Synthesis and Mossbauer Spectroscopic Studies of Chemically Oxidized Ferrocenyl(phenyl)phosphines

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The electrochemical potentials of $Fc_{3-x}PPh_x$, (**1**−**3**, $x = 0-2$) and $(FcPPh)_n$ (**4**) indicate that iodine should oxidize ferrocenyl(phenyl)phosphines. The molar conductivity of solutions of **1**−**3** increases sharply when the solutions are titrated with iodine, leveling off after the addition of >2 equiv of oxidant, consistent with formation of 1:1 electrolytes. Diamagnetic salts **6**−**9** are observed upon addition of a benzene solution of iodine to a benzene solution of **1**−**4** at ambient temperature in ratios of I_2/metallocene ranging from 1:1 to 2:1. Well-resolved ^1H and ^{31}P NMR spectra are obtained for **6**−**8**. Absorptions assigned to the I_3^- anion dominate the UV−vis spectrum of **6**−**8,** whereas characteristic absorptions for $[Fc][I_3]$ are absent. Mossbauer spectra of **7**−**9** reveal isomer shifts consistent with low-spin iron(II) in ferrocene derivatives rather than those in ferricenium ions. Small amounts of low-spin Fe^{III} appear to be present in **6**. Taken together, the results suggest that **6**−**9** are iodophosphonium salts and not ferricenium salts. Diferrocenyl(phenyl)phosphine oxide (**5**) reacts with iodine to produce a diamagnetic, dark solid **10**. Low-spin Fe^{II} is observed at 77 and 293 K in the Mossbauer spectra of **10** with no evidence for oxidation of Fe^{II} to Fe^{III}. Compound **10** is proposed to be a neutral complex between **5** and I_2. Reactions between **5** and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) yield $[Fc_2P(=O)][DDQ]_2$ (**11**). Mossbauer spectroscopy of **11** indicates the presence of a mixture of low-spin Fe^{II} and low-spin Fe^{III} at 77 K, suggesting that some electron transfer occurs from **5** to DDQ. The fraction of low-spin Fe^{III} increases at room temperature.

Introduction

Ferrocene is an attractive functional group in the design of electroactive ligands and polymers because of its readily accessible electrochemical potential and the reversibility of its one-electron oxidation.[1] Ferrocenyl(diphenyl)phosphine ($FcPPh_2$, **1**)[2] undergoes a reversible one-electron oxidation in both CH_2Cl_2 and acetonitrile.[3,4] Two oxidations separated by 0.16 V are observed for diferrocenyl(phenyl)phosphine (**2**) whereas three irreversible oxidations are reported for tris(ferrocenyl)phosphine (**3**) under the same conditions.[3] The first oxidation potentials for **1**−**3** are all more positive than those for ferrocene. This has been interpreted in terms of the electronic effect of the phosphorus substituent on the oxidation potential of the iron(II) center in **1**.[3,4] Additional ferrocene substituents in **2** and **3** appear to have little effect on the first oxidation potential. The first oxidation potential of poly(*n*-butyl ferrocenyl(phenyl)phosphine), however, is essentially the same as that of ferrocene with two subsequent oxidations at more positive potentials.[5] The electrochemistry of the polymer has been interpreted in terms of cooperative interactions between metal centers.

At first glance these conclusions are reasonable. The oxidation of triphenylphosphine occurs at potentials much more positive than those of ferrocene. In controlled potential coulometry studies of **1**−**3**, the reported blue-green colors of the oxidized solutions are consistent with the formation of ferricenium ions.[4] Interpretation of the electrochemistry of bis(diphenylphosphino)ferrocene, however, is different. Oxidation of $(\eta^5\text{-}C_5H_4PPh_2)_2Fe$ is believed to occur initially at iron but is followed by a rapid intramolecular transfer of one electron from phosphorus to iron, thereby regenerating the Fe^{II} center and creating a phosphonium ion radical.[6] The latter decomposes to a phosphine oxide by reaction with solvent. Similar explanations were recently proposed for the electrochemical oxidation of **1** and other ferrocene-substituted phosphines.[7,8]

To our knowledge, there is only a single report describing the chemical oxidation of ferrocenyl(phenyl)phosphines.[9] Reaction of diferrocenyl(phenyl)phosphine with iodine yielded $[Fc_2PPh][I_3]$ based on microanalysis. Mossbauer spectroscopy was used to identify the product as a localized, mixed-valent Fe^{II}/Fe^{III} compound. The electrochemical and chemical oxidation of $FcPPh_2Re(CO)_4Cl$, where the nonbonding electron pair on phosphorus is coordinated to a transition metal, also produces ferricenium ions.[10] In this paper we report on the chemical oxidation of **1**−**3** and poly(ferrocenylphenylphosphine) (**4**) with iodine and characterization of the products using a combination

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Table 1. NMR Spectral Data for Compounds **1**−**5** in CD_2Cl_2

compound	^1H	^{31}P	^{13}C
$FcPPh_2$ (**1**)	4.09 s (5 H, Cp) 4.13, 4.40 br s (4 H, C_5H_4) 7.35, 7.39 br s (10 H, Ph)	−17.8	69.4, 71.2, 73.4 76.1, 128.4, 133.8, 139.7
Fc_2PPh (**2**)	3.98, 4.20, 4.28, 4.33 br m (2 H each), 4.07 s (10 H, Cp)	−29.8	69.37, 70.31, 70.84 72.28, 73.19, 78.46, 128.2, 129.1, 134.3
Fc_3P (**3**)	4.04 s (15 H, Cp), 4.17 q (6 H) 4.30 t (6 H)	−59.9	69.3, 70.1, 73.1, 80.0
$[PhPFc]_y$ (**4**)	3.6−4.7 br m (10 H, Cp), 6.8−7.9 br, 5 H, Ph)	−31.5	
$Fc_2P(=O)Ph$ (**5**)[a]	4.50, 4.15, 4.08, 4.00 br s (2 H), 4.19 br s (10 H, Cp), 7.09, 7.95 m (5 H, PPh)	+26.7	

[a] In C_6D_6.

of cyclic voltammetry, molar conductivity, NMR, UV−vis, and Mossbauer spectroscopy methods. To examine the role of the phosphorus lone pair on the chemical oxidation of ferrocenyl(phenyl)phosphines, the reactivity of ferrocenyl(phenyl)phosphine oxide (**5**) with iodine and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) is also described.

Experimental Section

All compounds described in this work were handled using Schlenck techniques or in an M. I. Braun glovebox under purified argon or nitrogen atmospheres.[11] Ferrocenyl(diphenyl)phosphine (**1**), diferrocenyl(phenyl)phosphine (**2**), tris(ferrocenyl)phosphine (**3**),[3,12] poly(ferrocenylphenylphosphine) (**4**),[13] and diferrocenyl(phenyl)phosphine oxide (**5**)[3] were prepared by literature procedures. Iodine and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone were purchased from Aldrich Chemical Co. and used as received. Solvents were purified by refluxing over Na/benzophenone (toluene, benzene, tetrahydrofuran) or P_2O_5 (dichloromethane, 1,2-dichloroethane, acetonitrile) and distilled prior to use. Elemental analyses (C, H) were performed by Desert Analytics, Inc. Melting points were determined on an Electrothermal 9100 apparatus under argon in capillaries sealed with epoxy and are uncorrected.

NMR spectra were recorded at 300 MHz for ^1H and 121.4 MHz for $^{31}P\{^1H\}$ on a Varian XL300 spectrometer in 5-mm tubes equipped with a Teflon valve (Wilmad Glass, Inc.). Proton chemical shifts are relative to residual protons in the solvent ($CD\mathbf{H}Cl_2$ at δ 5.24 ppm). Carbon chemical shifts are reported relative to ^{13}C in the solvent ($\mathbf{C}D_2Cl_2$ at δ 53.8 ppm). Phosphorus chemical shifts are reported relative to external 85% $H_3\mathbf{P}O_4$ at δ 0.0 ppm. NMR data for **1**−**5** are summarized in Table 1.

UV−vis spectra were recorded in CH_2Cl_2 and CH_3CN solution on a Hewlett-Packard 8452A diode array spectrometer from 250 to 800 nm. Variable-temperature Mossbauer spectra were recorded in the solid state on a standard constant-acceleration apparatus and fit to standard independent Lorentzians.[14] Infrared spectra were obtained as KBr pellets on a Mattson Satellite FTIR interfaced with a Digital PC3000 computer.

Reaction of Ferrocenyl(diphenyl)phosphine (1) with Iodine. A solution of 144 mg (0.57 mmol, 1.0 equiv) of I_2 in 15 mL of benzene was added dropwise to an orange solution of 210 mg (0.57 mmol) of **1** in 15 mL of benzene at ambient temperature. Formation of a brown precipitate was observed after stirring for 20 min. The orange supernatant was rapidly decanted and the precipitate was washed with benzene (2 × 10 mL) until the washings were colorless. The brown tar was dried under vacuum, yielding 240 mg (68% yield) of **6a**. Accurate microanalyses could not be obtained for this product in part because of its tarlike consistency.

^1H (CD_2Cl_2): δ 4.30 s (6 H, Cp + one proton of the unsubstituted ring), 4.38 br m (1 H), 4.52 br m (1 H), 4.76 br m (1 H), 7.35 br m (4 H), 7. 39 br m (6 H).

$^{31}P\{^1H\}$ (CD_2Cl_2): δ −11.5 s.

IR (KBr): 420 w, 459 w, 493 s, 530 m, 570 m, 620 w, 692 s, 704 s, 727 w, 751 w, 825 w, 1108 w, 1123 m, 1184 w, 1437 m, 1542 m, 1626 s br, 2855 w br, 2930 w br, 3065 w br.

Using the procedure for **6a**, 513 mg (1.99 mmol, 1.5 equiv) of I_2 and 492 mg (0.133 mmol) of **1** were stirred for 16 h in benzene (60 mL) yielding **6b** as a sticky brown solid in ≈50% yield. Accurate microanalyses could not be obtained for this product in part because of its tarlike consistency and because the product was a mixture of compounds.

^1H (CD_2Cl_2): δ 4.26 s (5 H, Cp), 4.46 s (2 H, H_a), 4.76 s (2 H, H_b), 7.36 s (3 H, C_6H_6), 7.6−7.8 m (10 H, PPh_2).

$^{31}P\{^1H\}$ (CD_2Cl_2): δ 6.9 s (major), 50.8 s (minor).

^{13}C $\{^1H\}$ (CD_2Cl_2): δ 70.7 s, 73.0 d, 74.2 d, 128.5 s(C_6H_6), 129.6 d, 132.0 d, 134.5 s.

IR (KBr): 447 m, 473 s, 489 s, 518 m, 548 w, 567 m, 687 s, 703 m, 729 m, 745 m, 827 m, 870 w, 906 w, 924 w, 999 m, 1030 m, 1060 w, 1104 m, 1122 m, 1178 m, 1309 w, 1365 w, 1387 w, 1411 w, 1436 w, 1476 m, 2871 w, 2851 w, 2924 m, 2954 w, 3055 w, 3081 w.

UV−vis (CH_2Cl_2): 294, 364 nm.

Mossbauer: δ = 0.551 m/s, ΔE^Q = 2.269 mm/s.

Using the procedure for **6a**, 137 mg (0.54 mmol, 2.0 equiv) of I_2 and 100 mg (0.27 mmol) of **1** were stirred for 2 h in benzene (10 mL) at ambient temperature yielding 70 mg (30% yield) of **6c** as a brown solid (mp 137−140 °C). The product contained a mixture of products, as determined by NMR, which could not be readily separated.

^1H (CD_2Cl_2): δ 4.45 s (5 H, Cp), 4.60 q (2 H, J = 3 Hz), 5.02 q (2 H, J = 2 Hz), 7.6−7.8 m (10 H, PPh).

$^{31}P\{^1H\}$ (CD_2Cl_2): δ 15.1 s.

UV−vis (CH_2Cl_2): λ_{max} = 300, 368 nm.

Mossbauer (77 K): δ = 0.452 mm/s, ΔE^Q = 2.202 mm/s; δ = 0.431 mm/s, ΔE^Q = 0 mm/s; δ = 0.781 mm/s, ΔE^Q = 1.969 mm/s.

IR (KBr): 428 cm^{-1} w, 447 w, 477 s, 505 m, 616 w, 701, m, 723 m, 744 m, 776 m, 808 m, 822 m, 838 m, 1034 m, 1058 w, 1094 m, 1157 w, 1175 m, 1377 w, 1433 m, 1460 m, 2851 s, 2919 s, 2955 sh.

A second set of resonances accounting for 13% of the products (by integration) is assigned to $FcPPh_2{\cdot}{}^3/_2I_2$ (vide supra).

Reaction of Diferrocenyl(phenyl)phosphine (2) with Iodine. Using the procedure for **6a**, 104 mg (0.41 mmol, 1.0 equiv) of I_2 and 197 mg (0.41 mmol) of **2** were stirred for 16 h in benzene (30 mL) yielding 260 mg (87% yield) of **7a** (mp 165−168 °C). Anal. Calcd for $C_{26}H_{25}Fe_2I_2P{\cdot}{}^1/_3C_6H_6$: 44.34% C, 3.32% H. Found: 44.57% C, 3.45% H.

^1H (CD_2Cl_2): δ 4.36 s (10 H, Cp), 4.39 m (2 H), 4.56 m (2 H), 4.75 m (2 H), 4.79 m (2 H), 7. 35 s (2 H, C_6H_6), 7.62 m (2 H), 7.69−7.8 m (3 H).

$^{31}P\{^1H\}$ (CD_2Cl_2): δ −5.9 s.

IR (KBr): 420 cm^{-1} m, 434 m, 446 m, 470 s, 484 s, 554 m, 574 m, 617 m, 669 m, 684 m, 747 m, 826 m, 1027 m, 1106 m, 1181 m, 2855 w br, 2930 w br, 3065 w br.

UV−vis (CH_2Cl_2): 280, 355 nm.

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Using the procedure for **6a**, 164 mg (0.65 mmol, 1.5 equiv) of I_2 and 207 mg (0.43 mmol) of **2** were stirred for 16 h in benzene (30 mL) yielding 350 g (88% yield) of **7b** as an orange-red powder (mp 170−173 °C). Anal. Calcd for $C_{26}H_{25}Fe_2I_3P{\cdot}{}^1/_2C_6H_6$: 38.79% C, 2.92% H. Found: 38.82% C, 2.96% H.

^{1}H (CD_2Cl_2): δ 4.38 s (10 H, Cp), 4.47 m (2 H), 4.63 m (2 H), 4.84 m (2 H), 4.88 m (2 H), 7.35 s (3 H, C_6H_6), 7.62 m (2 H), 7.69−7.8 m (3 H).

^{31}P{^{1}H} (CD_2Cl_2): δ 3.7 s.

^{13}C{^{1}H} (CD_2Cl_2): 66.9, 68.1, 71.1, 72.2 (Cp), 74.1 d, 74.6 d, 75.1, 128.9 (C_6H_6), 130.1 d, 132.8 d, 134.9.

IR (KBr): 469 cm^{-1} s, 490 m, 556 w, 615 w, 689 w, 749 w, 822 m, 1002 m, 1028 m, 1055 w, 1065 w, 1100 m, 1184 s, 303 w, 1365 w, 1390 w, 1409 m, 1433 m, 1475 w, 1571 w, 1627 w, 3050 w br, 3090 w br.

UV−vis (CH_2Cl_2): 294, 364 nm.

Mossbauer: $\delta = 0.475$ mm/s, $\Delta E^Q = 2.30$ mm/s.

Using the procedure for **6a**, 36 mg (0.14 mmol, 2.0 equiv) of I_2 and 34 mg (0.071 mmol) of **2** were stirred for 2 h in benzene (10 mL) yielding 51 mg (73% yield) of **7c** as a brown powder (mp 100−104 °C). Anal. Calcd for $C_{26}H_{23}Fe_2I_4P{\cdot}C_6H_6$: 36.13% C, 2.75% H. Found: 35.90% C, 2.43% H.

^{1}H (CD_2Cl_2): δ 4.44 s (10 H, Cp), 4.57 br m (2 H), 4.72 br m (2 H), 4.96 br m (2 H), 5.00 br m (2 H), 7. 35 s (6 H, C_6H_6), 7.69 t (3 H, PPh), 7.77 t (2 H, PPh).

^{31}P{^{1}H} (CD_2Cl_2): δ 19.2 s.

UV−vis (CH_2Cl_2): $\lambda_{max} = 300$, 366 nm.

Mossbauer (77 K): δ 0.497 mm/s, $\Delta E^Q = 2.257$ mm/s.

IR (KBr): 444 cm^{-1} w, 479 s, 537 w, 565 w, 577 w, 613 w, 684 m, 715 w, 748 w, 826 m, 1002 m, 1031 s, 1107 w, 1178 s, 3050 br w.

Reaction of Tris(ferrocenyl)phosphine (3) with Iodine. Using the procedure for **6a**, 102 mg (0.40 mmol, 1.0 equiv) of I_2 and 235 mg (0.40 mmol) of **3** were stirred for 16 h in benzene (50 mL) yielding 335 mg (99% yield) of **8a** as an orange-red powder (mp 189−191 °C). Anal. Calcd for $C_{30}H_{27}Fe_3I_2P$: 42.89% C, 3.24% H. Found: 43.05% C, 3.14% H.

^{1}H (CD_2Cl_2): δ 4.37 s (6 H, Cp + one proton of the substituted ring), 4.40 m (1 H), 4.63 m (1 H), 4.81 m (1 H).

^{31}P{^{1}H} (CD_2Cl_2): δ 0.

IR (KBr): 420 cm^{-1} w, 446 w, 468 s, 484 m, 546 w, 575 w, 584 w, 593 w, 620 w, 640 w, 649 w, 659 w, 669 w, 688 m, 744 w, 808 w, 827 m, 1004 m, 1028 m, 1107 w, 1179 m, 2854 w br, 2929 w br, 3065 w br.

UV−vis (CH_2Cl_2): 270 sh, 340 nm.

Using the procedure for **6a**, 160 mg (0.63 mmol, 1.5 equiv) of I_2 and 246 mg (0.42 mmol) of **3** were stirred for 6 h in benzene (30 mL) yielding 365 mg (90% yield) of **8b** as an orange powder (mp 180−183 °C). Anal. Calcd for $C_{30}H_{27}Fe_3I_3P{\cdot}{}^1/_6C_6H_6$: 37.97% C, 2.88% H. Found: 37.49% C, 2.45% H.

^{1}H (CD_2Cl_2): δ 4.35 s (15 H, Cp), 4.60 q (6 H, $J = 1.9$ Hz), 4.84 q (6 H, $J = 1.8$ Hz), 7.35 s, (1 H, C_6H_6).

^{31}P{^{1}H} (CD_2Cl_2): δ 7.2 s.

^{13}C{^{1}H} (CD_2Cl_2): δ 71.8 s, 73.8 d, 74.2 d, 80.0 d, 110 s.

IR (KBr): 467 cm^{-1} s, 487 m, 621 w, 695 w, 827 m, 1001 m, 1026 m, 1056 w, 1107 w, 1178 m, 1194 w, 1303 w, 1364 w, 1410 w, 1955 w br, 3056 w br, 3082 w br.

UV−vis (CH_2Cl_2): 294, 364 nm.

Mossbauer: $\delta = 0.550$ mm/s, $\Delta E^Q = 2.268$ mm/s

Using the procedure for **6a**, 59.2 mg (0.23 mmol, 2.0 equiv) of I_2 and 68.4 mg (0.12 mmol) of **3** were stirred for 2 h in benzene (10 mL) yielding 110 mg (85% yield) of **8c** as an orange powder (mp 195−200 °C). Anal. Calcd for $C_{30}H_{27}Fe_3I_4P{\cdot}{}^1/_6C_6H_6$: 33.61% C, 2.55% H. Found: 33.51% C, 2.59% H.

^{1}H (CD_2Cl_2): δ 4.40 s (15 H, Cp), 4.66 q (6 H, $J = 3$ Hz), 4.92 q (6 H, $J = 3$ Hz), 7.35 s (1 H, C_6H_6).

^{31}P{^{1}H} (CD_2Cl_2): δ 22.9 s.

UV−vis (CH_2Cl_2): $\lambda_{max} = 280$, 364 nm.

Mossbauer: (77 K): δ 0.482 mm/s, $\Delta E^Q = 2.288$ mm/s.

IR (KBr): 463 cm^{-1} s, 543 w, 606 w, 619 w, 651 w, 678 m, 694 sh w, 830 m, 1003 m, 1027 m, 1057 m, 1107 m, 1179 s, 1242 w, 1304 w, 1365 w, 1388 w, 1411 w, 1634 br w, 2349 s, 2363 s, 3085 br w, 3428 br m.

Reaction of Poly(ferrocenylphenylphosphine) (4) with Iodine. Using the procedure for **6a**, 469 mg (1.8 mmol) of I_2 and 360 mg (1.3 mmol) of **4** were stirred for 16 h in benzene (30 mL) yielding 684 mg (82% yield) of **9a** as a brown solid insoluble in benzene and dichloromethane. The product loses I_2 as purple vapor above 230 °C. Anal. Calcd for $C_{16}H_{13}FeI_3P{\cdot}{}^1/_6C_6H_6$: 29.75% C, 2.16% H. Found: 29.57% C, 2.12% H.

IR (KBr): 469 cm^{-1} s, 490 s, 509 w, 556 w, 616 w, 690 w, 708 w, 749 w, 822 m, 1003 w, 1028 w, 1055 w, 1065 w, 1100 w, 1184 m, 1308 w, 1365 w, 1388 w, 1409 w, 1434 m, 1475 w, 2854 w br, 2922 w br, 2962 w br, 2962 w br, 3051 w br, 3087 w br.

Using the procedure for **6a**, 76.3 mg (0.30 mmol) of I_2 and 43.9 mg (0.15 mmol) of **4** were stirred for 16 h in benzene (30 mL) yielding 99 mg (82% yield) of **9b** as a brown solid insoluble in benzene and dichloromethane (mp 124−128 °C). Anal. Calcd for $C_{16}H_{13}FeI_4P$: 24.03% C, 1.64% H. Found, 24.30% C, 1.65% H.

^{1}H NMR (DMSO-d_6): 4.48 br (8 H), 7.51 br (5 H).

Mossbauer (77 K): δ 0.500 mm/s, $\Delta E^Q = 2.292$ mm/s.

IR (KBr): 460 cm^{-1} s, 550 m, 576 m, 619 m, 686 m, 717 m, 743 m, 831 s, 879 w, 910 w, 996 sh w, 1059 s, 1094 s, 1261 s, 1305 w, 1357 w, 1369 w, 1414 w, 1434 m, 1627 br w, 3087 br w, 3418 br m.

Reaction of Diferrocenyl(phenyl)phosphine Oxide (5) with 2.0 Equiv of Iodine. Using the procedure for **6a**, 107 mg (0.42 mmol) of I_2 and 105 mg (0.21 mmol) of **5** were stirred for 16 h in benzene (20 mL) yielding 89 mg (42% yield) of **10** as a black powder. Anal. Calcd for $C_{26}H_{23}FeI_3OP{\cdot}{}^1/_2C_6H_6$: 38.11% C, 2.80% H. Found: 38.22% C, 2.92% H.

^{1}H (CD_2Cl_2): 4.31 s (10 H, Cp), 4.42 br s (2 H), 4.6 br s (2 H), 4.7 br s (2 H), 4.8 br s (2 H), 7.3−7.8 br signals (8 H, C_6H_6, PPh).

^{31}P{^{1}H} (CD_2Cl_2): δ 51 br s.

UV−vis (CH_2Cl_2): $\lambda_{max} = 294$, 364 nm with a tail at ≈500 nm.

Mossbauer (77 K): $\delta = 0.387$ mm/s, $\Delta E^Q = 2.26$ mm/s; (298 K) $\delta = 0.468$ mm/s, $\Delta E^Q = 2.371$ mm/s.

IR (KBr): 480 cm^{-1} m, 575 m, 622 w, 695 w, 717 w, 751 w, 826 sh w, 870 br m, 1003 w, 1028 w, 1107 w, 1188 m, 1307 w, 1384 w, 1463 m, 2850 s, 2925 s, 2955 sh m.

Reaction of Diferrocenyl(phenyl)phosphine Oxide (5) with 1.0 Equiv of 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). An orange solution of 50.1 mg (0.122 mmol) of DDQ in benzene (20 mL) was added dropwise to a yellow solution of 97.4 mg (0.20 mmol) of **5** in benzene (20 mL) at ambient temperature. Formation of a dark precipitate was observed after several days. The orange supernatant was decanted and the brown precipitate was washed with 2 × 10 mL of benzene. The brown powder was dried under vacuum, yielding 47 mg (47% yield) of **11** as a brown solid (mp >280 °C, d). Anal. Calcd for $C_{42}H_{23}Cl_4Fe_2N_4O_5P$: 53.21% C, 2.45% H, 5.91% N. Found: 52.36% C, 2.34% H, 4.72% N.

UV−vis (CH_2Cl_2): $\lambda_{max} = 254$ nm ($\epsilon = 64\,000$), 338 (6800), 355 (6600), 582 (4120).

IR (KBr): 425 cm^{-1} w, 454 w, 480 m, 542 s, 575 w, 697 s, 721 s, 753 m, 789 w, 822 w, 904 w, 999 m, 1033 m, 1072 m, 1095 sh, 1121, 1163 w, 1189 s, 1352 s, 1412 s, 1560 br w, 1627 br w, 2227 w, 3076 w, 3095 w, 3446 br m.

Mossbauer (77 K): $\delta = 0.498$ mm/s, $\Delta E^Q = 2.322$ mm/s, $\delta = 0.465$ mm/s, $\Delta E^Q = 0.935$ mm/s.

Reaction of Ferrocene with DDQ.[15] Addition of a solution of 237 mg (1.0 mmol) of DDQ in benzene (8 mL) to a solution of 199 mg (1.1 mmol) of ferrocene in benzene (8 mL) at ambient temperature precipitates dark brown [Cp_2Fe][DDQ] as described in the literature. The product was collected by filtration, washed with hexane, and dried under vacuum. The yield was nearly quantitative. The product is essentially insoluble in all common solvents.

IR (KBr): 493 cm^{-1} w, 782 m, 848 m, 1041 m, 1182 m, 1416 w, 1457 w, 1543 s, 1580 s, 2209 m, 3079 m, 3116 m.

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(15) Brandon, R. L.; Osiecki, J. H.; Ottenberg, A. *J. Org. Chem.* **1966**, *31*, 1214.

Reaction of Ferrocene with Iodine.[30] A solution of 1280 mg (5.1 mmol) of I_2 in benzene (35 mL) was added to a solution of 500 mg (2.7 mmol) of ferrocene in benzene (15 mL). Ferricenium triiodide precipitates immediately. The purple supernatant containing the excess I_2 was decanted and the solid was washed with benzene until the washings were colorless. The product was dried under vacuum. Yield was nearly quantitative.

UV−vis (CH_2Cl_2): $\lambda_{max} = 294$, 364, and 500 nm.[30]

IR (KBr): 849 cm^{-1} s, 1006 m, 1110 w, 1412 m, 3098 m.

Reaction of Biferrocene with DDQ.[39] Addition of a solution of 41 mg (0.18 mmol) of DDQ in benzene (15 mL) to a solution of 115 mg (0.36 mmol) of biferrocene in benzene (15 mL) at ambient temperature precipitates dark brown [$CpFe(C_5H_4{-}C_5H_4)FeCp$][DDQ] as described in the literature. The solvent was evaporated under vacuum, and the precipitate was washed with hexane and dried under vacuum. The yield was nearly quantitative. The product is sparingly soluble (≤ 0.1 mM) in CH_2Cl_2.

IR (KBr): 435 cm^{-1} w, 475 w, 782 w, 819 w, 850 w, 1002 w, 1046 w, 1110 w, 1190 w, 1250 w, 1410 w, 1420 w, 1493 m, 1508 m, 1542 m, 1576 s, 2212 m, 3115 m.

UV−vis (CH_2Cl_2): 292 nm ($\epsilon = 10\,700$), 348 (6300), 434 (3440), 458 (3460), 548 (3068), 586 (3234).

Electrochemical Measurements. Oxidation potentials of **1**−**5** were determined on a BAS 100B electrochemical analyzer in CH_2Cl_2, CH_3CN, and 5% CH_2Cl_2/CH_3CN (v/v) solution (2 mM) containing 0.1−0.2 M [$^nBu_4N$][ClO_4] or [$^nBu_4N$][BF_4] as the supporting electrolyte. A 1.2-mm Au or 3-mm Pt disk working electrode (BAS), Pt counter electrode, and Ag/Ag^+ reference electrodes (Ag wire in 10 mM $AgNO_3$ and 0.1 M[NEt_4][BF_4] in CH_3CN)[10] were used. All experiments were performed under a nitrogen or argon atmosphere at a scan rate of 100 mV/s.

Conductivity Experiments. Solutions of **1**−**5** (0.010 M in 1,2-dichloroethane) were titrated with a solution of I_2 (0.089 M in 1,2-$C_2H_4Cl_2$). The resistivity of the resulting solution was determined using a Beckman Instruments model RC 16B2 conductivity bridge. Molar conductivities (cm^2/mol-Ω) of the solutions were calculated by literature methods.[16]

Titration of 1 and 3 with Iodine. Solutions of **1**, **3**, and iodine were prepared with ratios of I_2 to ferrocenyl(phenyl)phosphine equaling 0.5, 1, 1.5, 2, and 4:1 under argon in 5-mm NMR tubes equipped with Teflon valves in CH_2Cl_2. ^{31}P NMR spectra were recorded within 2 h of reaction and again after 24 h. The spectra were unchanged over this time period. The same samples were then analyzed by Raman spectroscopy on a SPEX-1877 triple spectrometer using a Coherent INNOVA 302 Kr^+ ion excitation source operating at 100 mW of power and a liquid-nitrogen-cooled CCD detector (Princeton Instruments). A Princeton Photonics Instruments Raman 101 spinner was used to spin the samples.

Results

Electrochemistry. The oxidation potentials of **1**−**4**, triphenylphosphine, and iodine were determined by cyclic voltammetry in dichloromethane, acetonitrile, and 5% CH_2Cl_2/CH_3CN solution with [$^nBu_4N$][ClO_4] or [$^nBu_4N$][BF_4] as the supporting electrolyte.[17] The results are summarized in Table 2. These data confirm that **1**−**3** are harder to oxidize than ferrocene (by ≈100 mV), but are considerably easier to oxidize than PPh_3. Poly(ferrocenylphenylphosphine) **4** oxidizes at essentially the same potential as **3** does in CH_2Cl_2. The electrochemical potentials for **1** and **2** are consistent with literature data.[4,7,10] Where comparisons are possible, electrochemical potentials in methylene chloride are slightly more positive than potentials in acetonitrile. A similar solvent dependence has been observed for oxidation potentials of alkylferrocenes.[18] The first oxidation potential for **3** is identical to that reported by Kotz and coworkers[4] but differs from the more recent value reported by Kagan et al.[7] by 100 mV. Differences in the supporting electrolyte ($LiClO_4$ vs [$^nBu_4N$][ClO_4]) and solvent may contribute to this discrepancy.

Table 2. Electrochemical Data for **1**−**5**

compound	$E_{1/2}$ (mV)[a]			solvent
Fc	92			CH_3CN
$FcPPh_2$ (**1**)	196			CH_3CN
Fc_2PPh (**2**)	180[b]	360	509	CH_3CN
Fc_3P (**3**)	352[b]	620[b]	782[b]	CH_2Cl_2
$[FcPPh]_x$ (**4**)	366[b]	731[b]	905[b]	CH_2Cl_2
$Fc_2P({=}O)Ph$ (**5**)	480[b]	689[b]		CH_3CN/CH_2Cl_2 (5%)
PPh_3	1090			CH_3CN
I_2	357			CH_3CN
	435			CH_3CN/CH_2Cl_2 (5%)
DDQ	534			CH_3CN/CH_2Cl_2 (5%)

[a] Experimental conditions: 2 mM solution containing 0.1−0.2 M [$^nBu_4N$][ClO_4] as the supporting electrolyte. Potentials relative to Ag/Ag^+ at a scan rate 100 mV/s. [b] Irreversible.

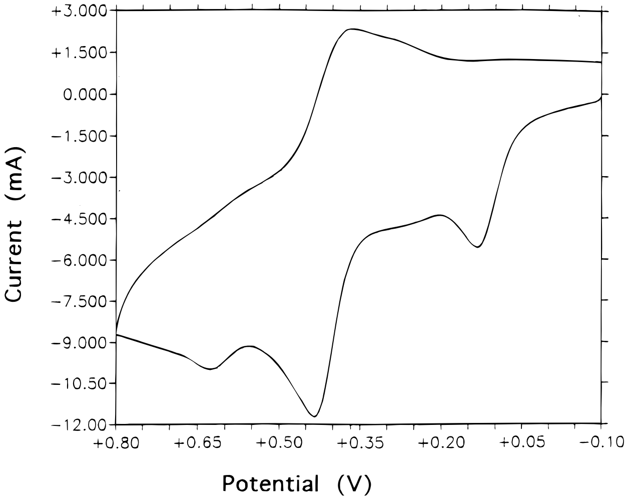

Figure 1. Cyclic voltammogram of Fc_2PPh, **2**.

The first oxidation wave for **1** in acetonitrile is reversible, consistent with conditions reported in the literature.[4] A second oxidation wave is not observed in acetonitrile although an irreversible oxidation at extremely positive potentials (+1400 mV vs SCE) is reported in acetonitrile containing 5% CH_2Cl_2.[8] At the scan rates used in our studies, the first oxidation of **2** in CH_3CN is irreversible even when the potential is reversed immediately after oxidation is detected (Figure 1). The second oxidation of **2** appears to be reversible ($\Delta E_{ia,\,ic} = 60$ mV) but the third oxidation is again irreversible. Others report[4] that both the first and second oxidations in **2** are reversible in CH_2Cl_2 but a third oxidation is not observed. Both **3** and **4** have insufficient solubility in pure acetonitrile for cyclic voltammetry studies. Three irreversible oxidations are observed for **3** in CH_2Cl_2 consistent with studies by Kotz et al.[4] Our results and those from Kagan's group[8] indicate a significantly larger separation between the three oxidation steps than that reported in the Kotz work.[4] A clear fourth oxidation wave is not observed for **3**, but the peak current for the final oxidation was larger than those for the first and second waves, suggesting that more than one electron may be transferred in this step. The irreversible behavior of **3** is consistent with adsorption of the oxidized product at the electrode as previously reported.[4] The cyclic voltammogram of **4** shows three irreversible oxidation waves, although the second

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(16) Shoemaker, D. P.; Garland, C. W.; Steinfeld, J. I. *Experiments In Physical Chemistry*; McGraw-Hill: New York, 1974.

(17) Subject to solubility considerations.

(18) Zanello, P.; Cinquantini, A.; Mangani, S.; Opromolla, G.; Pardi, L.; Janiak, C.; Rausch, M. D. *J. Organomet. Chem.* **1994**, *471*, 171.

oxidation appears as a shoulder on the final oxidation wave. Adsorption at the electrode again affects the electrochemistry.

Conductivity Studies. The molar conductivity of 1,2-dichloroethane solutions of **1**−**3** increases sharply when titrated with iodine leveling off after the addition of >2 equiv of oxidant. The molar conductivity of the final solution ($\Lambda_M \approx 20-25$ cm^2 Ω^{-1} mol^{-1}) in each case is consistent with formation of a 1:1 electrolyte after comparison with the molar conductivity of dichloroethane solutions of [NEt_4][Br] at comparable concentrations. The molar conductivities of the solutions are also similar to that of [$(FcPPh_2)_2Co(CO)_3$][BPh_4] in nitromethane.[3]

A dark precipitate forms immediately upon addition of the first aliquot of I_2 to a solution of poly(ferrocenylphenylphosphine) (**4**) in dichloroethane. Although a small increase in molar conductivity is observed, the presence of undissolved solids does not allow for comparison with the data obtained for **1**−**3**.

Titration of Ferrocenyl(phenyl)phosphines with Iodine. The reaction between ferrocenyl(phenyl)phosphines and iodine can be followed by ^{31}P NMR spectroscopy. A single resonance is observed at room temperature in each case. A steady downfield shift in the ^{31}P NMR resonance from −42 to 23 ppm is observed up to an I_2 to **3** ratio of 2:1. Reaction with additional I_2 up to a 4:1 ratio of I_2 to **3** leads to a much smaller downfield shift in the ^{31}P resonance from 23 to 26 ppm. A similar pattern is observed for titration of $FcPPh_2$ (**1**) with I_2. The results are consistent with the formation of a 2:1 complex between iodine and **1** or **3**.

Raman spectra of solutions containing a 1:1 ratio of I_2:**3** in CH_2Cl_2 have absorptions at 168 and 209 cm^{-1}. Absorptions in the 145−204 cm^{-1} range are assigned to P−I stretching in iodine complexes of aryl and alkyl phosphines, suggesting a similar assignment for the 168 cm^{-1} absorption in **3**.[19−22] The absorption at 209 cm^{-1} is assigned to free iodine.[22] An additional absorption at 288 cm^{-1} remains unassigned. Two different absorptions are observed at 226 and 337 cm^{-1} in solutions containing a 2:1 ratio of I_2 to **3**. It is possible that one of these peaks arises from ν(P−I) in [Fc_3PI][I_3]. The P−I stretch at 159 cm^{-1} in the Raman spectrum of $Ph_3P{\bullet}I_2$ is shifted to a higher frequency in [Ph_3PI][I_3] where either the 184 or the 202 cm^{-1} absorption corresponds to ν(P−I).[22]

Synthesis and Characterization of Triiodide Salts. The electrochemical data in Table 2 suggest that compounds **1**−**4** should all undergo chemical oxidation with iodine. Three ratios of iodine to ferrocenyl(phenyl)phosphines **1**−**3** (1:1, 1.5:1, and 2:1) were investigated. Rapid precipitation of diamagnetic iodide salts, **6**−**8**, is observed upon addition of benzene solutions of iodine to benzene solutions of **1**−**3** at ambient temperature for the entire range of iodine-to-iron ratios. Benzene was chosen as the solvent because of the ease of isolation of the products by filtration. Products **7** and **8** are generally isolated in good yields (75−90%) by decanting the supernatant, and washing the product with benzene and drying it in a vacuum. Compounds **6a**−**c** prove to be oils or sticky solids even after repeated washings and drying at 80 mTorr contributing to the lower isolated yields for this product. Compound **6c** does appear to solidify after storage for several weeks in a glovebox and contains a mixture of products by NMR. Attempts at separating and purifying **6c** proved unsuccessful. Polymer **4** was reacted with iodine in dichloromethane because it is insoluble in benzene. Evaporation of the solvent and washing the product with benzene yields **9**. Acceptable elemental analyses were obtained for the triiodide salts **7**−**9**. Analysis of compounds **7** and **8** indicated that they retained variable amounts of benzene even after being dried under vacuum. The presence of benzene in **7** and **8** is confirmed by ^{1}H NMR spectroscopy.

^{1}H NMR spectra of **6**−**8** (Table 3) consist of a singlet for the five protons on the C_5H_5 ring and either two (**6b**,**c** and **8b**,**c**), three (**6a** and **8a**), or four (**7a**−**c**) multiplets assigned to the protons of the phosphorus-substituted cyclopentadienyl rings. All of the resonances are shifted downfield relative to the starting ferrocene compounds. A similar downfield shift for all resonances was observed in phosphonium salts of the general formula [$Fc_xPPh_{3-x}Me$][I].[3] Within a series of compounds differing only in the ratio of iodine to iron (e.g., **7a**−**c**) the largest downfield shifts in the ^{1}H resonances are observed for the product with the greatest amount of iodine (e.g., **7c**). By analogy to NMR studies of **1**−**3**, the furthest downfield resonances of the substituted ring protons are assigned to protons attached to the 3 and 4 positions of the ring (Scheme 1). Three sets of resonances for the substituted ring protons in **6a** and **8a** result from an overlap of the Cp proton with one of the CH protons of the substituted rings.

The four resonances for the substituted ring protons in **7** are the result of chemical inequivalence of the four protons of the unsubstituted ring from slow inversion about the phosphorus. The resonances for the substituted ring protons in **6**−**8** show a more complicated splitting than the expected AB pattern. Multiplets are observed for **6**, whereas quartets are observed for **7** and **8**. Quartets can be rationalized by considering coupling to the adjacent as well as coupling to the cross-ring protons as proposed in the literature for **1**−**3**.[3]

The ^{31}P NMR spectra of **6**−**8** consist of singlet resonances shifted downfield from the resonances of the starting materials. The spectra for **6** again reveal the presence of a mixture of products. The downfield progression of the ^{31}P resonances within a series of compounds (e.g., **8a**−**c**) was discussed in the previous section. Identical spectra are obtained for compounds prepared from **1**−**3** and 2 equiv of iodine in dichloromethane.

Solutions of **6**−**8** in CH_2Cl_2 are yellow rather than the characteristic blue-green color of the ferricenium ion in [Fc][BF_4]. An absorption in the visible region of the spectrum at 444 nm for **1**−**3** disappears upon reaction with iodine. Absorptions at 620 and 498 nm observed for [Fc][BF_4] and [Fc][I_3], respectively, are absent in the UV−vis spectrum. A strong absorption in the UV at 254 nm is replaced by two absorptions at 294 and 364 nm characteristic of the I_3^- anion in **6c**−**8c**.[23] The latter absorption has a broad "tail" extending out to 550 nm. The absorptions assigned to the I_3^- ion obscure the region where the charge-transfer bands of ferricenium ion in [Fc][BF_4] (316 and 364 nm) are typically observed. These charge-transfer bands are also not observed in [Fc][I_3]. In products **7a**,**b** and **8a**,**b** two absorptions are observed at slightly higher energies than those in **7c**−**8c** (e.g., 280 and 355 nm in **7a**,**b**). A similar trend is seen in the UV−vis spectra of $Ph_3P{\bullet}I_2$.[23] In **6a** and **b**, the absorptions at ≈270−290 nm are obscured by intenseabsorptions at 255 nm from the ferrocenyl(diphenyl)phosphine moiety.

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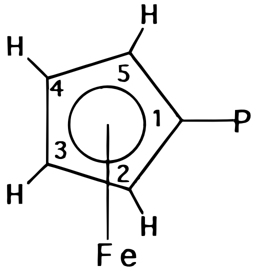
Table 3. NMR Spectral Data for Compounds **6**−**8** and **10** in CD_2Cl_2

compound	^1H	^{31}P
$FcPPh_2I_2$ (**6a**)	4.30 s (6 H, Cp + 1 H), 4.38 br m (1 H), 4.52 br m (1 H), 4.76 br m (1 H), 7.35 br m (4 H), 7. 39 br m (6 H)	−11.5
$FcPPh_2I_{3/2}$ (**6b**)	4.26 s (5H, Cp), 4.46 s (2H, $H_{3,4}$), 4.76 s (2H, $H_{2,5}$), 7.36 s (3H, C_6H_6), 7.6−7.8 m (10H, PPh_2)	6.9
$[FcPPh_2I][I_3]$ (**6c**)	4.45 s (5 H, Cp), 4.60 q (2 H, $H_{3,4}$ $J_{23} = 3$ Hz, $J_{34} = 2$ Hz), 5.02 q (2 H, $H_{2,5}$) 7.6−7.8 (10 H, Ph)	15.1
$Fc_2PPhI_2 \cdot 1/3\ C_6H_6$ (**7a**)	4.36 s (10 H, Cp), 4.39 m (2 H), 4.56 m (2 H), 4.75 m (2 H), 4.79 m (2 H), 7.62 m (2H), 7.69−7.8 m (3 H)	−5.9
$Fc_2PPhI_{3/2} \cdot 1/2\ C_6H_6$ (**7b**)	4.38 s (10 H, Cp), 4.47 m (2 H), 4.63 m (2 H), 4.84 m (2 H), 4.88 m (2 H), 7.35 s (3 H, C_6H_6) 7.62 m (2 H), 7.69−7.8 m (3 H)	3.7
$[Fc_2PPhI][I_3] \cdot C_6H_6$ (**7c**)	4.44 s (10 H, Cp), 4.57 br m (2 H), 4.72 br m (2 H), 4.96 br m (2 H), 5.00 br m (2 H), 7.35 s (3 H, C_6H_6) 7.69 t (3 H, Ph), 7.77 t (2 H, Ph), 7.35 s (6 H, C_6H_6)	19.2
Fc_3PI_2 (**8a**)	4.37 s (6 H, Cp + 1 H), 4.40 m (1 H), 4.63 m (1 H), 4.81 m (1 H), 7.35 s (1 H, C_6H_6)	0
$Fc_3PI_{3/2} \cdot 1/6\ C_6H_6$ (**8b**)	4.35 s (15 H, Cp), 4.60 q (6 H, $J = 1.9$ Hz), 4.84 q (6 H, $J = 1.8$ Hz), 7.35 s (1 H, C_6H_6)	7.2
$[Fc_3PI][I_3] \cdot 1/6\ C_6H_6$ (**8c**)	4.40 s (15 H, Cp), 4.66 q (6 H, H_3 $J_{35} = 3$ Hz, $J_{23} = 4.5$ Hz), 4.92 q (6 H $H_{2,5}$) 7.35 s (1 H, C_6H_6)	22.9
$Fc_2P({=}O)PhI_3 \cdot 1/2\ C_6H_6$ (**10**)	4.31 s (10 H, Cp), 4.42 br s (2 H), 4.7 br s (2 H), 4.8 br s (2 H), 7.3−7.8 br (8 H, Ph, C_6H_6)	51

Scheme 1. Numbering of Phosphorus-Substituted Cp Rings in $Fc_{3-x}PPh_x$



Mossbauer Spectroscopy. Mossbauer spectra of **6**−**9** salts reveal isomer shifts ($\delta \approx 0.45{-}0.50$ mm/s) and quadrupole splittings ($\Delta E^Q \approx 2.30$ mm/s) that are nearly identical to those of the starting materials **1**−**4**. Mossbauer spectra of low-spin iron(II) in ferrocene derivatives consistently show isomer shifts between 0.300 and 0.400 mm/s and quadrupole splits about 2.20−2.30 mm/s.[24] "Ferrocenium-like", low-spin iron(III) compounds typically have isomer shifts similar to that of ferrocene but with much smaller quadrupole splits (≈0.5 mm/s). For example, ferricenium triiodide has an isomer shift of 0.417 mm/s and a quadrupole split of 0.156 mm/s at 300 K.[30] We find no evidence for a species with an isomer shift of 0.380 mm/s and near-zero quadrupole split in the Mossbauer spectrum of **7b** as reported earlier for $[Fc_2PPh][I_3]$.[9] Only for **6c** are additional species detected in the Mossbauer spectrum. A compound with an isomer shift of 0.431 mm/s and zero quadrupole shift suggests the presence of low-spin Fe^{III}. A third compound with Mossbauer parameters typical for low-spin Fe^{II} ($\delta = 0.781$ mm/s and $\Delta E^Q = 1.969$ mm/s) is also observed.

Reaction of Diferrocenyl(phenyl)phosphine Oxide (5) with Iodine and 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). The electrochemistry of **5** shows two oxidations at 0.480 and 0.689 V in acetonitrile containing 5% CH_2Cl_2. The first oxidation is reversible, but the second is irreversible. Comparison with the electrochemical potential of iodine (Table 1) under the same conditions suggests that oxidation of **5** with I_2 should not occur but reaction between **5** and DDQ is favorable.

Addition of 1.5 equiv of iodine to a benzene solution of **5** nevertheless precipitates a dark solid **10** which analyzes for $Fc_2P({=}O)PhI_3 \cdot {}^1/_2C_6H_6$. Room temperature ^1H and ^{31}P spectra of **10** are broadened relative to those observed for **5**−**8**. The ^{31}P resonance for **10** is shifted upfield from 26 ppm in **5** to 51 ppm in **10**. The ^1H NMR spectrum of **10** consists of a singlet for the unsubstituted Cp rings and four broad resonances for the protons of the substituted rings. The peak width at half-height for the Cp resonance increases from <2 Hz in **5** to 25 Hz in **10**. As in **2** and **7**, the two ferrocene groups are inequivalent due to restricted rotation. These resonances are shifted downfield relative to those of diferrocenyl(phenyl)phosphine oxide.

Absorptions at 254 and 440 nm for **5**[25] in the UV−vis spectrum are replaced by absorptions at 294 and 364 nm in **10**. As in compounds **6**−**8**, these absorptions are characteristic of the I_3^- anion. The UV−vis spectrum of **10** does show a broad feature centered at ≈500 nm. This "tail" on the 364 nm absorption is observed at approximately the same wavelength as the 500 nm absorption of $[Fc][I_3]$ but is not clearly resolved from the former.

The infrared spectrum of **10** is very similar to the spectrum of the starting material. A band at 1188 cm^{-1} (KBr) in **10** assigned to the P═O stretch is well within the range of frequencies for P═O vibrations in triaryl and trialkyl phosphine oxides.[26] The P═O stretch in **5** has been reported as 1180

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(24) Greenwood, N. N.; Gibbs, T. C. *Mossbauer Spectroscopy*; Chapman & Hall: London, U.K., 1971.

(25) The same UV−vis absorptions were reported previously: Neuse, E. W. *J. Organomet. Chem.* **1967**, *7*, 349.

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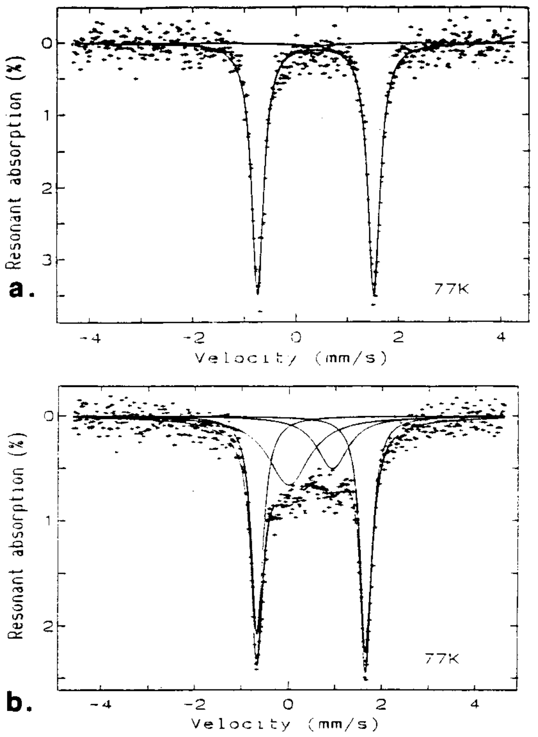

Figure 2. Mossbauer spectra of (a) $Fc_2P({=}O)Ph{\cdot}I_2$ (**10**) and (b.) $Fc_2P({=}O)Ph{\cdot}DDQ$ (**11**) at 77 K.

cm^{-1} in Nujol.[12] We observe two strong absorptions at 1192 and 1178 cm^{-1} in KBr, either of which could be assigned to the P=O stretch in $Fc_2P({=}O)Ph$. The lower energy absorption is also seen in Fc_2PPh (**2**) and in **7** suggesting that the absorption at 1192 cm^{-1} is due to P=O stretching. The out-of-plane bend for ferrocene C−H bonds at 826 cm^{-1} in **10** is essentially unchanged from that of **5**. Absorptions assigned to ferrocene−phosphorus, phosphorus−phenyl, and phenyl group vibrations are observed at energies in the range reported for **5** and monosubstituted ferrocenes.[12] Mossbauer spectra of **10** at both 77 and 293 K clearly show the presence of low-spin iron(II) ($\delta = 0.387$ mm/s, $\Delta E^{Q} = 2.26$ mm/s; $\delta = 0.468$ mm/s, $\Delta E^{Q} = 2.371$ mm/s, respectively, in Figure 2a).

Titration of **5** with iodine in dichloroethane leads to an increase in the molar conductivity but the titration profile and final molar conductivity are quite different from those of reactions between I_2 and **1**−**3**. The molar conductivity increases linearly to a value of 9 cm^2/mol-Ω at an I_2/**5** ratio of 3:1. This is different from the sharp rise in Λ upon addition of the second equivalent of I_2 to **2**. A slower increase to $\approx$12 cm^2/mol-Ω is observed as the I_2 to **5** ratio reaches 9:1, a value 25% lower than that for a similar ratio of I_2 to **2**.

Addition of an orange benzene solution of DDQ to a yellow solution of **5** precipitates a paramagnetic, dark brown solid **11** after being stirred at room temperature for several days. For comparison, the reaction between ferrocene and DDQ to form $[Cp_2Fe][DDQ]$ is instantaneous in benzene. Microanalysis of **11** indicates a 1:2 stoichiometry of **5** to DDQ, $[Fc_2P({=}O)Ph][DDQ]_2$. Solid **11** is sparingly soluble in 1,2-dichloroethane and other common solvents, thereby preventing measurement of molar conductivity. The infrared spectrum of **11** has a sharp, strong absorption at 1189 cm^{-1} which is assigned to the P=O stretch. The P=O stretch occurs at slightly lower energy than that in $Fc_2P({=}O)Ph$. Bands assigned to ferrocene−phosphine, phenyl−phosphine, ferrocene C−C stretching, and C−H out-of-plane bending for **5** in the literature and in our measurements are essentially unchanged in **11**. The ν_{CN} at 2226 cm^{-1} is observed at lower energy than it is in DDQ ($\nu_{CN} = 2233$ cm^{-1}). The intense C=O stretch at 1676 cm^{-1} and the ν(C=C) at 1550 cm^{-1} in DDQ are missing in **11**. The change in ν_{CN} in **11** is much smaller than that in $[Cp_2Fe][DDQ]$ (2209 cm^{-1}) or $[CpFe(C_5H_4{-}C_5H_4)FeCp][DDQ]$ (2212 cm^{-1}). Strong aromatic $\nu_{C=C}$ of the $DDQ^{\bullet-}$ radical anion at 1580 and 1543 cm^{-1} in $[Cp_2Fe][DDQ]$[27] or 1576 and 1542 cm^{-1} in $[CpFe(C_5H_4{-}C_5H_4)FeCp][DDQ]$ are absent in **11**.

The UV−vis spectra of **11** in acetonitrile and dichloromethane are dominated by absorptions by the DDQ portions of the molecules. Four absorptions at $\lambda_{max} = 258$, 346, 434, and 546 nm and the corresponding extinction coefficients are similar to those observed for $[CpFe(C_5H_4{-}C_5H_4)FeCp][DDQ]$ and other ferrocenium complexes containing the $DDQ^{\bullet-}$ radical anion.[27]

Significantly, the Mossbauer spectra (Figure 2b) at 77 K reveal that **11** contains primarily low-spin Fe^{II} with an isomer shift of 0.498 mm/s and a quadrupole split of 2.322 mm/s. There is clear evidence for another iron species with an isomer shift of 0.465 mm/s and a quadrupole split of 0.935 mm/s. The value of the quadrupole split is smaller than that in the valence detrapped, mixed valent $Fe^{II/III}$ species ("$Fe^{2.5}$") observed in $[Cp_2{*}Fe_2(pentalene)][BF_4]$ ($\delta = 0.41$ mm/s, $\Delta E^{Q} = 1.30$ mm/s at 4.2 K) and $[Cp_2{*}Fe_2(s\text{-indacene})][BF_4]$ ($\delta = 0.55$ mm/s, $\Delta E^{Q} = 1.67$ mm/s at 4.8 K), but larger than that in low-spin Fe^{III} in $[Cp_2{*}Fe_2(pentalene)][BF_4]_2$ ($\delta = 0.54$ mm/s, $\Delta E^{Q} = 0.80$ mm/s at 4.2 K).[28] The Mossbauer parameters for **11** are very different from those in valence trapped $[Cp_2{*}Fe_2(as\text{-indacene})][BF_4]$ ($\delta = 0.49$ mm/s, $\Delta E^{Q} = 0.43$ mm/s and $\delta = 0.50$ mm/s, $\Delta E^{Q} = 2.29$ mm/s at 77 K). The fraction of mixed valent $Fe^{II/III}$ species increases at ambient temperature.

Discussion

Taken together, the results of our molar conductivity, NMR, UV−vis, and Mossbauer spectroscopy studies demonstrate that the final product of reactions between ferrocenyl(phenyl)-phosphines and iodine are iodophosphonium salts and not ferricenium salts. The observation of well-resolved NMR spectra is consistent with diamagnetic, low-spin Fe^{II} complexes rather than paramagnetic, low-spin, Fe^{III} ferricenium complexes such as ferricenium triiodide, $[Fc^+][I_3^-]$.[29] Mossbauer spectroscopy confirms that the products contain low-spin Fe^{II}.

Compounds **7**−**9** closely resemble the iodophosphonium salt isolated from reactions between triphenylphosphine and iodine (eq 1).[22] Reaction of PPh_3 with 1 equiv of iodine produces a

$$\mathrm{Ph_3P} \xrightarrow{I_2} [\mathrm{Ph_3PI}][\mathrm{I}] \xrightarrow{I_2} [\mathrm{Ph_3PI}][\mathrm{I_3}] \tag{1}$$

charge-transfer adduct between I^- and Ph_3PI^+ which reacts with additional iodine to form iodotriphenylphosphonium triiodide.[22] Like $[Ph_3PI][I_3]$, **7** and **8** are 1:1 electrolytes in dichloroethane solution and have UV spectra consistent with the presence of triiodide ions. Based on Mossbauer evidence, it seems likely that poly(ferrocenylphenylphosphine) **4** also forms an iodo-(ferrocenylphenylphosphonium) polymer similar to poly-[{ferrocenyl(phenyl) (methyl)phosphonium}triflate].[30] Proposed structures for **6**−**9** are shown in Figure 3. Not surprisingly,

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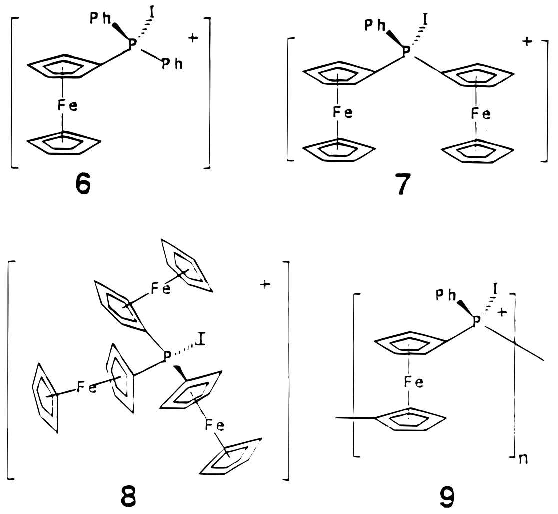

Figure 3. Proposed structures for iodo(ferrocenylphenyl)phosphonium salts **6**−**9** with [I_n^-] anions (n = 1, 3).

compounds **7** and **8** resemble the diamagnetic, methyl iodide salts of **2** and **3** reported over two decades ago.[3] The first member of the series, **6**, is always isolated as a mixture of compounds. In many respects, **6** is similar to **7** and **8** in its NMR spectroscopy, molar conductivity, UV−vis, and IR spectroscopy. The major component of **6** is likely to have a structure similar to those shown for **7**−**9** in Figure 3. The Mossbauer spectrum of **6**, however, reveals the presence of a mixture of iron compounds. The major component is a low-spin Fe^{II} compound similar to **7**−**9**. There is evidence for low-spin Fe^{III} as well as a second low-spin Fe^{II} species with a different isomer shift and quadrupole split. Further characterization of these three complexes has been thwarted by our inability to separate and purify **6**.

The reported isolation of [Fc_2PPh][I_3][9] prompted the synthesis of **6b**−**9b**. Our results for the reaction between ferrocenyl(phenyl)phosphines **1**−**4** and 2 equiv of iodine are different from those reported in the literature. Whereas we find no evidence for low-spin Fe^{III} in the Mossbauer spectrum of our samples of **7b**, Wei and co-workers report that reaction of **2** with 1.5 equiv of I_2 produces a compound containing at least some low-spin Fe^{III}. The percent of oxidation at iron is not reported.

One possible explanation we considered for the disparity in the results is the reaction of small amounts of diferrocenyl(phenyl)phosphine oxide, **5**, present as an impurity in commercial samples of **2**, with iodine. In principle, the reaction at the phosphorus seen in **2** is avoided by oxidation of the phosphorus(III) to phosphorus(V). Reaction of **5** with I_2 produces a dark solid **10** with a formula $Fc_2P({=}O)Ph{\cdot}I_3$ containing only low-spin iron(II) at both ambient temperature and 77 K by Mossbauer spectroscopy. Clearly, the ferrocene has not been oxidized to ferricenium. It is highly unlikely that further reaction occurs at the phosphorus in **5** because there is only one documented example of anodic oxidation of a formally phosphorus(V) compound.[31] Reaction of triphenylphosphine chalcogenides $Ph_3P{=}E$ (E = O, S, Se) with iodine, however, yields products with a 1:1 stoichiometry between phosphine and iodine.[32,33] The $Ph_3P{=}O{\cdot}I_2$ complex readily loses iodine, but the sulfur and selenium derivatives have been crystallographically characterized and contain monomeric $Ph_3P{=}E{-}I{-}I$ units with a linear E−I−I linkage (Figure 4a). The structure of a 2:3 adduct between $Ph_3P{=}S$ and I_2 (Figure 4b) was determined earlier and found to contain two molecules of $Ph_3P{=}S{\cdot}I_2$ linked by a third I_2 corresponding to an empirical formula $Ph_3P{=}SI_3$.[34]

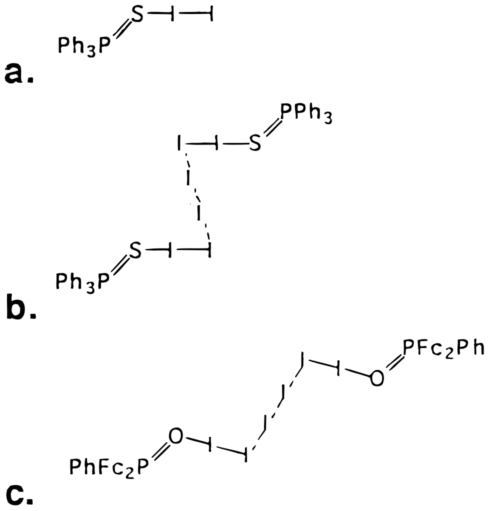

Figure 4. Structures for (a) $Ph_3P{=}S{\cdot}I_2$ and (b) $(Ph_3P{=}S{\cdot}I_2)_2(\mu\text{-}I_2)$, and (c) one possible structure for **10**.

The similarity in reaction chemistry of $Fc_{3-x}PPh_x$ (**1**−**3**) and triphenylphosphine with iodine makes it tempting to draw similar conclusions for the corresponding phosphine oxides **5** and $Ph_3P{=}O$. In the absence of an X-ray structure, structural assignments for **10** must rely on spectroscopy. The ν(P=O) for $Ph_3P{=}O{\cdot}I_2$ occurs at lower energy than for the parent $Ph_3P{=}O$ by 15 cm^{-1}. A strong absorption corresponding to the P=O stretch in **5** is observed at 1192 cm^{-1} in KBr. In compound **10** a less intense absorption at 1188 cm^{-1} is consistent with the donation of electron density from O to the iodine. The UV−vis spectrum of $Ph_3P{=}O{\cdot}I_2$[35] showed two absorptions typical of the I_3^- anion and identical to those observed for **10**. Further support for the presence of I_3^- in **10** is found in the molar conductivity data ($\Lambda \approx 9$ cm^2/mol-Ω). The similarity of the spectroscopy for **10** and $Ph_3P{=}O{\cdot}I_2$ leads us to propose the structure for **10** in Figure 4c as a charge-transfer complex between iodine and the oxygen of **5**. The stoichiometry of **10** ($Fc_2P({=}O)Ph{\cdot}I_3$) further suggests the dimeric structure seen for $(Ph_3P{=}S)_2(I_2)_3$.

Ferrocene and alkylferrocenes readily form π-complexes with *p*-benzoquinone, chloranil, tetracyanoethylene, and perfluorophenanthrene.[36,37] In cases where the electrochemical potentials of the acceptors do not allow for electron transfer from ferrocene, neutral complexes are isolated. Stronger oxidants such as DDQ oxidize ferrocene,[15] biferrocene,[38] and decamethylferrocene[27] yielding ionic, charge-transfer complexes containing low-spin Fe^{III} and the $DDQ^{\bullet-}$ radical anion. The crystallographically characterized [$Cp^*{}_2Fe^{\bullet+}$][$DDQ^{\bullet-}$] adopts the

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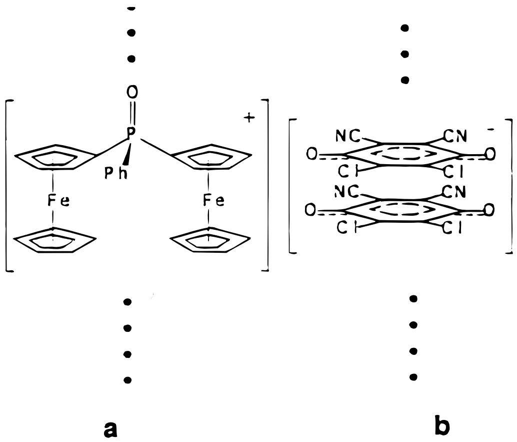

Figure 5. Proposed segregated stack Structures for complex **11**.

"mixed stack" structure of alternating donor and acceptor molecules arranged in linear $\cdots\cdot D^{+}A^{-}D^{+}A^{-}D^{+}A^{-}D^{+}A^{-}\cdots$ chains. Diferrocenyl(phenyl)phosphine oxide **5** is harder to oxidize than ferrocene but the electrochemical potentials of **5** and DDQ indicate that electron transfer is favorable. Unlike the typical 1:1 ratio in metallocene DDQ salts, reaction of **5** with DDQ precipitates **11** containing a 1:2 ratio of **5** to DDQ. The same stoichiometry is observed in a related ferrocene donor−acceptor complex, $[Fe(C_5H_4Me)_2][TCNQ]_2$.[3939] The latter compound has been structurally characterized and adopts a segregated stack structure containing parallel chains of donor cations and acceptor anions.

The insolubility of **11** has prevented the growth of single crystals for X-ray structure determination. Some insight into the structure of **11** is obtained from spectroscopy. UV−vis spectra of **11** are consistent with the presence of $DDQ^{\bullet-}$ radical anions as in other metallocene DDQ salts.[27,28] The absence of the carbonyl stretch in **11** is consistent with electron transfer from iron to DDQ. Electrochemical potentials suggest that oxidation of only one iron center in **5** by DDQ is favorable. As a result, both of the DDQs in $[Fc_2P({=}O)Ph][DDQ]_2$ (**11**) are unlikely to be present as $DDQ^{\bullet-}$ radical anions. Interactions between the two DDQ molecules in **11** may be responsible for the differences in the IR spectra of **11** and other DDQ salts of metallocenes. Dimerization of anions in metallocene salts of organic acceptors (e.g., TCNE, TCNQ) is frequently observed in segregated stack structures consisting of parallel $\cdots D^{+}D^{+}D^{+}D^{+}\cdots$ and $\cdots A^{-}A^{-}A^{-}A^{-}\cdots$ chains.[40] Although confirmation of segregated stack structures for metallocene salts of DDQ by X-ray diffraction has not been reported, the dimerization of $DDQ^{\bullet-}$ has been confirmed in a tetrathiafulvalene salt.[41] On this basis, we propose that the structure of complex **11** contains segregated chains of diferrocenyl(phenyl)phosphine oxide radical cations and chains of DDQ units (Figure 5).

The Mossbauer spectra of **11** confirm the presence of two types of iron. The values for the quadrupole split in **11** bear a strong resemblance to valence-averaged "$Fe^{2.5+}$" found in other dinuclear ferrocenes. One interpretation of the Mossbauer spectrum is that **11** is delocalized on the Mossbauer time scale (10^{-6} s). The difference between the first and second oxidation potential for **5** (209 mV) is less than the typical value for delocalized biferrocenes, but is consistent with communication between metal centers on the electrochemical time scale (10^{-3} s). The observation of intervalence charge-transfer bands in the near-IR spectrum of electrochemically generated $\mathbf{5}^{+}$ has been cited[42] as evidence for delocalization in $\mathbf{5}^{+}$.

The Mossbauer spectra of **11** also indicate that electron transfer is incomplete at 77 K. The percentage of oxidized species is less than 50% but appears to increase as the temperature increases. These observations may simply reflect differences in the recoil-free fraction as a function of temperature or a temperature-dependent solid-state redox process in **11** which favors electron transfer from iron to DDQ at higher temperatures and reduction of Fe^{III} at low temperature. Similar spectral changes have been reported for $[Cp^{*}Fe]_2(\mu\text{-pentalene})$ oxygen complexes[43] and recently for polyiodide salts of *N*,*N*′-bis(ferrocenylmethylidene)-*p*-phenylene diamine.[28] Further investigations of the temperature-dependent redox process in **11** by magnetic susceptibility and ESR spectroscopy are in progress.

Conclusions

A combination of NMR, UV−vis, and Mossbauer spectroscopy methods demonstrates that iodine reacts with ferrocenyl(phenyl)phosphines yielding iodo(ferrocenyl)(phenyl)phosphonium salts and not ferricenium salts. The correlation of our results with the electrochemistry of ferrocenyl(phenyl)phosphines is difficult because the potential oxidant has an alternative pathway available. Reactions of ferrocenyl(phenyl)phosphines with oxidants lacking coordinating anions are in progress. The results of these and related spectroelectrochemical studies on ferrocenyl(phenyl)phosphines will be reported in a separate paper. In cases where the phosphorus lone pair is unavailable and electron transfer is feasible, charge-transfer complexes are observed.

Acknowledgment. The authors thank Professor William M. Reiff for assistance in obtaining the Mossbauer spectra.

Supporting Information Available: Mossbauer and NMR spectra of **3** and **8c**, Mossbauer spectra of **6c**, plots of molar conductivity, and ^{31}P chemical shifts as a function of $I_2{:}Fc_{3-x}PPh_x$ ($x = 0-2$). This material is available free of charge via the Internet at http://pubs.acs.org.

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