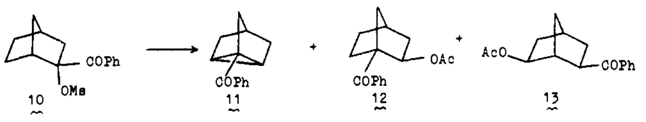
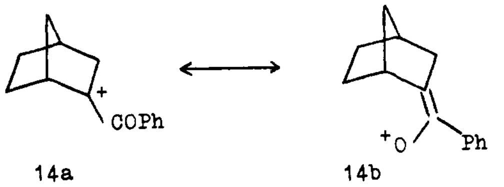
In support of this hypothesis, mesylate **10** has been prepared.[10] Acetolysis of **10** ($k = 1.35 \times 10^{-5}$ s^{-1} at 75 °C) gave the products shown and strongly suggests the involvement of an α-keto cation.



However, in terms of rate, the effect of the benzoyl group relative to hydrogen is quite small.[12] Solvolysis rates of **10** and *endo*-2-norbornyl mesylate ($k = 2.6 \times 10^{-5}$ s^{-1} at 75 °C)[13] are comparable, despite the inductively electron-withdrawing benzoyl group in **10**.

How would one expect the benzoyl group to effect the solvolysis rate of **10**? To answer this question, consider first the effect of a benzoyl group on the solvolysis of 2-phenyl-2-propyl chloride (cumyl chloride). *p*-Benzoylcumyl chloride[14] solvolyzed 79 times slower than cumyl chloride. Normally the effect of substituents on solvolysis rate is attenuated when that substituent is insulated from the cationic center by the aromatic ring of the cumyl chloride. For example, a *p*-methyl substituent increases the solvolysis rate of cumyl chloride by a factor of 27,[4] while substitution of a methyl for hydrogen directly on a cationic center gives rate increases from 10^5 to 10^8.[15] A *p*-cyclopropyl group increases the solvolysis rate of cumyl chloride by a factor of 154,[4] while substitution of a cyclopropyl group for hydrogen directly on a cationic center increases the rate of greater than 10^9.[7b] A *p*-trifluoromethyl group retards the solvolysis of cumyl chloride by a factor of 600,[4] while substitution for hydrogen directly at a cationic center[16] retards the rate by 10^5–10^6. One might then expect that, in the absence of other factors, the unattenuated benzoyl group might slow the solvolysis of **10** by a large factor, perhaps as large as 10^4–10^5. Some other factor must therefore increase the solvolysis rate of **10** so that its rate is comparable to that of *endo*-2-norbornyl mesylate. We believe that at least part of this factor is carbonyl group stabilization of the α-keto cation **14** via forms such as **14b**.



This suggestion, on the basis of our experimental results, is in agreement with the recent theoretical study of Houk and Paddon-Row[17] which indicates that a formyl group in a conjugating conformation can stabilize a cationic intermediate relative to a nonconjugating (perpendicular) formyl group.

Acknowledgment is made to the donors of the Petroleum Research fund, administered by the American Chemical Society, for support of this research.

Supplementary Material Available: Details of arguments against the involvement of **8** (4 pages). Ordering information is given on any current masthead page.

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(10) Reaction of norcamphor with diethyl-1-(trimethylsiloxy)-1-phenylmethanephosphonate carbanion[11] followed by hydrolysis gave the alcohol precursor to **10**. Treatment with $CH_3SOCl–Et_3N$ followed by *m*-chloroperbenzoic acid oxidation gave **10**.

(11) Koenigkramer, R. E.; Zimmer, H. *J. Org. Chem.* **1980**, *45*, 3994–3998.

(12) Our previous study[1] found a rate ratio of $10^{7.3}$ in the solvolysis of *exo*-2-methylbicyclo[2.2.1]heptan-*endo*-2-yl tresylate and carbonyl analogue *exo*-3-methylbicyclo[2.2.1]heptan-2-on-*endo*-3-yl tresylate. This is the α-CH_2/α-keto ratio and *not* the α-H/α-keto ratio as has been implied in the various references to our work. These systems are not suitable for determining the effect of the carbonyl group relative to hydrogen. The present system, **10**, gives such an α-H/α-keto ratio.

(13) Estimated from the tosylate rate assuming the tosylate rate is 2 times the mesylate rate. See: Schleyer, P. v. R.; Donaldson, M. M.; Watts, W. E. *J. Am. Chem. Soc.* **1965**, *87*, 375–376.

(14) This chloride was prepared by reaction of the grignard reagent derived from 4-bromobenzophenone dimethyl ketal with acetone followed by treatment with concentrated hydrochloric acid.

(15) Fry, J. L.; Harris, J. M.; Bingham, C. R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2540–2542.

(16) Koshy, K. M.; Tidwell, T. T. *J. Am. Chem. Soc.* **1980**, *102*, 1216–1218.

(17) Paddon-Row, M. N.; Santiago, C.; Houk, K. N. *J. Am. Chem. Soc.* **1980**, *102*, 6561–6563.

Syntheses of Trifluoromethylated Thiadiphosphanorbornadiene and Thiadiphosphole[1]

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Previously, we reported that 2,3,5,6-tetrakis(trifluoromethyl)-1,4-diphosphabenzene (**2**) was obtained by thermolysis of 2,3,5,6,7,8-hexakis(trifluoromethyl)-7-methoxy-7,8-dihydro-1,4-diphosphabarrelene (**1**) and that **2** was thermally stable but reactive to dienophiles and oxygen.[2] Now, we have used this high reactivity of **2** for the synthesis of a new ring system, thiadiphosphanorbornadiene (**3**), which was further converted to a thiadiphosphole. Since **2** is very sensitive to air, we thermolyzed **1** in situ in this experiment.

Thermolysis of **1** with excess of sulfur in pentane in a sealed tube at 100 °C for 48 h gave an adduct of **2** with sulfur, 2,3,5,6-tetrakis(trifluoromethyl)-7-thia-1,4-diphosphanorbornadiene (**3**), which was purified by preparative GLC.[3] **3**: an air-stable yellow oil; $\nu_{C=C}$ 1610 cm^{-1}; ^{19}F NMR (pentane) δ[4] -6.8 ($J_{PF} = 24.8$ Hz); high-resolution MS, *m/e* 418 (M^+). Anal. Calcd. for $C_7F_9P_2S$ ($M - CF_3$): 348.905. Found: 348.906. In the attempted desulfurization of **3** with triphenylphosphine, the formation of **2** was confirmed by ^{19}F NMR spectroscopy. Treatment of **2** with 0.5 molar equiv of cyclohexene thioxide gave **3** and a cycloadduct (**4**) of **2** with cyclohexene in nearly quantitative yields, estimated by ^{19}F NMR spectroscopy, both of which were separated by preparative GLC.[3] **4**: mp 130–132 °C (pentane); ν_{C-H} 2950, 2870, ν_{C-F} 1240, and 1140 cm^{-1}; *m/e* 468 (M^+). This reaction shows that **2** has a high affinity for sulfur.

Compound **3** seemed likely to react with **2** as a dienophile, since hexakis(trifluoromethyl)diphosphabarrelene (**5**) was known to be a good dienophile.[5] The adduct **6** could be a good precursor for the thiadiphosphole compound **7**, since dihydrodiphosphabarrelene **1** was easily cleaved to **2** and the ethylene compound. Therefore, we thermolyzed **1** with 0.5 molar equiv of sulfur and obtained the thiadiphosphole **7** and **5** in nearly quantitative yields, estimated by ^{19}F NMR spectroscopy. The reaction mixture was cooled, the precipitate of **5** was filtered off, and the solvent was removed under vacuum to give a very air-sensitive oil which was nearly pure **7** by ^{19}F NMR spectroscopy. **7**: ν_{C-F} 1238, 1175 cm^{-1}; ^{19}F NMR (pentane) δ -12.8 ($J_{PF} = 51$ Hz); λ_{max} (hexane) 248 ($\epsilon > 1100$), 322 nm ($\epsilon > 850$). The air sensitivity of **7** is comparable to that of **2**, both of which have planar structures. This is very interesting, since **3** and **5** of the cage structure are stable to air. Compound **7** was found to be a good diene in the Diels–Alder reaction. Thus the reaction of **7** with hexafluoro-2-butyne gave **3** quantitatively. Further, the treatment of **7** with maleic anhydride in pentane gave an adduct (**8**) in 57% yield, which was precipitated from the reaction mixture. **8**: mp 135–136°C (hexane–C_6H_6); ν_{C-H} 2980,

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(1) A part of this work was presented at 9th International Symposium on Fluorine Chemistry, Sept. 1979, Avignon, France.

(2) Y. Kobayashi, I. Kumadaki, A. Ohsawa, and H. Hamana, *Tetrahedron Lett.*, **1976**, 3715.

(3) Ohkura gas chromatograph, Model 701. Column DEGS 3-mm i.d., 3-m long, at 70 °C. Isolation yield 7.4% (58% based on ^{19}F NMR spectroscopy).

(4) Benzotrifluoride as an external standard: higher field is shown by +.

(5) Y. Kobayashi, I. kumadaki, H. Hamana, and S. Fujino, *Tetrahedron Lett.*, **1976**, 4815.

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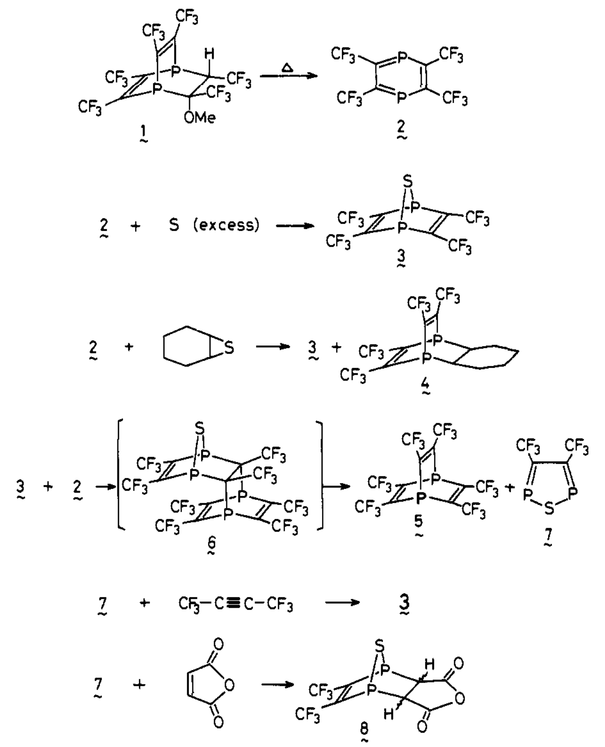
Chart I



$\nu_{C=O}$ 1860, 1790, $\nu_{C=C}$ 1610, ν_{C-F} 1270, 1170 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.13 (d, J_{P-H} = 14 Hz); ^{19}F NMR (CDCl$_3$) δ −9.6 (J_{P-F} = 27.1 Hz); high resolution MS, m/e 354 (M$^+$). Anal. Calcd. for $C_8H_2O_3P_2SF_6$: 353.910. Found: 353.908. These results are summarized in Chart I.

The driving force of the last step from the adduct **6** to **7** and **5** may be explained by some aromaticity of **7**, as **1** was easily cleaved to **2** partially due to the aromaticity of the latter.[5] High thermal stability of **7** seems to support its aromaticity.

Reversible, Nitrogen-Assisted Migration of a Phenyl Group from Phosphorus to Iron in CpFe(CO)[PhP(OCH$_2$CH$_2$)$_2$NH]$^+$PF$_6^-$

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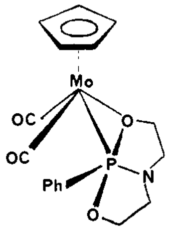
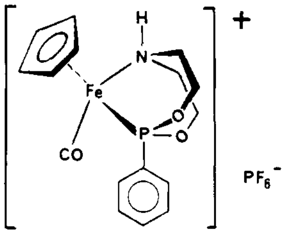
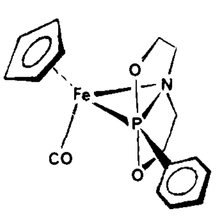
Our recent synthesis of the transition-metal–phosphoranide adduct **1**[1] led us to investigate the action of a base on CpFe(CO)[PhP(OCH$_2$CH$_2$)$_2$NH]$^+$PF$_6^-$ (**2**),[2,3] in order to abstract the proton bound to nitrogen. This was expected to give either a phosphoranide adduct (such as **3** or a product analogous to **1**) or the amide adduct **4**. In fact neither of these alternatives was realized; rather a new reaction has been discovered which leads to compound **5**.



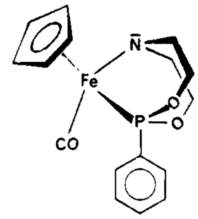
1



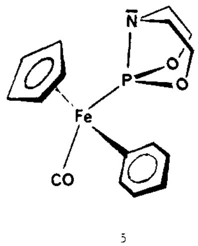
2



3



4



5

Infrared spectroscopy was used to monitor the reaction of **2** with LiMe; the ν_{CO} vibration of **2** at 1975 cm^{-1} can be made to disappear completely, while a new absorption develops at 1920 cm^{-1}, by heating it for 4 h in THF with a slight excess (ca. 1.5 M equiv) of the base. After chromatography (SiO$_2$/Et$_2$O) of the reaction product, an amber-colored crystalline material was isolated in 30% yield. Its spectral characteristics, however, are compatible neither with the phosphoranide structures, such as **1** or **3**, nor with the amide structure, such as **4**. While the spectral properties of **2** and its molybdenum analogue CpMo(CO)$_2$[PhP(OCH$_2$CH$_2$)$_2$NH]$^+$PF$_6^-$ are very similar (with, for example, ^{31}P resonances at 208 and 198 ppm, respectively), the ^{31}P resonance of the new compound, at 218 ppm, is very different from that found for the phosphoranide adduct **1** (16.5 ppm). A ^{31}P resonance of 218 ppm alone *could* indicate a phosphanoamido iron chelate, as in **4**;[4,5] however, the absence of coupling between the ^{13}C nuclei of the phenyl group and ^{31}P is not compatible with the amide structure **4**.

The structure of the reaction product has therefore been established by X-ray diffraction (by using conventional, heavy-atom methods). The monoclinic crystals crystallize in the space group $P2_1/n$ with unit-cell parameters a = 7.776 (1), b = 14.477 (3), c = 14.083 (1) Å; β = 102.04 (1)°; V = 1550.5 Å;^{3} D_m = 1.52, D_c = 1.539 g cm^{-3}; Z = 4. Of 2846 independent measured reflections (Mo Kα radiation), 2000 were used for the refinement of the structure (R_w = 0.056, R = 0.073). The hydrogen atoms were located by a Fourier difference synthesis at this stage of the refinement. The final R factors converged to R_w = 0.035 and R = 0.057.

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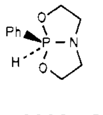
† Member of the Université Scientifique et Médicale de Grenoble.

[1] Wachter, J.; Riess, J. G.; Mentzen, B. *Angew Chem.*, in press.

[2] Compound **2** was obtained by the action of bicyclophosphorane on CpFe(CO)$_2$Br, through the same experimental procedure as was previously reported for the molybdenum analogue.[4]



[3] The analyses of the new compounds were done by the Service Central de Microanalyse du CNRS and are all satisfactory.

[4] Wachter, J.; Jeanneaux, F.; Riess, J. G. *Inorg. Chem.* **1980**, *19*, 2169.

[5] Pradat, C.; Riess, J. G.; Bondoux, D.; Mentzen, B. F., Tkatchenko, I., Houalla, D. *J. Am. Chem. Soc.* **1979**, *101*, 2234.

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