1**. C: black. P: orange, F: yellow green. Fe: red brown. Hydrogen atoms have been omitted for clarity.

Crystallographic studies of single crystals of **3** and **4** confirmed the proposed formulations. In **3** and **4**, the fluorophosphonium centers are pseudo-tetrahedral. In **3** the P-F bond is 1.574(3) Å, while in **4** the P-F bonds are shorter, averaging 1.545(2) Å. In both cases these observations are typical of fluorophosphonium cations. Unsurprisingly the phosphonium moieties in **4** are oriented so as to maximize the distance between the cationic centres in the solid state.

Attempts to synthesize a fluorophosphonium cation derived from a phosphinoferrocenophane were undertaken. To this end, the species PhP(η^5-C_5H_4)$_2$Fe **5** was prepared following a slightly modified literature methods.[49] Addition of a solution of XeF_2 to solutions of **5** in dichloromethane rapidly yielded an insoluble intractable dark solid, suggesting the possibility of polymeric products. Similarly, attempts to form the fluorophosphonium cation directly by fluoronium ion transfer from Selectfluor or fluoropyridines were also unsuccessful. Interestingly, Manners has noted that the chlorophosphine analogue ClP(C_5H_4)$_2$Fe was unstable at temperatures above -20°C.[49] Nonetheless, compound **5** could be methylated upon addition of methyl triflate generating the triflate salt [PhMeP(η^5-C_5H_4)$_2$Fe][O_3SCF_3] **6** (Scheme 2). Although this species was not isolated, treatment of the solution of **6** with one equivalent of [$SiEt_3$][B(C_6F_5)$_4$] effected anion exchange providing access to the salt [PhMeP(η^5-C_5H_4)$_2$Fe][B(C_6F_5)$_4$] **7** (Scheme 2). The formulation of **7** and the quaternization of the phosphorus centre was confirmed crystallographically (Figure 4). The metric parameters are unexceptional.

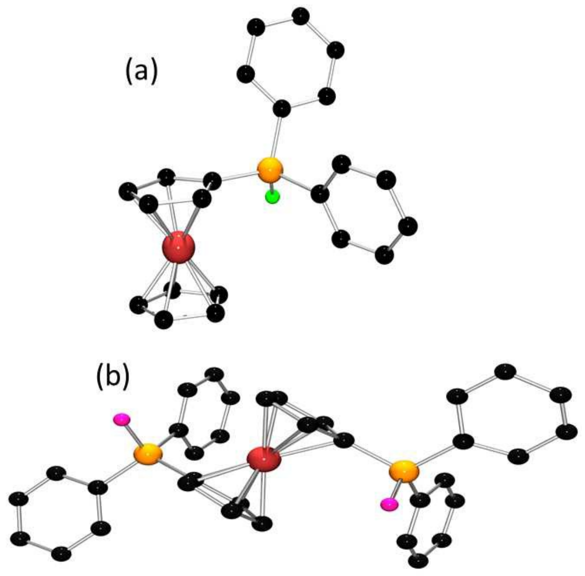
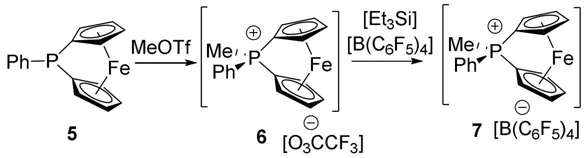


Figure 3 POV-ray depiction of cations of (a) **3** and (b) **4**. C: black. P: orange, F: yellow green. Fe: red brown. Hydrogen atoms and the anions have been omitted for clarity.



Scheme 2. Synthesis of **7**.

Oxidation of the Fe(II) centre of **3** or **4** was investigated. Compound **3** exhibited a quasi-reversible oxidation wave (see SI) and efforts to generate the nominally Fe(III) species by the addition of AgX (X = F, Cl) did exhibit the color change characteristic of Fe oxidation from light orange to a deep turquoise. However, all efforts to isolate the oxidized species were fraught with difficulty and ultimately unsuccessful.

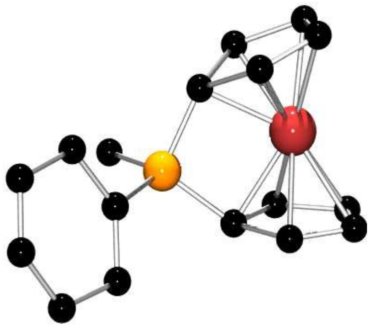
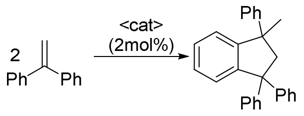
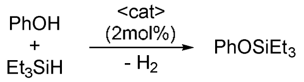
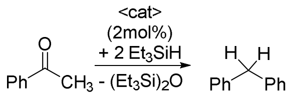
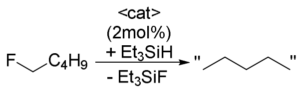


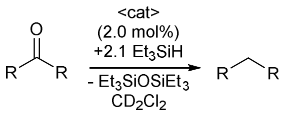
Figure 4 Pov-ray depiction of cation of **7**. C: black. P: orange. Fe: red brown. Hydrogen atoms and the anion have been omitted for clarity.

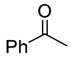
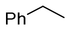
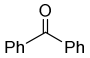
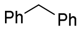
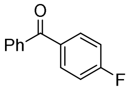
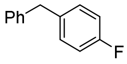
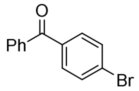
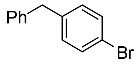
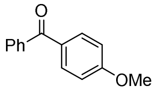
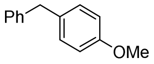
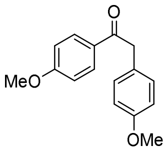
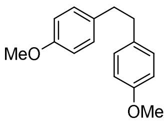
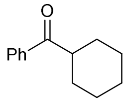
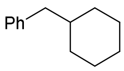
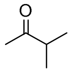
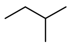
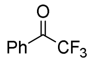
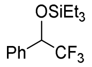
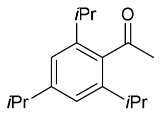
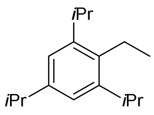
Table 1. Lewis acid catalysis by **3**, **4** and **7**

	**3** 10% (96 h, 50 °C) **4** >99% (48 h, 25 °C) **7** 0% (72 h , 50 °C)
	**3** 97% (7 d, 50 °C) **4** >99% (24 h, 25 °C) **7** 0% (72 h, 50 °C)
	**3** 27% (96 h, 50 °C) **4** >99% (24 h, 25 °C) **7** 0% (72 h, 50 °C)
	**3** <1% (96 h, 50 °C) **4** 55% (24 h, 25 °C) **7** 0% (72 h, 50 °C)

Having generated several ferrocene-derived phosphonium cations, the catalytic activities of the salts **3**, **4** and **7** were probed (Table 1). Consistent with the observed reactivity of established EPCs of types A, B, C, D, and E, dication **4** was shown to quantitatively catalyze Friedel-Crafts dimerization of 1,1-diphenylethylene, dehydrocoupling of phenol and triethylsilane, and deoxygenation of acetophenone in the presence of 2.1 equivalents of $HSiEt_3$ as a hydride source. Compound **4** also mediated the hydrodefluorination of 1-fluoropentane in the presence of $HSiEt_3$ in 55% yield after 7 days at 25°C. In contrast, the monocation **3** was less reactive, requiring heating to 50 °C to catalyze 10% dimerization of diphenylethylene. Nonetheless, **3** did catalyze the dehydrocoupling of phenol and triethylsilane (97%) albeit over the course of 7 days. Similarly heating **3** for 3 days only catalyzed the deoxygenation of acetophenone to 27% yield. At the same temperature **3** exhibited essentially no ability to mediate hydrodefluorination converting only 1% of 1-fluoropentane to pentane. Interestingly, neither **3** nor **4** catalyzed the hydrosilylation of olefins with either $HSiEt_3$ or $PhSi(Me_2)H$, in contrast to other EPCs. In stark contrast to **3** and **4**, compound **7** showed neither catalytic nor stoichiometric activity in any of these transformations. This is consistent with our previous observations that electron-withdrawing substituents are essential to lower the energy of the σ* LUMO enhancing the electron acceptor properties of such phosphonium cations.[28] In addition, ferrocene is comparatively sterically demanding and may inhibit access to the σ* LUMO on P.

Table 2. Catalytic deoxygenation of ketones mediated by **3** and **4**



Substrate	Cat	T[° C]	t(d)	Conv. %	Product
	**3** **4**	50 25	7 1	27[a] >99	
	**3** **4**	50 25	7 5	>99 >99	
	**3** **4**	50 25	7 2	>99 >99	
	**3** **4**	50 25	7 2	95 91	
	**3** **4**	50 25	5 2	99 98[b]	
	**3** **4**	50 25	5 2	>99 >99	
	**3** **4**	50 25	7 4	7 92	
	**3** **4**	50 25	5 4	74 76	
	**3** **4**	50 25	7 5	>10 89	
	**3** **4**	50 25	7 4	60 91	

Conversion determined according to ^1H NMR spectroscopy. [a]Significant quantities of $PhCH_2CH_2SiEt_3$ derived from the hydrosilylation of styrene were observed. [b]80% isolated yield obtained for this product.

To further probe the reactivity of **3** and **4** in deoxygenation of ketones, a broader range of substrates was investigated (Table 2). Catalyst **4** proved capable of carrying out deoxygenation of a range of substrates at ambient temperatures over the course of 24-120 h. For example, acetophenone is deoxygenated to ethyl benzene during a 1 day treatment with Et_3SiH and the catalyst **4**. In contrast, the analogous use of **3** as the catalyst is much less efficient in this case, giving a 27% yield of ethylbenzene together with $PhCH_2CH_2SiEt_3$ after 4 days at 50°C. Benzophenone is deoxygenated to diphenylmethane in the presence of silane and either **3** or **4** although **3** requires 7 days at 50°C for complete conversion whereas **4** is done after 5 days at 25°C. The *para*-substituted aromatic ketones $PhC(O)C_6H_4X$ (X = F, Br, OMe) and 2,4,6-*i*PrPhC(O)CH_3 are reduced using either **3** and **4** as the catalyst (Table 2). The ketone $MeOC_6H_4C(O)CH_2C_6H_4OMe$ was effectively reduced under similar conditions. Aliphatic ketones $PhC(O)C_6H_{11}$ and $CH_3C(O)CH(CH_3)_2$ were also deoxygenated, although for the latter, a reduced yield of the deoxygenated product was obtained. This results from competing elimination pathways giving small amounts of alkene products.[36] $PhC(O)CF_3$ underwent hydrosilylation in the presence of catalyst **4** at 50°C, however only the hydrosilylation product was obtained. In contrast, the corresponding reaction with **3** gave minimal conversion.

Comparing these activities to those previously reported, we note that the phosphonium dications of types B, C, and D have shown to be active catalysts for ketone deoxygenation under similar conditions.[31, 36] In general, the dicationic catalysts are significantly more active than **3** or **4**, effecting the catalysis at ambient temperatures.[31, 36] Interestingly, dicationic catalysts of type C with bridges of one or two carbon atoms proved generally more active in catalysis than **4**. On the other hand, type C cations with three to five carbon linkers are much less active, suggesting that that enhanced reactivity results from the enforced proximity of the two phosphonium centres. In contrast, this is not the case for **4** where the cationic centers on each Cp-ring are oriented so as to maximize the separation of the charged centers. Nonetheless, the presence of the second phosphonium center in **4** inductively enhances the Lewis acidity of the other, although it is unlikely that these centers act in a cooperative fashion. As a result **4** exhibits catalytic activity that is certainly above that of the $[Ph_3PF][B(C_6F_5)_4]$ but somewhat less than that of diphosphonium dications derived from $Ph_2P(CH_2)_nPPh_2$ (n = 1, 2), where the proximity of the cationic centers is imposed.

Conclusions

The species $[CpFe(\eta^5\!-\!C_5H_4PFPh_2)][B(C_6F_5)_4]$ **3** and $[Fe(\eta^5\text{-}C_5H_4PFPh_2)_2]$ $[B(C_6F_5)_4]_2$ **4**, are easily prepared from commercially or readily available phosphine precursors by oxidation with XeF_2 and subsequent fluoride abstraction. These Lewis acids are effective catalysts for Friedel-Crafts dimerization of 1,1-diphenylethylene, dehydrocoupling of phenol and triethylsilane, hydrodefluorination of 1-fluoropentane and the deoxygenation of a series of ketones. The present systems show activities that are comparable to several of the EPC systems we have previously reported, although the monocation **3** showed lower activity than the dication **4**. This further indicates the enhanced Lewis acidity that results from a dicationic Lewis acidic phosphonium cation. We are continuing to explore and develop the range of EPCs that are effective Lewis acid catalysts for a broadening range of useful organic transformations.

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Notes and references

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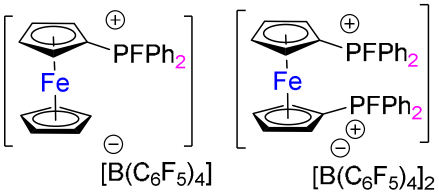
TOC GRAPHIC



LEWIS ACID CATALYSTS

Ferrocenyl-derived electrophilic phosphonium cations are catalysts for a series of reactions including the deoxygenation of a series of ketones.