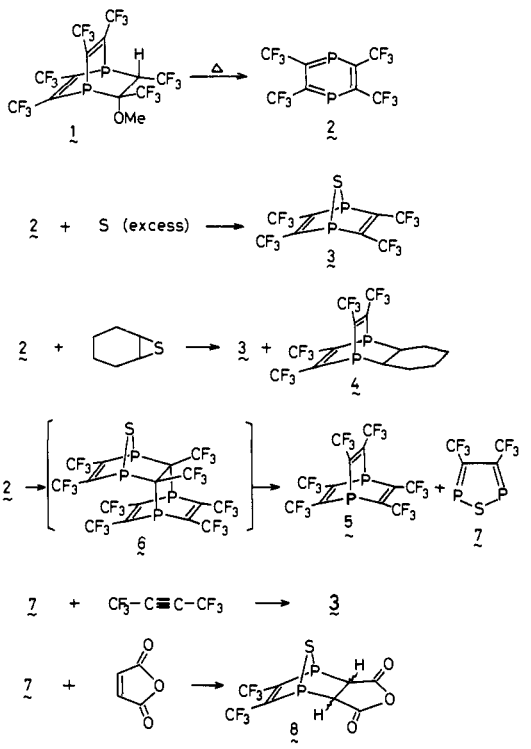
Chart I



$\nu_{C=O}$ 1860, 1790, $\nu_{C=C}$ 1610, $\nu_{C-F}$ 1270, 1170 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 4.13 (d, $J_{P-H}$ = 14 Hz); $^{19}F$ NMR ($CDCl_3$) $\delta$ -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 $CpFe(CO)[PhP(OCH_2CH_2)_2NH]^+PF_6^-$

Pierre Vierling and Jean G. Riess*

*Laboratoire de Chimie Minérale Moléculaire*
*Equipe Associée au C.N.R.S., Université de Nice*
*Parc Valrose, 06034 Nice, France*

André Grand†

*Laboratoire de Chimie Organique Physique (ERA 674)*
*Département de Recherches Fondamentales*
*Centre d'Etudes Nucléaires 85X*
*38041 Grenoble, France*

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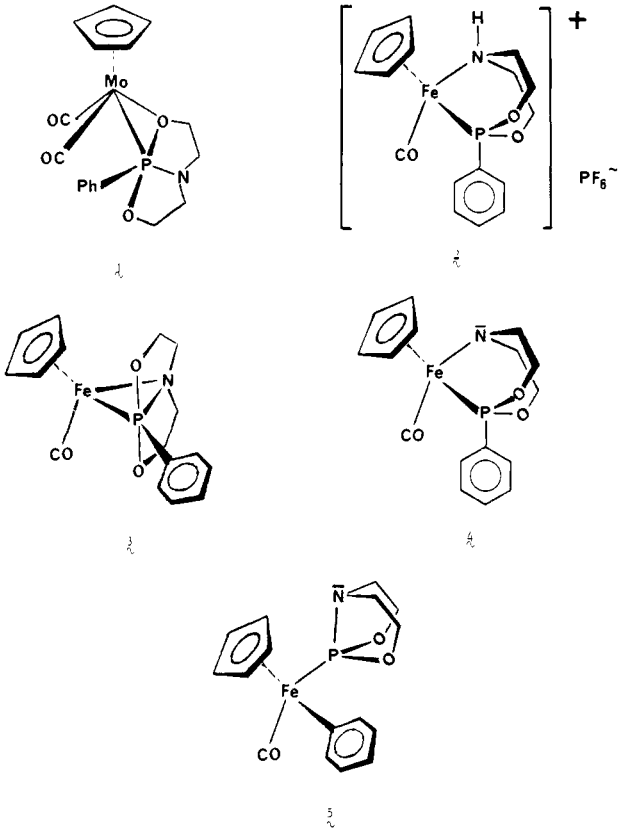
Our recent synthesis of the transition-metal-phosphoranide adduct **1**[1] led us to investigate the action of a base on $CpFe(CO)[PhP(OCH_2CH_2)_2NH]^+PF_6^-$ (**2**),[2,3] in order to abstract the proton bound to nitrogen. This was expected to give either a phosphoranide adduct (such as **3** or a 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**.



Infrared spectroscopy was used to monitor the reaction of **2** with LiMe; the $\nu_{CO}$ 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 ($SiO_2/Et_2O$) 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 $CpMo(CO)_2[PhP(OCH_2CH_2)_2NH]^+PF_6^-$ 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; $\beta$ = 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 K$\alpha$ 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.

† 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 $CpFe(CO)_2Br$, 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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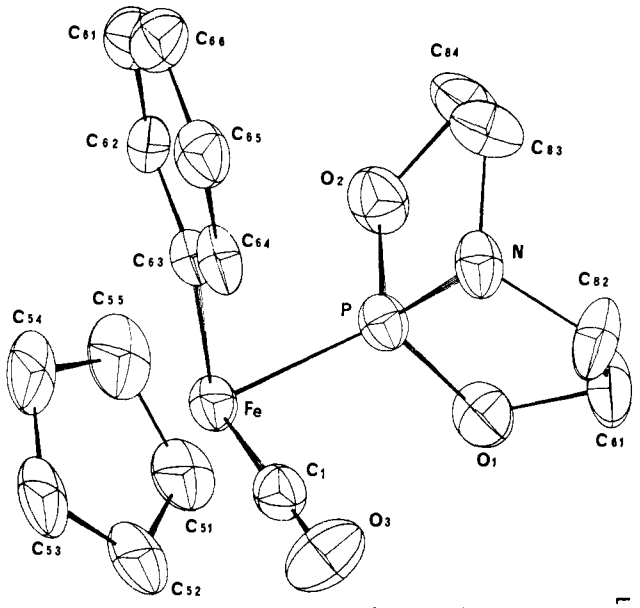


**Figure 1.** Molecular structure of $(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_6H_5)(CO)Fe[P(OCH_2CH_2)_2N]$. Selected bond lengths: Fe-P 2.105 (2), Fe-C1 1.715 (5), Fe-C63 2.037 (5), Fe-Cp(mean) 2.102 (5), P-N 1.692 (4), P-O1 1.620 (3), P-O3 1.602 (4) Å. Angles: P-Fe-C1 90.6(2), C63-Fe-C1 94.5 (2), C63-Fe-P 83.9 (2), Fe-P-N 123.3 (2), Fe-P-O1 114.5 (2), Fe-P-O2 115.5 (2), P-N-C82 108.6 (3), P-N-C83 107.4 (3), C82-N-C83 117.6 (4)°.

An ORTEP picture of the structure is shown in Figure 1. Its most unexpected feature is that the phenyl group is no longer bound to phosporus, but to iron, while the ligand has undergone a rearrangement into a bicyclic entity, as a result of the formation of a P-N bond. The iron atom lies in the plane of the phenyl group, and the Fe-C(phenyl) $\sigma$ bond is short (2.04 Å) when compared to that found in $(\eta^5\text{-Cp})Fe(CO)(PPh_3)(\eta^1\text{-}C_6H_5)$ (2.14 Å).[6] The P-Fe bond distance of 2.105 Å is also much shorter than that (2.23 Å) of the $PPh_3$ derivative **6**; it appears to be the shortest P-Fe bond found so far in an iron(II) compound.[7] This may originate both from a lessening of steric hindrance when triphenylphosphane is replaced by the much more compact bicyclic ligand and from the expected increase in $\sigma$ character of the phosphorus hybrid orbital binding iron, due to the greater electronegativity of the phosphorus substituents in the bicyclic ligand.[8] The P-N bond is also remarkably short (1.69 Å) and is comparable with bond distances found in aminophosphanes for which it is customary to invoke a $p_\pi$-$d_\pi$ contribution[9,10] ($Me_2N\text{-}PCl_2$ : 1.69 Å),[11] in spite of the fact that here the nitrogen atom is markedly pyramidal (sum of the angles around nitrogen: 333.6 ± 1.0°).. This bond length is also shorter than the 1.75 Å found when N is coordinated to a $BH_3$ group in the bis(borane)-bicyclophosphane adduct $H_3B{\cdot}P[OC(CH_3)_2CH_2]_2N{\cdot}BH_3$.[9] The free bicyclic ligand has lately been synthesized;[12] in its uncoordinated form it is, however, unstable at room temperature with respect to polymerization.

Another very surprising observation is that the migration of the phenyl group is *reversible*: when gaseous HCl is bubbled through a THF solution of **5** at room temperature, the color changes from orange to deep red. The conversion is quantitative, as shown by the IR spectrum of the solution. The addition of $NH_4^+PF_6^-$ allows the recovery, in 60% yield, of compound **2**.

This new behavior of the cyclic P/N ligand appears to have no precedent in the literature. The rearrangement cannot be compared, for example, to the observation that $PPh_3$ can undergo oxidative addition to zero-valent metals, as observed, for example, by Fahey and Mahan,[13] since there is neither a change of oxidation state and coordination number for the metal nor a change of the phosphane into a phosphide ligand. It cannot be compared, either, to the irreversible transfer of a phenyl group from a phosphonium ion to iron, as observed by Ellis[14] or from a phosphorus ylide to nickel, as reported by Keim et al.[15] This original behavior clearly entails the assistance of the NH group. We suggest that it is the action of an acid or a base on that group that triggers a redistribution of bonds about phosporus and iron, probably in a synchronous pair of 1,2 shifts at the P-Fe bond, that is perhaps uniquely attributable to the transannular relationship of N and P in this flexible ligand.

**Supplementary Material Available:** A table of atomic positions and thermal parameters and a table of bond lengths and angles (2 pages). Ordering information is given on any current masthead page.

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## Acanthifolicin, a New Episulfide-Containing Polyether Carboxylic Acid from Extracts of the Marine Sponge *Pandaros acanthifolium*

Francis J. Schmitz,* Ravi S. Prasad,
Yalamanchili Gopichand, M. Bilayet Hossain, and
Dick van der Helm*

*Department of Chemistry, University of Oklahoma
Norman, Oklahoma 73019*

Paul Schmidt

*Oklahoma Medical Research Foundation
Oklahoma City, Oklahoma 73104*

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Bacteria and other microorganisms present in marine sponges as endosymbionts or as a result of filter feeding by the sponges are suspected of being the source of some of the metabolites isolated from the entire sponge assemblages.[1] While unambiguous determination of the ultimate source of specific metabolites from sponge assemblages is obviously difficult, a reasonable assignment might be made in cases where metabolites known to be unique to certain microorganisms are isolated. In our bioassay-guided search for antitumor agents in marine organisms, we now have isolated a highly cytotoxic compound, acanthifolicin (**1**),[2] from extracts of the sponge *Pandaros acanthifolium*, and have established by X-ray analysis that it is a novel episulfide-containing member of the polyether antibiotic class of compounds[3] isolated heretofore only from bacteria. Acanthifolicin is the first polyether carboxylic acid reported from marine sources. Its episulfide functionality, rare in any natural product, is an unprecedented feature among the known polyether antibiotics that have attracted much attention during the last decade.[3] The isolation of this

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