Inorganica Chimica Acta 450 (2016) 30-38

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Chemical oxidation of ferrocenyl(phenyl)phosphines and ferrocenyl (phenyl)phosphine chalcogenides



^a Department of Chemistry and Chemical Biology, Northeastern University, Boston, MA 02115, United States

^b Department of Chemistry, Colby College, Waterville, ME 04901, United States

^c Department of Chemistry, Wellesley College, Wellesley, MA 02481, United States

ARTICLE INFO

Article history: Received 4 December 2015 Received in revised form 2 May 2016 Accepted 3 May 2016 Available online 11 May 2016

Keywords: Ferrocene Phosphine Electrochemistry Oxidation

ABSTRACT

The electrochemistry of ferrocene-substituted phosphines suggests electron loss from a largely ferrocene-based HOMO with significant phosphorus character rather than the exclusive oxidation of iron. In contrast, studies of the chemical oxidation of ferrocenylphosphines are limited. Reactions between FcPPh₂ (1) and silver salts (AgCF₃CO₂, AgBF₄, and AgOTf) lead to the silver-phosphine complexes [(FcPPh₂)₂Ag][CF₃CO₂] (11), [(FcPPh₂)₃Ag][BF₄] (13), and [(FcPPh₂)₃Ag][OTf] (16), respectively, with no evidence for oxidation of Fe^{II} to Fe^{III}. Compound 13 reacts with traces of water forming FcP(OBF₃)Ph₂ (15) which crystallizes in the Pī space group with *a* = 10.326(4) Å, *b* = 10.326(4) Å, *c* = 17.445(6) Å, α = 104.068(6)°, β = 99.970(7)°, and γ = 100.542(7)°. Reaction of 1 with excess AgOTf, however, yields a green, paramagnetic, Fe^{III} complex: [(FcPPh₂)₃Q][OTf]₂ (17) based on elemental analysis, ESR and Mössbauer spectroscopy. Reaction of 1 with bromine yields paramagnetic FcPh₂Br₃ (10) by ESR spectroscopy. Reactions between ferrocenyl(phenyl)phosphines, Fc_nPPh_{3-n} (1-3, Fc = C₅H₅FeC₅H₄, *n* = 1-3), and sulfur or selenium yield the corresponding ferrocenyl(phenyl)-phosphine chalcogenides, Fc_nP(E) Ph_{3-n} (4-9, *n* = 1-3, E = S, Se). The crystal structures of (FcP(S)Ph₂ (4) are reported; *P*21/*c* space group, *a* = 14.5187(16) Å, *b* = 10.5915(12) Å, *c* = 12.0004(13) Å, α = 90°, β = 96.891(2)°, γ = 90°. Reaction of 4 with bromine is accompanied by the loss of sulfur also yields 10.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

A growing number of reports on the electrochemical oxidation of ferrocene substituted phosphines suggest electron loss occurs from a largely ferrocene-based HOMO with significant phosphorus character rather than oxidation of the iron. These studies include ferrocenyl(phenyl)phosphines Fc_nPPh_{3-n} (**1–3**, where n = 1-3, respectively, and $Fc = C_5H_5FeC_5H_4$) [1], 1,1'-bis(diphenylphosphino)ferrocene (dppf) [2], 1,1'-bis(diisopropylphosphino) ferrocene (dippf) [3], Josiphos [4], and BoPhoz derivatives (e.g. (*R*)-*N*-diphenylphosphino-*N*-methyl-[(*S*)-*N*-(diphenylphosphino)ferrocenyl]ethylamine) [5]. Evidence for electrochemical oxidation of phosphorus in ferrocenes with phosphorus substituted cyclopentadienyl rings has also been reported for phosphinobipyridylferrocenes [6], 1'-(diphenylphosphino)ferrocene carboxylic acid [7], [bis(2-cyclopentadienylethyl)phenylphosphine]iron [8], diphenylphosphineferrocenecarboxaldehyde and its imine derivatives [9]. Nevertheless, the first report of the electrochemical oxidation of ferrocenyl(diphenyl)phosphine, **1**, and [(η^{5} -C₅H₄) CMe₂}₂PCy]Fe describes blue-green solutions after controlled potential coulometry consistent with formation of ferroceniumlike, Fe^{III} cations [10].

The presence of covalent P=O, P=S, or P=Se bonds in ferrocenyl phosphine chalcogenides means the phosphorus lone pair electrons are no longer available and oxidation of the ferrocene should be observed. Consistent with this hypothesis, reversible anodic electrochemistry is observed for $Fc_2P(O)Ph$ while only the first oxidation in Fc_2PPh appears to be reversible [1]. Electrochemistry similar to $Fc_2P(O)Ph$ is reported for dppfO₂, dippfO₂, dppfS₂, dippfS₂ and 1,1'-bis(di^tbutylpropyl-phosphino)ferrocene disulfide, dtbpfS₂ [2b,11]. The corresponding selenides (dppfSe₂, dippfSe₂, dippfSe₂, and Fc_3PSe) [1a,2a,3,11] show irreversible anodic electrochemistry due to rapid reactions of the radical cations on the electrochemical timescale. The observation that the anodic





Inorganica Chimica Acta

^{*} Corresponding author at: Department of Chemistry and Chemical Biology, Northeastern University, 360 Huntington Avenue, Boston, MA 02115, United States. *E-mail address*: r.kirss@neu.edu (R.U. Kirss).

¹ Present address: Cummings School of Veterinary Medicine, North Grafton, MA 01536, United States.

² Present address: Department of Chemistry, Stanford University, 335 Campus Drive Stanford, CA 94305, United States.

electrochemistry of dtbpfSe₂ mimics that of bis(^tbutyl) biphenylphosphine selenide suggests that the ferrocene moiety in phosphinoferrocene chalcogenides may simply act as an aryl group.

The chemical oxidation of ferrocenyl phosphines has received considerably less attention. Reaction of Fc_nPPh_{3-n} and $Fc_2P(O)Ph$ with DDQ yields products containing mostly low spin Fe^{II} with only a trace of low-spin Fe^{III} detected by Mössbauer spectroscopy [1b]. The formation of a Se—Se bond upon chemical oxidation of 1,1'-bis(di-tert-butylpropylphosphino)ferrocene diselenide (dtbpfSe₂) with acetylferrocenium cation is established by the crystal structure of [dtbpfSe₂][BF₄]₂ while [7a] oxidation of Ferro-TANE selenides by [NO][BF₄] is accompanied by loss of selenium [5].

In this paper we explore the reaction of ferrocenyl(phenyl) phosphines, Fc_nPPh_{3-n} (1–3) and ferrocenyl(phenyl)phosphine chalcogenides, $Fc_nP(E)Ph_{3-n}$ (4–9, E = S, Se, n = 1-3, Scheme 1) with oxidizing agents. Pure, characterizable products have been obtained only for reactions of 1 with bromine and silver ion. Whereas $FcP(S)Ph_2$ (4) [12], $FcP(Se)Ph_2$ (5) [13,14], and $Fc_2P(S)Ph$ (6) [15] are reported in the literature, only brief descriptions of the synthetic procedures (for 4 and 5), yields, and little characterization data are provided. Thus, details of the synthesis and characterization of 4–6 are provided here along with the remaining three members of the series: $Fc_2P(Se)Ph$ (7), $Fc_3P(S)$ (8), and $Fc_3P(Se)$ (9).

2. Experimental

2.1. General methods

All compounds described in this work were handled using Schlenk techniques under a nitrogen atmosphere. Ferrocenyl(phenyl) phosphines **1–3** were prepared by literature methods [16]. Solvents were purified by refluxing over Na (toluene, petroleum ether b.p. 36-68 °C), CaH₂ (acetonitrile) or P₂O₅ (dichloromethane) followed by distillation prior to use. Elemental analyses (C, H) were performed by Columbia Analytical Services, Inc.

NMR spectra were recorded at 300 or 400 MHz for ¹H and 75.4 MHz for ¹³C{¹H} on a Varian Mercury VX300 spectrometer. Proton chemical shifts are reported relative to residual protons in the solvent (CHCl₃ at δ 7.24 ppm, C₆D₅H at δ 7.15 ppm, CD₂HCN at δ 1.97 ppm, or CD₃C(O)CD₂H at d 2.04 ppm). Carbon chemical shifts are reported relative to solvent (CHCl₃ t at δ 77.0 ppm). Phosphorus chemical shifts (162 MHz) are reported relative to 85% H₃PO₄ at d 0.00 ppm.

IR spectra were recorded from evaporated solutions (neat) on KBr plates on a Bruker Alpha-T FTIR spectrometer between 400 and 4000 cm⁻¹. ESR spectra were recorded on a Bruker EMX X-band spectrometer or on an EleXsys E-500 X-band spectrometer equipped with an Oxford Instruments ESR900 liquid helium cryostat. A constant acceleration Mössbauer spectrometer (SEE Co, Minneapolis, MN) and Igor Pro 6 software (using Lorentzian fit-

ting functions, WaveMetrics, Portland, OR) were used to record and analyze ⁵⁷Fe spectra [17]. Isomer shifts are reported relative to Fe foil at ambient temperature. Magnetic measurements were made at ambient temperature (293 K) on solid samples using a Johnson-Matthey Magnetic Susceptometer.

Electrochemical measurements were made under nitrogen on a BAS 100 B/W electrochemical workstation at 22 °C using 1.0×10^{-3} M solutions in dry CH₂Cl₂ with 0.1 M ⁿBu₄NPF₆ as supporting electrolyte at a scan rate of 100 mV/s. The working electrode was a 3 mm Pt disk with a Pt wire as auxiliary electrode. A silver wire was used as a pseudo-reference electrode. Ferrocene was added as an internal standard to which all potentials are referenced to ($E_{1/2} = 0.00$ V).

2.2. Synthesis of ferrocenyl(phenyl)phosphine chalcogenides

2.2.1. Ferrocenyl(diphenyl)phosphine sulfide (4)

59 mg (1.8 mmol) sulfur was added to a solution of 752 mg (2.03 mmol) 1 in 20 mL toluene. The mixture was refluxed for 2 h, cooled to ambient temperature and filtered to remove any remaining sulfur. Solvent was evaporated from the filtrate and the crude yellow-orange product chromatographed on a neutral alumina column. A single yellow band was eluted with CHCl₃ yielding 560 mg (1.4 mmol, 76%) of ferrocenyl(diphenyl)phosphine sulfide (4) upon evaporation of the eluent. Single crystals of 4 suitable for X-ray diffraction studies were isolated from dichloromethane solutions layered with ether at -20 °C. M.p. 144-146 °C. Anal. Calc. for C22H19FePS: C, 65.69, H, 4.76. Found: C, 65.62, H, 4.80%. ¹H NMR (C_6D_6): δ 4.08 s (5H, Cp), 4.32 m (2H, C_5H_4), 4.65 m (2H, C_5H_4), 6.99 m (6H, Ph), 7.85 m (4H, Ph); ¹³C {¹H} NMR (CDCl₃): δ 68.69, 70.25, 71.65 d (J_{CP} = 10.5 Hz), 73.14 d $(J_{CP} = 12.9 \text{ Hz})$, 128.42 d $(J_{CP} = 12.3 \text{ Hz})$, 131.44, 131.86 d $(J_{CP} = 10.9 \text{ Hz})$, 134.32 s ${}^{31}P{}^{1}H$ NMR $(C_6D_6) \delta$ 41.2 s. IR (KBr, thin film) $v_{P=S}$ 541, 655 cm⁻¹.

2.2.2. Ferrocenyl(diphenyl)phosphine selenide (5)

When completed analogously to **4**, the reaction of 217 mg (2.75 mmol) selenium with 1020 mg (2.75 mmol) **1** in 20 mL toluene yielded 430 mg (0.95 mmol, 39%) ferrocenyl(diphenyl)-phosphine selenide (**5**). M.p. 128–129 °C *Anal.* Calc. for C₂₂H₁₉FePSe: C, 58.83, H, 4.26. Found: C, 58.73, H, 4.55%. ¹H NMR (C₆D₆): δ 4.00 m (2H), 4.08 s (5H), 4.42 m (2H), 6.97 m (6H), 7.84 m (4H). ¹³C{¹H} NMR (C₆D₆): δ 70.84, 72.28 d (J_{CP} = 9.7 Hz), 73.94 d (J_{CP} = 12.4 Hz), 128.47 d (J_{CP} = 12.4 Hz), 131.29, 132.77 d (J_{CP} = 10.6 Hz), 135.5. ³¹P{¹H} NMR (C₆D₆) δ 32.6 s (J_{PSe} = 757 Hz). IR (KBr, thin film) $\nu_{P=Se}$ 533, 573 cm⁻¹.

2.2.3. Diferrocenyl(phenyl)phosphine sulfide (6)

A mixture of 63.3 mg (2.0 mmol) sulfur and 757 mg (1.58 mmol) **2** in 20 mL diethyl ether was stirred overnight at ambient temperature. The same workup described above yielded 578 mg (1.1 mmol, 72%) of diferrocenyl(phenyl)phosphine



Scheme 1. Structures of 1-9.

sulfide (**6**) as red cubes. The compound decomposed without melting above 180 °C. *Anal.* Calc. for $C_{26}H_{23}Fe_2PS$: C, 61.21, H, 4.54. Found: C, 61.01, H, 4.83%. ¹H NMR (C_6D_6): δ 4.01 m (2H), 4.07 m (2H), 4.16 s (10H), 4.26 m (2H), 4.55 m (2H), 7.03 m (3H), 8.10 m (2H). ¹³C{¹H} NMR (C_6D_6): δ 70.23 d (J_{CP} = 10.0 Hz), 70.63, 72.00 d (J_{CP} = 9.8 Hz), 72.35 d (J_{CP} = 13.0 Hz), 73.40 d (J = 12.6 Hz), 78.41, 79.72, 131.13, 132.14 d (J_{CP} = 10.4 Hz), 135.48, 136.60. ³¹P {¹H} NMR (C_6D_6) δ 38.8 s. IR (KBr, thin film) $\nu_{P=S}$ 550, 667 cm⁻¹.

2.2.4. (Phenyl)diferrocenyl phosphine selenide (7)

The reaction between 137 mg (1.74 mmol) selenium and 781 mg (1.60 mmol) **2** in 20 mL toluene carried out as described for **5** above yielded 374 mg (0.67 mmol, 41%) diferrocenyl(phenyl)phosphine selenide (**7**). The compound decomposed without melting above 170 °C. *Anal.* Calc. for $C_{26}H_{23}Fe_2PSe:$ C, 56.06, H, 4.16. Found: C, 56.04, H, 4.42%. ¹H NMR (C_6D_6): δ 4.02 m (2H), 4.07 m (2H), 4.18 s (10H), 4.26 m (2H), 4.55 m (2H), 7.01 m (3H), 8.13 m (2H). ¹³C{¹H} NMR (C_6D_6): δ 70.81 s, 71.21 d ($J_{CP} = 9.8$ Hz), 72.74 d ($J_{CP} = 12.7$ Hz), 73.77 d (J = 12.7 Hz), 77.46, 78.84, 131.9, 132.80 d ($J_{CP} = 10.3$ Hz); ³¹P{¹H} NMR (C_6D_6) δ 29.1 s ($J_{PSe} = 761$ Hz). IR (KBr, thin film) $\nu_{P=Se}$ 576, 629 cm⁻¹.

2.2.5. Triferrocenylphosphine sulfide (8)

A mixture of 41.8 mg (1.3 mmol) sulfur and 120 mg (0.21 mmol) **3** in 20 mL toluene was refluxed for 4 h, yielding 83 mg (0.13 mmol, 64% yield) of triferrocenylphosphine sulfide (**8**) as orange needles after chromatography and re-crystallization how CHCl₃/petroleum ether. The compound decomposed without melting above 160 °C. *Anal.* Calc. for C₃₀H₂₇Fe₃PS: C, 58.29, H, 4.40. Found: C, 57.70, H, 4.71%. These analyses are slightly outside the ±0.4% standard for purity but represent the best values obtained to date and taken together with NMR spectra suggest a pure compound. ¹H NMR (C₆D₆): δ 4.10 m (2H), 4.23 s (5H), 4.50 m (2H). ³¹P{¹H} NMR (C₆D₆): δ 36.9 s IR (KBr, thin film) $\nu_{P=S}$ 677 cm⁻¹.

2.2.6. Triferrocenylphosphine selenide (9)

The reaction between 114.7 mg (1.5 mmol) selenium and 149 mg (0.25 mmol) **3** in 20 ml refluxing toluene for 4 h yielded 77 mg (0.12 mmol, 46% yield) of triferrocenylphosphine selenide (**9**) as an orange powder after chromatography and re-crystallization from chcl₃/petroleum ether. The compound decomposed without melting above 155 °C. *Anal.* Calc. for C₃₀H₂₇Fe₃PSe: C, 54.18, H, 4.09. Found: C, 53.74, H, 4.38%. ¹H NMR (C₆D₆): δ 4.11 m (2H), 4.24 s (5H), 4.52 m (2H). ³¹P{¹H} NMR (C₆D₆): δ 23.6 s (J_{PSe} = 757 Hz) IR (KBr, thin film) $v_{P=Se}$ 570 cm⁻¹.

2.3. Reaction with chemical oxidants

2.3.1. Reaction of ferrocenyl(diphenyl)phosphine (1) with bromine

A diethylether solution of bromine (5.4 mL, 0.1 M Br₂, 0.54 mmol) was added dropwise to a yellow solution of 111 mg (0.30 mmol) 1 in 20 mL diethylether at ambient temperature. The color of the solution gradually changed to a deep red and precipitated an oily black material upon stirring overnight. After decanting the ether away, the crude product was purified by precipitation from CH₂Cl₂/hexanes (1:3). The black product was dried under vacuum at 100 °C for several hours to remove any excess bromine, yielding 94 mg (51%) of a dark black, paramagnetic solid, FcPPh₂Br₃ (**10**). This product did not melt and the dark color of the compound prevented an accurate assessment of decomposition temperature. Anal. Calc. for C₂₂H₁₉FePBr₃: C, 43.32, H, 3.14. Found: C, 43.56, H, 3.43%. IR (KBr, thin film) 454 w, 492 s, 532 m, 569 s, 626 w, 692 s, 704 s, 728 s, 751 m, 1123 s, 1261 s, 1275 m, 1418 m, 1437 s, 1457 s, 1472 m, 1488 m, 1497 m. UV–Vis (CH₂Cl₂): λ_{max} = 394, 407, 473 nm. μ_{eff} (293 K)

= 5.98 $\mu_{\rm B}$. ¹H NMR (CD₃CN) δ 3.7 v br (9H), 7.8 v br (10H). ³¹P {¹H} NMR (CDCl₃) broad resonances at ≈43 and 25 ppm (1:1 ratio).

2.3.2. Reaction of $FcP(S)Ph_2$ (4) with bromine

The dropwise addition of a diethylether solution of bromine (2.5 mL, 0.1 M Br₂, 0.25 mmol) to an orange–red solution of **4** (97 mg, 0.24 mmol) in 10 mL CH₂Cl₂ at ambient temperature led to a rapid color change to deep red. No further color changes were observed after stirring overnight. Filtration and evaporation of solvent under vacuum yielded a red oily product. Heating the crude product under vacuum at 100 °C for several hours yielded a dark, solid material. Crystallization from CH₂Cl₂/hexane mixtures precipitated 24 mg (4 mmol, 17%) of **10**. Unreacted **4** (55 mg) was recovered from the mother liquor and identified by ¹H and ³¹P NMR. The IR spectrum of the product was identical to that for the product from reactions between **1** and Br₂ above. *Anal.* Calc. for C₂₂H₁₉FePBr₃: C, 43.32, H, 3.14. Found: C, 43.44, H, 3.16%.

2.3.3. General procedure for reactions between ferrocenyl(diphenyl) phosphine (1) and silver salts

The following general procedure was used for reactions of **1** with several silver salts in dichloromethane or acetonitrile. A solution of **1** was added to a solution (or slurry) of the silver salt under nitrogen at ambient temperature. After stirring for 2-3 h, the solution was filtered through a small amount of Celite and the solvent volume was reduced to 1-2 mL. Addition of petroleum ether or diethylether and cooling precipitated the product.

2.3.4. Reaction of 1 with 0.5 equivalent $AgCF_3CO_2$ in CH_2Cl_2 to form 11

The reaction between 144 mg (0.39 mmol) **1** and 32 mg (0.19 mmol) AgCF₃CO₂ in 25 mL CH₂Cl₂ yielded 138 mg (0.14 mmol, 78%) of the orange microcrystalline solid bis[ferrocenyl(diphenyl)phosphine] silver trifluoroacetate, (**11**). The sample darkened from orange to dark red above 130 °C without melting before turning black above 140 °C. *Anal.* Calc. for C₄₆H₃₈Fe₂AgP₂F₃-O₂: C, 57.47, H, 3.96. Found: C, 57.56, H, 3.92%. ¹H NMR (CDCl₃) δ 4.01 s (5H), 4.14 m (2H), 4.39 m (2H), 7.35 m (6H), 7.47 t (4H). ³¹P{¹H} NMR (CDCl₃) very broad resonance at \approx -1 ppm.

2.3.5. Reaction of 1 with 0.5 equivalent AgCF₃CO₂ in CH₃CN to form 11

The reaction between 104 mg (0.28 mmol) **1** and 27 mg (0.16 mmol) AgCF₃CO₂ in 20 mL CH₃CN followed by crystallization from CH₂Cl₂/petroleum ether yielded 66 mg (0.08 mmol, 50%) of an orange microcrystalline solid that was spectroscopically identical to **11**.

2.3.6. Reaction of 1 with PPh_3 and $\mathsf{AgCF}_3\mathsf{CO}_2$ in $\mathsf{CH}_2\mathsf{Cl}_2$ to form 11 and 12

The reaction between 89 mg (0.24 mmol) **1**, 57 mg (0.22 mmol) PPh₃, and 40 mg (0.24 mmol) AgCF₃CO₂ in 20 mL CH₂Cl₂ yielded 115 mg (0.095 mmol, 44%) of a mustard yellow powder, [(FcPPh₂) (PPh₃)₂Ag][CF₃CO₂] (**12**) as a solvate with one equivalent of CH₂Cl₂. Evaporation of the mother liquor yielded a yellow solid spectroscopically identified as **11**. M.p. the sample darkened from orange to dark red above 160 °C and then turned black by 170 °C. *Anal.* Calc. for C₆₀H₄₉FeAgP₃F₃O₂·CH₂Cl₂: C, 61.02, H, 4.28. Found: C, 60.97, H, 4.62%. ¹H NMR (CDCl₃) δ 4.02 s (5H, Cp), 4.21 m (2H), 4.39 m (2H), 5.30 s (2H, CH₂Cl₂) 7.25–7.40 m and 7.49 m (40H). ³¹P{¹H} NMR (CDCl₃) two broad resonances at 1 and 7 ppm.

2.3.7. Reaction of 1 with 0.5 equivalent of AgBF₄ in CH₂Cl₂ to form 13

A yellow-orange solution of 420 mg (1.1 mmol) **1** in 10 mL CH₂-Cl₂ was added dropwise to a colorless solution of 100 mg (0.51 mmol) AgBF₄ in 10 mL CH₂Cl₂. The solution initially turned green, but as more **1** was added the color changed to a deep orange. After stirring overnight, the solution was filtered and the filtrate concentrated to about 4 mL. Petroleum ether (~10 mL) was carefully layered on top of the CH₂Cl₂ solution and the resulting mixture was cooled to -20 °C, depositing a red-orange oil. After several weeks of periodically agitating the mixture, 348 mg (0.27 mmol, 25%) of yellow-orange solid $[(FcPPh_2)_3Ag][BF_4]$ (13) was isolated by filtration. The crude product was crystallized from acetonitrile, diethyl ether and a small amount of petroleum ether. Crystallization was challenging as the compound forms oils if precipitated too quickly. The sample appears to decompose upon heating above 100 °C (darkens) without melting. Anal. Calc. for C₆₆H₅₇P₃Fe₃AgBF₄: C, 60.72, H, 4.40. Found: C, 59.95, H, 4.72%. These analyses are outside the ±0.4% standard for purity but represent the best values obtained to date after numerous attempts at purification. ¹H NMR (CDCl₃): δ 4.02 s (5H, Cp), 4.35 m (2H), 4.51 m (2H), 7.44 m (4H), 7.56 m (6H). ³¹P{¹H} NMR (CD₃CN) very broad resonance at ≈ 4 ppm.

2.3.8. Reaction of **1** with excess $AgBF_4$ in CH_2Cl_2 to form mixture **14**

The reaction between 157 mg (0.42 mmol) **1** and 161 mg (0.83 mmol) AgBF₄ in 20 mL CH₂Cl₂ yielded 151 mg of (**14**) as a paramagnetic, green solid. Samples of **14** do not melt upon heating and the dark color of the sample prevented evaluation of a decomposition temperature. Mössbauer (90 K) indicates a mixture of products: δ 0.47 mm/s, $\Delta E_Q = 2.1$ mm/s (70%) and δ 0.5 mm/s, $\Delta E_Q = 0.25$ mm/s (30%). UV–Vis (CH₂Cl₂): λ_{max} 616 nm.

2.3.9. Reaction of 1 with 1 equivalent of $AgBF_4$ in CH_2Cl_2 to form 14 and 15

The reaction between 101 mg (0.27 mmol) **1** and 58.4 mg (0.30 mmol) AgBF₄ (inadequately dried) in 20 mL CH₂Cl₂ followed by addition of hexane yielded 30 mg (0.07 mmol, 25%) of yellow crystals of a boron trifluoride adduct of ferrocenyl(diphenyl)phosphine oxide, FcPh₂PO·BF₃ (**15**). The composition of **15** was determined by single crystal X-ray diffraction. An additional 79 mg of product isolated from the mother liquor as a yellow–green powder contained a mixture of **14** and **15**. ¹H NMR (CDCl₃) δ 4.34 m (5H), 4.51 m (2H), 4.64 m (2H), 7.55 m and 7.68 m (10H). ³¹P{¹H} NMR (CDCl₃) δ –6.6 br s.

2.3.10. Reaction of 1 with 0.33 equivalent of AgOTf in CH_2Cl_2 to form 16

A yellow–orange solution of 385 mg (1.0 mmol) **1** in 10 mL CH₂-Cl₂ was added dropwise to a colorless solution of 81 mg (0.31 mmol) AgOTf in 15 mL CH₂Cl₂. The solution initially turned green, but as more **1** was added, a deep orange color solution was obtained. After stirring for 3 h, the solution volume was reduced to \approx 4 mL under a N₂ stream, Then 10 mL of petroleum ether was carefully layered on top of the CH₂Cl₂ solution. Cooling to –20 °C overnight precipitated a yellow solid which was washed with more petroleum ether and dried. The addition of more petroleum ether to the mother liquor precipitated a second batch of product. A total of 275 mg (0.21 mmol, 65%) of [(FcPPh₂)₃Ag][CF₃-SO₃] (**16**) was isolated.

The sample appears to decompose upon heating above 100 °C (darkens) without melting. *Anal.* Calc. for $C_{67}H_{57}P_3Fe_3AgSO_3$: C, 58.85, H, 4.20. Found: C, 58.33, H, 4.82%. These analyses are slightly outside the ±0.4% standard for purity but represent the best values obtained to date after numerous attempts at purification. ¹H NMR (CDCl₃) δ 4.00 s (5H, Cp), 4.29 m (2H), 4.41 m (2H), 7.39 m (4H), 7.58 m (6H). ³¹P{¹H} NMR (CDCl₃) broad resonances at \approx 5 ppm.

2.3.11. Reaction of 1 with excess AgOTf in CH₂Cl₂ to form 17

To a solution of 159 mg (0.43 mmol) **1** in 15 mL CH_2Cl_2 was added 241 mg (0.94 mmol) AgOTf in 15 mL CH_2Cl_2 yielding a dark green solution. After stirring for 3 h, the mixture was filtered and the filtrate volume reduced by half under vacuum, precipitating

138 mg (0.18 mmol, 41%) of a paramagnetic, green solid, [(FcPPh₂) Ag][CF₃SO₃]₂, **17**. Samples of **17** do not melt upon heating and the dark color of the sample prevented evaluation of a decomposition temperature. UV–Vis spectra could not be obtained as **17** did not re-dissolve in CH₂Cl₂ or any other common solvents tested. *Anal.* Calc. for C₂₄H₁₉AgS₂O₆PF₆Fe: C, 37.14, H, 2.47. Found: C, 36.84, H, 2.72%. Mössbauer (90 K) δ 0.54 mm/s, $\Delta E_0 = 0$ mm/s.

2.4. Crystal structures of 4 and 15

The selected crystals of **4** and **15** were glued with epoxy onto the tip of a glass rod drawn out to a fiber. The X-ray intensity data were measured with phi and omega scans at 297 K on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda = 0.71073$ Å). The data were integrated with the Bruker SAINT software package, solved by direct methods, and refined using the Bruker SHELXTL version 6.1 Software Package using literature scattering factors (Wilson, A.J.C., Ed. International Tables for Crystallography; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.). Compounds 4 and 15 crystallize in the monoclinic $C2_1/c$ and triclinic $P\overline{1}$ space groups, respectively both with Z = 4. All non-hydrogen atoms were modeled anisotropically. Hydrogen atoms were placed at calculated distances and using a riding model, such that positional and thermal parameters are derived from the atom each hydrogen atom is bound to while maintaining the calculated distance and optimal angles.

3. Results

3.1. Synthesis of ferrocenyl(phenyl)phosphine chalcogenides 4-9

The reaction of Fc_nPPh_{3-n} (1–3) with elemental sulfur and selenium proceeds smoothly in refluxing toluene or ether to yield the corresponding ferrocenyl(phenyl)phosphine chalcogenides (4-9). Compounds **4–9** are isolated in 39–76% yield after purification by chromatography on alumina followed by re-crystallization if necessary. Yields for the selenides (5, 7 and 9) are generally lower than for the sulfides (4, 6 and 8). The products are all diamagnetic, airstable, orange to red-orange solids and have elemental analyses consistent with the proposed composition. Compounds 4-9 are soluble in chloroform, dichloromethane, and benzene but only 4 and 6 have appreciable solubility in CH₃CN. The selenides 5 and 7 are very sparingly soluble in acetonitrile whereas the triferrocenylphosphine chalcogenides 8-9 are insoluble. ¹H NMR spectra of **4–9** consist of a singlet for the protons on the unsubstituted C_5H_5 ring. Two signals are observed for the protons on the substituted ring in **4** and **5**, while four signals (multiplets) are observed in the spectra of 6-9. The latter are likely the result of restricted rotation about the Fc-P bonds as seen in iodophosphonium salts of 2-3 [18]. The chemical shifts for the aryl protons are typical for an aryl phosphine. The ³¹P NMR spectra (Table 1) for **4-9** consist of singlets with J_{PSe} for **5**, **7** and **9** between 757 and 761 Hz. The values for J_{PSe} are greater than those for $Ph_3P=S$ (730 Hz) and dppfSe₂ (736 Hz) but less than for $Fc[P(furyl^{Me})_2]_2$ (788 Hz) [19]. Comparison of the IR spectra of Fc_nPPh_{3-n} (1–3) with 4–9 reveals two new absorptions in the region between 350 and 800 cm⁻¹ assigned to the P=E vibrations (Table 1). The data for 4-5 and **7–9** are consistent with the reported [15] $v_{P=S}$ for **6** (667 cm⁻¹, s and 550 w).

3.2. Crystal Structure of 4

Compound **4** (Fig. 1) crystallizes in the $P2_1/c$ space group. The P=S distance is 1.9363(8), the C–P–S bond angles range between

|--|

Table 1

lectrochemical, "IR," and NMR ^c data for ferrocenyl(phenyl)phosphines (1–3) and ferrocenyl(phenyl)phosphine chalcogenides (4–9).							
Compound	$E_{1/2}^{0/+}$ (mV)	$E_{1/2}^{+/2+}$ (mV)	$\Delta E (mV)$	$K_{\rm comp}^{j}$	$v_{(P=E)} (cm^{-1})^b$	³¹ P (ppm)	
$FcPPh_2(1)$	64 ^d					-17.8 ⁱ	
	80 ^e						
$Fc_2PPh(2)$	20	300 ^f	280 ^g			-29.8 ⁱ	
$Fc_3P(3)$	-2	$\approx 50^{h}$	52			-59.9 ⁱ	
$FcP(S)Ph_2(4)$	248				655, 541	41.2	
$FcP(Se)Ph_2(5)$	243				573, 533	32.6	
$Fc_2P(S)Ph(6)$	201	423	222	$5.6 imes 10^3$	667, 550	38.8	
$Fc_2P(Se)Ph(7)$	179	472	293	$8.9 imes 10^4$	629, 576	29.1	

190

290

E

345

450

vs FcH/FcH⁺ 22 °C using 1.0 × 10⁻³ M solutions in dry CH₂Cl₂ with 0.1 M ⁿBu₄NPF₆ as supporting electrolyte at a scan rate of 100 mV/s. Precision ±5 mV.

Thin film on KBr.

^c In CDCl₃.

 $Fc_{3}P(S)(8)$

 $Fc_3P(Se)(\mathbf{9})$

d

See Ref. [10].

In MeCN see Ref. [29]. $E_{1/2}^{2+/3+} = 425 \text{ mV g}.$

^g $E_{1/2}^{2+/3+} = 770 \text{ mV}.$

^h Irreversible.

ⁱ In CD₂Cl₂ see Ref. [18].

^j Log K_{comp} = 16.9 $\Delta E_{1/2}$ for one electron processes see Ref. [38].

155

160



Fig. 1. Thermal ellipsoid (30% probability) view of the crystal structure of 4. Hydrogen atoms have been omitted for clarity.

112° and 114° while the C-P-C bond angles are a little smaller, between 104° and 107°. Thus the structure of **4** is comparable to that of Ph₃P=S with very similar P=S distances, C-P-S and C-P-C bond angles [20].

3.3. Electrochemistry of 4-9

Compounds **4–9** are oxidized at more positive potentials than 1–3 in CH₂Cl₂ solution (Table 1). The number of ferrocene units has a greater effect on the electrochemical potential than the identity of the chalcogen; the electrochemical potentials for 4 and 5 are found to be between 40 and 60 mV more positive than the electrochemical potentials for the first oxidation of **6** and **7** with a further 20–25 mV decrease in the potential for 8 and 9. The second wave in the cyclic voltammograms of 6 and 7 indicates a separation between the electrochemical potentials between 222 and 293 mV, respectively, for the first and second oxidation waves. The 110–150 mV separation between the anodic (E_a) and cathodic (E_c) waves for **6–7** suggests quasi-reversible electrochemistry in CH₂Cl₂ compared to ferrocene (60 mV). The reversible anodic electrochemistry of **6** has been previously reported [11] in acetonitrile (0.62 and 0.76 mV versus Ag/AgCl, $E_a - E_c = 61-62$ mV). Two additional waves in the cyclic voltammograms of 8 and 9 are assigned to $E_{1/2}^{1+/2+}$ (reversible, $E_a - E_c = 60$ mV) and $E_{1/2}^{2+/3+}$ (irreversible). The very large differences in cathodic and anodic peak currents for the second and third oxidation processes in 8 suggest the possibility for absorption of the reactants of products on the electrode [21]. The choice of electrolyte may also be critical as the electrochemistry of 9 showed three reversible oxidations when [NBu₄][B (C₆F₅)₄] rather than [NBu₄][PF₆] was used as the supporting electrolyte [1a].

677

570

36.9

23.6

3.4. Chemical oxidation with bromine

 8.0×10^{4}

Reaction of ferrocenyl(diphenyl)phosphine (1) or ferrocenyl (diphenyl)phosphine sulfide (4) with two equivalents of bromine yields a dark solid product whose composition by elemental analysis is consistent with the empirical formula FcPPh₂Br₃ (10, Scheme 2). The absorptions at 655 and 541 cm⁻¹ assigned to $v_{P=S}$ in the IR spectra of 4 disappear completely upon reaction with bromine, consistent with the loss of sulfur. The ESR spectrum of 10 consists of a single broad transition centered on g = 4.2 with a line width of approximately 400 gauss. Due to the size and shape of the crystals examined together in the sample tube, the signal broadness may be due to many crystal orientations being present. The same product is obtained in lower yield from reactions of ferrocenyl(diphenyl)phosphine (1) with bromine. The strong absorbances at 394 and 407 nm in the UV-Vis spectrum of 10 is consistent with the Br₃⁻ anion [22]. The magnetic moment at ambient temperature (293 K) is found to be 5.98 $\mu_{\rm B}$ very close to the spin only value for a high spin, S = 5/2, Fe^{III}. NMR spectroscopy of **10** reveal very broad resonances consistent with a paramagnetic compound but also confirm that both Cp (δ 3.7) and Ph (δ 7.8) groups are present in 10. Two broad phosphorus signals in the ³¹P NMR spectrum confirm that phosphorus is present in **10** but suggest that **10** contain more than one "FcPPh₂Br₃" unit.

Despite considerable effort, it was not possible to extend the chemistry observed for 4 to other members of the ferrrocenyl(phenyl) phosphine chalcogenide family (5-9). Infrared spectra of the products from reactions between 5-7 and elemental bromine also reveal a decrease in the intensity of the $v_{P=E}$ absorption of the



Scheme 2. Reaction of FcPPh₂ (1) and FcP(S)Ph₂ (4) with bromine.

starting material, however, analytically pure products were not isolated in these cases. While chalcogen loss is suggested in reactions with Br_2 , pure products were also not obtained. Pure, characterizable products could also not be isolated in reactions between **4–9** and silver salts.

3.5. Chemical oxidation with silver ion

The reaction between two equivalents of 1 and AgCF₃CO₂ in CH₂Cl₂ yields the silver-phosphine complex [(FcPPh₂)₂Ag][CF₃CO₂] (11) in modest yield. Compound 11 is diamagnetic with a wellresolved ¹H NMR spectrum. The ambient temperature ³¹P NMR spectrum of 11 consists of a single, extremely broad resonance at ≈ -1 ppm (peak width at half-height = 260 Hz). Cooling an acetone/CDCl₃ solution of **11** to $-50 \,^{\circ}$ C leads to a further broadening of the ³¹P resonance without coalescence or resolution into two doublets. Warming the sample to 50 °C gives a sharper ³¹P signal (peak width at half-height = 146 Hz), consistent with restricted rotation in **11**. The effect of two naturally occurring isotopes of silver, ¹⁰⁷Ag and ¹⁰⁹Ag, on ³¹P NMR spectra of ferrocenyl phosphine complexes has been observed in the 2:1 complex [(FcCH₂PPh₂)₂-Agl[OTf]: a single broad resonance at ambient temperature is resolved into two doublets centered at 8.6 ppm with $J_{P=107Ag}$ = 320 Hz and $J_{P=107Ag}$ = 368 Hz at -60 °C in CDCl₃ [23]. Our inability to resolve the coupling constants for ¹⁰⁷Ag-P and ¹⁰⁹Ag-P coupling does not necessarily exclude this explanation for the ³¹P spectra of **11**. The same product (**11**, Scheme 3) is isolated from reactions between 1 and AgCF₃CO₂ (2:1 ratio) in acetonitrile with no evidence in the ¹H NMR or IR spectra for the presence of CH₃CN in this product.

The broadness of the ³¹P signal prevents comparisons of the spectrum for **11** with known triphenylphosphine silver compounds where the ³¹P chemical shift correlates with the stoichiometry, i.e. the phosphine to silver ratio [24]. Thus the composition of **11** is based on elemental analysis and ¹H NMR spectroscopy. Obtaining structural data to confirm the coordination number for the silver ion in **11** has been thwarted by an inability to grow X-ray quality crystals of **11**.

The reaction between equimolar amounts of silver trifluoroacetate, triphenylphosphine and **1** yields the diamagnetic silver phosphine complex **12** (Scheme 3) containing a 3:1 ratio of phosphines to silver. The ¹H NMR chemical shifts for **12** are sharp, well resolved and slightly downfield of those for **1**. Elemental analysis and integration of the ¹H resonances are consistent with the formulation of **12** as [(FcPPh₂)(PPh₃)₂Ag][CF₃CO₂] containing one equivalent of CH₂Cl₂ (¹H NMR δ 5.30). The ambient temperature ³¹P NMR spectrum of **12** consists of two extremely broad resonances at 1 and 7 ppm that are shifted further downfield from both **1** and **11**.

Slow addition of a solution of **1** to a solution of AgBF₄ in CH₂Cl₂ initially produces a green-colored solution, however, when the

ratio of 1:Ag⁺ exceeds one, the green color dissipates to eventually give an orange solution from which the diamagnetic, silver-phosphine complex $[(FcPPh_2)_3Ag]^+BF_4^-$ (13) is isolated. The spectroscopy of 13 is similar to that of the trifluoroacetate salt, 11 described above, with a well-resolved ¹H NMR spectrum but a very broad ³¹P resonance at ambient temperature.

Compound **1** reacts with excess AgBF₄ to yield a green, paramagnetic solid, **14**, which gave an elemental analysis that couldn't be matched to a single reasonable product. Consistent with this, the Mössbauer spectrum of **14** at 90 K suggests the presence of both ferrocene-like, low-spin Fe^{II} (δ = 0.47 mm/s, ΔE_Q = 2.1 mm/s, 70%) and ferrocenium-like low-spin, Fe^{III} (δ = 0.50 mm/s, ΔE_Q = 0.25 mm/s, 30%) compounds in the sample [25].

Compound **14** also proved to be moisture sensitive. If water is added to **14** or if the reaction between **1** and $AgBF_4$ is carried out using slightly damp silver salt (e.g., undried $AgBF_4$, as this compound is hygroscopic), a yellow solid, **15**, is isolated. This product was identified by X-ray crystallography as the BF₃ adduct of ferrocenyl(diphenyl)phosphine oxide, FcPh₂P=O·BF₃ (Fig. 2).

The P=O distance in **15** (1.5273(19) Å) is quite close to the P=O distance in FcPh₂P=O (1.477 Å) [26] but is significantly longer than the B–F bond distances (1.33–1.37 Å), enabling a clear distinction between the two of them in the structure. A prominent absorption at 1184 cm⁻¹ in the IR spectrum of **15** compares favorably with the $v_{P=O}$ for Fc₂PhP=O (1200 cm⁻¹) [15] and Ph₃P=O (1190 cm⁻¹) [27]. Although the precise mechanism for the formation of **15** is not known, the conversion of **1** to FcPh₂P=O in the presence of air and water in CH₂Cl₂ solution is slower than the formation of **15** in the reaction, (also supported by the presence of BF₃ in the product).

Reaction between **1** and $AgCF_3SO_3$ in a 3:1 ratio yields a yellow, diamagnetic product, [(FcPPh₂)₃Ag][CF₃SO₃] (**16**), however, when excess silver triflate is used in the reaction, a green paramagnetic solid is isolated that analyzes as [(FcPPh₂)Ag][CF₃SO₃]₂ (**17**). The Mössbauer spectrum of 17 at 90 K indicates that 17 contains exclusively ferrocenium-like low-spin, Fe^{III} (δ = 0.50 mm/s, ΔE_Q = 0 mm/ s). The extremely poor solubility of 17 has hampered purification and thwarted attempts at crystal growth. Solid samples of 17 were ESR silent down to 200 K, however, below 26 K a very broad, complicated anisotropic spectrum spanning 10000G was observed. While considerable additional modeling of the spectrum is needed, the spectrum suggests magnetic coupling between the ${\rm Fe}^{\rm III},\,{\rm Ag}^{\rm I}$ (I = 1/2) and possibly P (I = 1/2). Addition of **1** to a slurry of **17** yields a yellow mixture that appears to contain some 16 but a clean product was not obtained. Addition of a solution of 16 to AgCF₃SO₃ very slowly leads to a green solution that likely contains 17.

As in the case of ferrocenyl (phenyl) phosphine chalcogenides (**5–9**), all reactions of **2–3** with silver salts seem to result in mixtures from which we have been unable to isolate and characterize pure products. Efforts to investigate the reactions of **1–3** with other





Fig. 2. Thermal ellipsoid (30% probability) view of the crystal structure of 15. Hydrogen atoms have been omitted for clarity. This compound has two independent molecules in the asymmetric unit (both are shown).

oxidants were limited by the availability of oxidants with appropriate electrochemical potentials. Reactions between **1–3** and readily available oxidants such as NO⁺ ($E^{\circ} = 1.00$ V in CH₂Cl₂ versus Fc/Fc⁺) and Fe(η^{5} -C₅H₄COMe)Cp⁺ ($E^{\circ} = 0.27$ V in CH₃CN versus Fc/Fc⁺) did not yield pure, characterizable products.

4. Discussion

The electrochemical potential of 1 suggests that mild chemical oxidants such as I_2 ($E^{\circ\prime} = -14$ mV in CH₃CN versus Fc) [28] should not lead to oxidation of **1** ($E^{\circ\prime}$ = 80 mV in CH₃CN versus Fc) [29], consistent with the isolation of iodo(phenyl)(ferrocenyl)phosphonium salts from such reactions [18]. Elemental analysis, UV–Vis and Mössbauer spectroscopy revealed that reaction between 2 and I₂ yielded a diamagnetic product: [Fc₂PPh][I₃]·0.5 C₆H₆ [18]. Literature data suggests that bromine is a slightly stronger oxidant $(7 \text{ mV for } Br_2 \text{ versus } -140 \text{ mV for } I_2 \text{ in MeCN versus } Fc/Fc^+)$ [28] than iodine and might oxidize 1 depending on the effect of solvent on E° . Indeed, the reaction between **1** and Br₂ in CH₂Cl₂ yields a paramagnetic solid, FcPh₂PBr₃ (10). The ESR data for 10 is consistent with paramagnetic Fe^{III} . The high field signal at g = 4.2 is similar to the values reported for ferrocenium radical cations [30] and inconsistent with literature data for a phosphorus-centered radical cation (g = 2.006 for Ph₃P⁺) [31]. Additional evidence for a $Br_3^$ anion in **10** is provided by the intense absorbances at $\lambda_{max} = 394$ and 407 nm in the UV-Vis spectrum [22]. Magnetic measurements on **10** (μ_{eff} = 5.98 μ_{B}) are consistent with paramagnetic, high spin (S = 5/2) Fe^{III}. The spin on Fe in **10** is unusual; ferricenium ion itself contains low spin Fe^{III} in both the solid state and in solution [32]. Oxidation of diferrocenyl[bis(vinyldithio)tetrathiofulvane] with HBF₄, however, yields a mixed valent derivative that contains 66% high spin Fe^{III} at 290 K as measured by Mössbauer spectroscopy suggesting that the high spin nature of **10** is possible [33].

The reaction of **4** with bromine also leads to formation of **10** resembling the chemistry of triphenylphosphine sulfide, Ph_3PS .

The reaction between Ph_3PS and Br_2 leads to loss of S (as SBr_2) and isolation of $[Ph_3PBr][Br]$ [18]. The similarity in the reactivity between (phenyl)ferrocenephosphine chalcogenides and Ph_3PS is also seen in reactions with I_2 ; **6** and Ph_3P both react with iodine to form charge transfer complexes $Fc_2P(S)P\cdot I_2$ and $Ph_3PS\cdot I_2$, respectively [15,34].

The electrochemical potential for silver ion is solvent dependant [18]. One predicts that oxidation of $1 (E^{\circ'} = 80 \text{ mV} \text{ in } \text{CH}_3\text{CN} \text{ versus}$ Fc) [18,29], by Ag⁺ is unlikely in CH₃CN (40 mV versus Fc/Fc⁺ for the CF₃CO₂ salt) [28]. The isolation of diamagnetic [(FcPh₂P)₂Ag] [CF₃CO₂] (11) from acetonitrile is therefore not surprising. Triphenylphosphine reacts with AgBF₄ in acetonitrile to form [(Ph₃P)₂-Ag(CH₃CN)][BF₄] which loses CH₃CN upon drying to yield the two-coordinate silver-phosphine complex [(Ph₃P)₂Ag][BF₄] [35] suggesting that 1 and PPh₃ have similar coordination chemistry with silver ion in Lewis basic solvents.

Silver ion in dichloromethane solution has a more positive electrochemical potential ($E^{\circ\prime}$ = 650 mV in CH₂Cl₂ relative to ferrocene) [28]. Therefore, the reaction between **1** ($E^{\circ\prime}$ = 64 mV in CH₂Cl₂ versus Fc) [10] and Ag⁺ in dichloromethane should lead to electron transfer. The isolation of a diamagnetic, silver coordination complex [(FcPh₂P)₂Ag][CF₃CO₂] (**11**, Scheme 4) under these conditions is surprising. The electrochemical potential of $FcCH_2PPh_2$ ($E^\circ =$ -40 mV Fc in CH₃CN) [36] is even closer to that of ferrocene than 1 and hence even easier to oxidize than 1, yet there is no evidence for electron transfer in reactions between AgOTf and FcCH₂PPh₂ in CH₂Cl₂. Two diamagnetic silver complexes of [(ferrocenyl)methyl] (diphenyl)phosphine, [(FcCH₂PPh₂)₂Ag][OTf] and [(FcCH₂PPh₂)₃-Ag][OTf], have been isolated and characterized [23]. This suggests that **1** can also behave like PPh₃ and FcCH₂PPh₂ in its coordination chemistry with silver ion even in solvents where oxidation seems favorable based on electrochemical potentials.

The lower phosphine to silver ratio in **11** compared to $[(Ph_3P)_2-Ag(CH_3CN)][BF_4]$ and $[(FcCH_2PPh_2)_3Ag][OTf]$ may reflect a steric effect of the ferrocene moiety relative to a phenyl or ferrocenyl-



Scheme 4. Reaction of FcPPh₂ (1) with AgX (X = CF₃CO₂, BF₄, and CF₃SO₃).

methyl group. The isolation of the silver phosphine complex $[(FcPh_2P)(PPh_3)_2Ag][CF_3CO_2]$ (12) with a 3:1 ratio of phosphine to Ag^+ supports the argument that sterics may control the stoichiometry in 11 and 12. In the latter compound the smaller triphenylphosphine ligand allows the coordination of a third phosphine ligand. Sterics may also be at least partially responsible for the lack of success in isolating pure silver complexes of 2 and 3. The counterion also clearly affects the stoichiometry in 11, 13 and 16 with the traditionally regarded less-coordinating BF₄⁻ and triflate anions favoring a higher phosphine to silver ratio.

The oxidation of **1** appears to depend on both the counterion and the ratio of **1** to Ag⁺ ion. Using an excess of silver ion and changing the silver salt from silver trifluoroacetate to silver tetrafluoroborate or silver triflate leads to the oxidation of Fe^{II}. When AgBF₄ is used in excess, **1** is partially oxidized to an impure, green product (**14**) identified by Mössbauer spectroscopy as a mixture of low spin Fe^{II} and Fe^{III}. Complex **14** hydrolyzes rapidly to form a Lewis acid-base complex of BF₃ and (diphenylphosphino)ferrocene oxide, **15**. Two explanations for the formation of a phosphine oxide in **15** appear reasonable: the hydrolysis of the BF₄⁻ in **14** by adventitious water in the solvent or partially hydrolyzed AgBF₄ [37] and reaction of the ferrocenyl(phenyl)phosphine radical cations with water as reported for 1,1'-bis(diphenylphosphino) ferrocene and [(η^5 -C₅H₄)CMe₂]₂PCy]Fe [2b,10a].

When **1** is reacted with *excess* silver triflate, however, the pure iron(III) compound **17**, $[(FcPPh_2)Ag][CF_3SO_3]_2$, is isolated. Mössbauer spectroscopy confirms that **17** contains only low spin, ferrocenium-like Fe^{III}, the result of oxidation of the iron center in **1**. The ESR spectrum of solid **17** is complex; anisotropic and suggestive of magnetic coupling of Fe^{III} to silver ion. Additional work is needed in modeling and spectral simulation before further interpretation of the ESR spectrum is attempted. The resulting cation derived from **1** (**1**⁺) is still a sufficiently strong Lewis base to coordinate a silver ion leading to the cation, **17**. The larger positive charge on **17** undoubtedly contributes to the low solubility of **17** in the common solvents explored to date.

Comparing the reaction between $FcCH_2PPh_2$ with silver ion and the reaction between **1** and excess Ag^+ , the formation of **17** is a surprisingly different result. The former reaction yields a low spin iron (II) coordination compound, [(FcCH₂PPh₂)₂Ag][OTf] even though the electrochemical potential for oxidation of FcCH₂PPh₂ is more favorable than for **1** [23]. The isolation of **17** supports the characterization given for the blue–green solutions of **1**⁺ reported four decades ago in bulk electrolysis experiments as a ferrocenyl(diphenyl)phosphine radical cation [10].

5. Conclusions

Some of the chemistry of ferrocenyl(diphenyl)phosphine (1) and ferrocenyl(diphenyl)phosphine sulfide (4) resembles that reported for PPh₃ and Ph₃PS. Under appropriate conditions, 1 reacts with silver ion to form diamagnetic phosphine complexes. The difference in size between ferrocene and phenyl groups

accounts for the differences in coordination numbers found for silver complexes derived from these phosphines. Thus it appears that despite favorable electrochemical potentials, silver ion does not *necessarily* oxidize ferrocenyl phosphines. In other words, in some reactions with Ag⁺, **1** can act like a large aryl phosphine rather than a substituted ferrocene. Isolation of **17** demonstrates that oxidation of **1** with silver ion is also possible, but depends on the ratio of silver to **1**, solvent and the choice of counterion. Ferrocenyl(phenyl)phosphine can also behave as a substituted ferrocene. Work continues toward the isolation of additional complexes amenable to structural characterization of ferrocenyl(phenyl)phosphine silver complexes and the interesting ferrocenyl(phenyl)phosphine radical cations.

Acknowledgments

The authors wish to thank Mr. Eric Berquist, Professor David Budil (Northeastern University), Professor Sean Elliot and Dr. Pierre Ceccaldi (Boston University) for the ESR spectra. We are grateful to Professor Theodore Betley, Mr. Matthew Wilding and Ms. Diana Ionvan at Harvard University for help in obtaining Mössbauer spectra. We also acknowledge support from the Natural Science Foundation for funding the X-ray crystallography equipment at Colby College.

Appendix A. Supplementary material

CCDC 1447706 and 14407707 for **4** and **15** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2016.05.010.

References

- [1] (a) F. Barrière, R.U. Kirss, W.E. Geiger, Organometallics 24 (2005) 48;
- (b) D.A. Durfey, R.U. Kirss, C. Frommen, W.M. Reiff, Inorg. Chim. Acta 357 (2004) 311
- [2] (a) C. Nataro, A.N. Campbell, M.A. Ferguson, C.D. Incarvito, A.L. Rheingold, J. Organomet. Chem. 673 (2003) 47;
- (b) G. Pilloni, B. Longato, B. Corain, J. Organomet. Chem. 420 (1991) 57.
 [3] J.H.L. Ong, C. Nataro, J.A. Golen, A.L. Rheingold, Organometallics 22 (2003)
- 5027.
 [4] B.L. Ghent, S.L. Martinak, L.A. Sites, J.A. Golen, A.L. Rheingold, C. Nataro, J. Organomet. Chem. 692 (2007) 2365.
- [5] C.L. Mandell, S.S. Kleinbach, W.G. Dougherty, W.S. Kassel, C. Nataro, Inorg. Chem. 49 (2010) 9718.
- [6] J. Podlaha, P. Stepnicka, J. Ludvik, I. Cisarova, Organometallics 15 (1996) 543.
- [7] I.R. Butler, M. Kalji, L. Nehrtlich, M. Hursthouse, A.I. Karaulov, K.M. Abdul-
- Malik, J. Chem. Soc., Chem. Commun. (1995) 459. [8] J.J. Adams, O.J. Curnow, G. Huttner, S.J. Smail, M.M. Turnbull, J. Organomet. Chem. 577 (1999) 44.
- [9] A. Masson-Szynczak, O. Riant, A. Gref, H.B. Kagan, J. Organomet. Chem. 511 (1996) 193.
- [10] (a) J.C. Kotz, C.L. Nivert, J.M. Lieber, R.C. Reed, J. Organomet. Chem. 91 (1975) 87;
 - (b) T. Höcher, A. Cinquantini, P. Zanello, E. Hey-Hawkins, Polyhedron 24 (2005) 1340.

- [11] (a) F.N. Blanco, L.E. Hagopian, W.R. McNamara, J.A. Golen, A.L. Rheingold, C. Nataro, Organometallics 25 (2006) 4292;
- (b) B.D. Swartz, C. Nataro, Organometallics 24 (2005) 2447.
- [12] F. Mathey, J.P. Lampin, J. Organomet. Chem. 128 (1977) 297.
- [13] M.N. Chevykalova, L.F. Manzhukova, N.V. Artemova, Yu.N. Luzikov, I.E. Nifant'ev, E.E. Nifant'ev, Russ. Chem. Bull. 52 (2003) 78.
- [14] B. Milde, M. Lojan, C. Schreiner, T. Rüffer, H. Lang, Eur. J. Inorg. Chem. (2011) 5437.
- [15] N. Bricklebank, S.J. Coles, S.D. Forder, M.B. Hursthouse, A. Poulton, P.J. Skabara, J. Organomet. Chem. 690 (2005) 328.
- [16] (a) G.P. Sollott, H.E. Mertwoy, S. Portnoy, J.L. Snead, J. Org. Chem. 28 (1963) 1090;
- (b) G.P. Sollott, W.R. Peterson, J. Organomet. Chem. 4 (1965) 491.
- [17] Mössbauer spectra recorded at Harvard University: G.T. Sazama, T.A. Betley, Inorg. Chem. 53 (2014) 269.
- [18] D.A. Durfey, R.U. Kirss, C. Frommen, W. Feighery, Inorg. Chem. 39 (2000) 3509.
- [19] D. Roy, S. Mom, S. Royer, D. Lucas, J.-C. Hierso, H. Doucet, ACS Catal. 2 (2012) 1033
- [20] P.W. Codding, K.A. Kerr, Acta Crystallogr., Sect. B 34 (1978) 3785.
- [21] V.M. Nemykin, C.D. Barrett, R.G. Hadt, R.I. Subbotin, A.Y. Maximov, E.V. Polshin, A.Y. Koposov, Dalton Trans. (2007) 3378.
- [22] G. Steinfeld, V. Lozan, H.-J. Krüger, B. Kersting, Angew. Chem., Int. Ed. 48 (2009) 1954
- [23] E.M. Barranco, O. Crespo, M.C. Gimeno, A. Laguna, P.G. Jones, B. Ahrens, Inorg. Chem. 39 (2000) 680.
- [24] (a) E.L. Muetterties, C.W. Alegranti, J. Am. Chem. Soc. 94 (1972) 6386;
 (b) R.G. Goel, P. Pilon, Inorg. Chem. 17 (1978) 2876;

(c) P.F. Barron, J.C. Dyason, P.C. Healy, L.M. Engelhardt, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans. (1986) 1965.

- [25] N.N. Greenwood, T.C. Gibbs, Mössbauer Spectroscopy, Chapman and Hall Ltd., London, UK, 1971.
- [26] T.-J. Kim, J.-H. Lee, S.-C. Kwon, K.-H. Kwon, J.-K. Uhm, H. Lee, S.-I. Byun, Bull. Korean Chem. Soc. 12 (1991) 116.
- [27] M.J. Frazer, W. Gerrard, R. Twaits, J. Inorg. Nucl. Chem. 25 (1963) 637.
- [28] N.G. Connelly, W.E. Geiger, Chem. Rev. 96 (1996) 877. We have been unable to find data for the effect on the counterion on the electrochemical potential of Ag+.
- [29] M.A. Bennett, S.K. Bhargava, A.M. Bond, I.M. Burgar, S.-X. Guo, G. Kar, S.H. Priver, J. Wagler, A.C. Willis, A.A.J. Torriero, Dalton Trans. 39 (2010) 9079.
- [30] S.K. Pal, K. Alagesan, A.G. Samuelson, J. Pebler, J. Organomet. Chem. 575 (1999) 108.
- [31] (a) G.F. Kokoszka, F.E. Brinckman, J. Chem. Soc., Chem. Commun. (1968) 349;
 (b) A. Hasegawa, G.D.G. McConnachie, M.C.R. Symons, J. Chem. Soc., Faraday Trans. 1 (80) (1984) 1005;
- (c) C.J. Rhodes, M.C.R. Symons, J. Chem. Soc., Chem. Commun. (1989) 1393.
- [32] D.N. Hendrickson, Y.S. Sohn, H.B. Gray, Inorg. Chem. 10 (1971) 1559.
- [33] H.-J. Lee, D.-Y. Noh, A.S. Underhill, C.S. Lee, J. Mater. Chem. 9 (1999) 2359.
 [34] W.I. Cross, S.M. Godfrey, S.L. Jackson, C.A. McAuliffe, R.G. Pritchard, J. Chem. Soc., Dalton Trans. (1999) 2225.
- [35] R.E. Bachman, D.F. Andretta, in: J. Chem. Soc., Dalton Trans. 37 (1998) 5657.
- [36] A.J. Downard, N.J. Goodwin, W. Henderson, J. Organomet. Chem. 676 (2003) 62.
- [37] M. Ghiladi, R.J. Josev, J. Jiang, C.J. McKenzie, S. Morup, I. Sotofte, J. Unstrup, J. Chem. Soc., Dalton Trans. (1999) 2675.
- [38] K.D. Demadis, C.M. Hartshorn, T.J. Meyer, Chem. Rev. 101 (2001) 2655.