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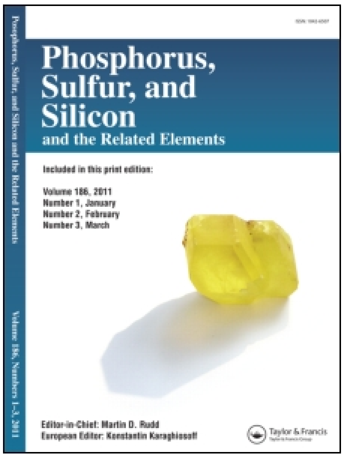

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SYNTHESES OF FERROCENYLFLUOROPHOSPHINIC ACID AND RELATED COMPOUNDS[1]

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SYNTHESES OF FERROCENYLFLUOROPHOSPHINIC ACID AND RELATED COMPOUNDS[1]

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Ferrocenylfluorophosphinic acid ($(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4POH(O)F)$), ferrocenyldifluorophosphine oxide ($(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4POF_2)$) and ferrocenyltetrafluorophosphorane ($(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4PF_4)$) are prepared from the reaction of ferrocene with PF_5 in CH_2Cl_2 and are characterized by proton, carbon, fluorine and phosphorus resonance spectra.

Key words: Ferrocenylfluorophosphinic acid; ferrocenylidifluorophosphine oxide; ferrocenyltetrafluorophosphorane; ferrocene; phosphorus pentafluoride; nmr.

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Reactions of ferrocene with trivalent Lewis acids such as PCl_3, $AsCl_3$, AsI_3, $SbCl_3$ and $BiCl_3$ give, in every case, unsubstituted ferrocenium salts.[2–6] Ferrocene is oxidized by $CH_3NO_2/EF_5(E = P, Sb)$ in liquid HF to give high yields of the corresponding paramagnetic ferrocenium hexafluorometallates.[7] Here we report that monosubstituted ferrocene compounds $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4PF_4)$ **I**, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4POF_2)$, **II** and $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4POH(O)F)$, **III** are synthesized from the reaction of ferrocene with PF_5 in CH_2Cl_2 solution. Ferrocenylfluorophosphinic acid, **III**, has a doublet in both the fluorine and phosphorus resonance spectra with a splitting of 998 Hz and is assigned as YPFXX'. The proton and carbon resonance spectra both show sharp singlets for the unsubstituted C_5H_5 ring and are consistent with a monosubstituted ferrocene species of type $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4R)$. The identity of **III** has also been confirmed by an X-ray structural study.[8] The phosphorus spectrum for ferrocenyldifluorophosphine oxide, **II**, has a triplet with a coupling constant of 1,079 Hz. A well resolved quintet is observed in the phosphorus spectrum of ferrocenyltetrafluorophosphorane **I**, with a coupling constant of 937 Hz. The fluorine resonance spectra for **I** and **II** each have a set of doublets with coupling constants of 946 and 1,077 Hz respectively. Thus the spectra of compounds **I** and **II** are consistent with species of types YPF_4 and YPF_2X respectively. The proton and carbon spectra for **I** and **II** also show resonances for the unsubstituted C_5H_5 ring and are assignable to a monosubstituted ferrocene species. Compound **II** arises from partial hydrolysis of **I** with trace water during the workup and further hydrolysis gives **III**, since, when solutions of **I** and **II** are exposed to air, only **III** is observed from the fluorine and phosphorus resonance spectra. The reaction of ferrocene and PF_5 is therefore, a new and direct route to phosphorus substituted ferrocenes.

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EXPERIMENTAL

Phosphorus pentafluoride from the supplier's cylinder was stored over phosphorus pentoxide in a bulb on a vacuum line. The fluorine resonance spectrum of this gas showed no evidence for phosphorus oxyfluoride. Ferrocene was recrystallized from hexane before use. Methylene chloride and hexane were purified,[9] distilled from phosphorus pentoxide and stored under vacuum. Magnetic resonance spectra were obtained in CH_2Cl_2 on a "Brucker AM 400" spectrometer at a magnetic field strength corresponding to a resonance frequency of 400 MHz for protons. Proton and carbon chemical shifts are reported with respect to tetramethylsilane although the inert compound, neopentane, was actually used as internal reference and appropriate corrections applied. Fluorine resonance shifts are reported relative to internal $CFCl_3$ and phosphorus resonance shifts relative to external 85% H_3PO_4. C and H microanalyses were performed by Mr. H. Seguin of the National Research Council, Canada and fluorine analysis by Canadian Microanalytical Service Ltd. Melting points (uncorrected) were obtained on a Gallenkamp apparatus.

General procedure for Preparation of **I** *and* **II**. The reaction was carried out in a reaction vessel consisting of two 20 mL "Pyrex" tubes separated and joined by an inverted L-shaped "Teflon" high vacuum stopcock. The first of these tubes was closed by another L-shaped "Teflon" high vacuum stopcock to allow removal of the apparatus from the vacuum line without exposure of its contents to the atmosphere. The second tube of the apparatus had an nmr tube attached to it as a side arm. Ferrocene (0.112 g, 0.6 mmol) was weighed and placed in the first tube of the reactor and 2 mL of CH_2Cl_2 was added by vacuum transfer. An equimolar quantity of PF_5 (0.076 g) was then transferred into the same tube. After one day at room temperature, all volatile species were removed by pumping under vacuum.[10] A mixed solvent (2 mL CH_2Cl_2 and 10 mL hexane) was added to the residual solid and after shaking the yellow-orange supernatant liquid was carefully decanted from the remaining insoluble solid and into the second tube. The solvents were pumped off under vacuum and the orange solid (mixture of **I** and **II**) obtained was redissolved in CH_2Cl_2 along with the nmr reference compounds, decanted into the nmr tube as side arm and sealed under vacuum. For **II**, ^1H nmr: δ 4.39 (S, C_5H_5); 4.64–4.71 (m, C_5H_4); ^{13}C nmr: δ 70.8 (C_5H_5), 72.7, 72.4 73.7, 73.8 (C_5H_4); ^{19}F nmr: δ −59.5 (d, $J_{FP} = 1077$ Hz), ^{31}P nmr: δ 23.1 (t, $J_{PF} = 1079$ Hz). For **I**, ^1H nmr: δ 4.40 (s, C_5H_5), 4.60–4.70 (m, C_5H_4); ^{19}F nmr: δ −52.9 (d, $J_{FP} = 946$ Hz); ^{31}P nmr: δ −35.1 (quintet, $J_{PF} = 937$ Hz).

General Procedure for Preparation of **III**. The compound was prepared in a 20 mL reaction vessel from equimolar quantities of ferrocene (0.533 g) and PF_5 (0.360 g) in 3 mL CH_2Cl_2. After one day at room temperature the reaction mixture was diluted with 5 mL CH_2Cl_2 followed by 15 mL hexane and the solution was filtered. Yellow crystals of **III** were obtained from the filtrate at 4°C, isolated yield 37%. For $C_{10}H_{10}FFePO_2$ Calc. %C = 44.80, %H = 3.73, %F = 7.09. Found %C = 43.73, %H = 3.59, %F = 6.64. M.P. = 119 – 121°C. ^1H nmr: δ 4.38 (s, C_5H_5), 4.58, 4.63 (2m, C_5H_4); ^{13}C nmr: δ 70.2 (C_5H_5), 71.7, 71.9, 72.1, 72.3 (C_5H_4); ^{19} F nmr: δ −54.1 (d, $J_{FP} = 998$ Hz); ^{31}P nmr: δ 29.0 (d, $J_{PF} = 999$ Hz).

REFERENCES

1. Issued as NRCC No. 29524.
2. A. G. Landers, M. W. Lynch, S. B. Raaberg, A. L. Rheingold, J. E. Lewis, N. J. Mammano and A. Zalkin, *J. Chem. Soc., Chem. Commun.* 931 (1976).
3. N. J. Mammano, A. Zalkin, A. G. Landers and A. L. Rheingold, *Inorg. Chem.* **16,** 297 (1977).
4. A. L. Rheingold, A. G. Landers, P. Dahlstrom and J. Zubieta, *J. Chem. Soc., Chem. Commun.* 143 (1979).
5. M. R. Churchill, A. G. Landers and A. L. Rheingold, *Inorg. Chem.* **20,** 849 (1981).
6. A. L. Rheingold, A. D. Uhler and A. G. Landers, Ibid. **22,** 3255 (1983).
7. H. Schumann, *Chemiker-Zeitung.* **111,** 111 (1987).
8. The crystals are orthorhombic in space group $P2_1nb$ with $a = 6{\cdot}0376(7)$, $b = 9.7228(8)$, $c = 18.039(3)$ Å and $Z = 4$. E. J. Gabe and F. L. Lee, unpublished results.
9. D. D. Perrin, W. L. F. Armarego and D. R. Perrin, "Purification of Laboratory Chemicals", 2nd Ed., Pergamon Press, Oxford (1980).
10. In a separate experiment at this point the volatiles were transferred to an nmr tube. The fluorine resonance spectrum showed the presence of PF_5 and POF_3, but no HF nor SiF_4.