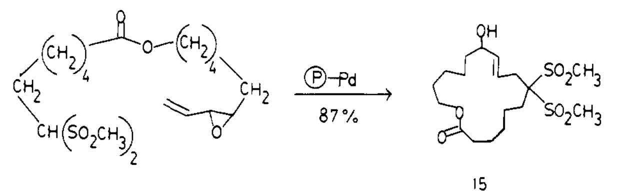
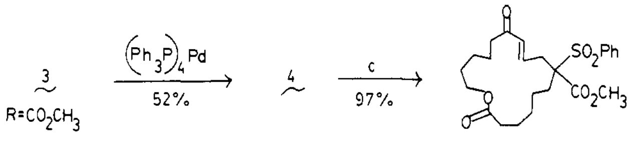
cyclization conditions. Interestingly, this cyclization to **15**[10,11] was the fastest (15 min vs. 3 h for **3** R = $PhSO_2$) even though **14** must be less acidic than either **3** (R = CO_2CH_3) or **3** (R = $PhSO_2$) by comparing the pK_a's of **11** → **13**.



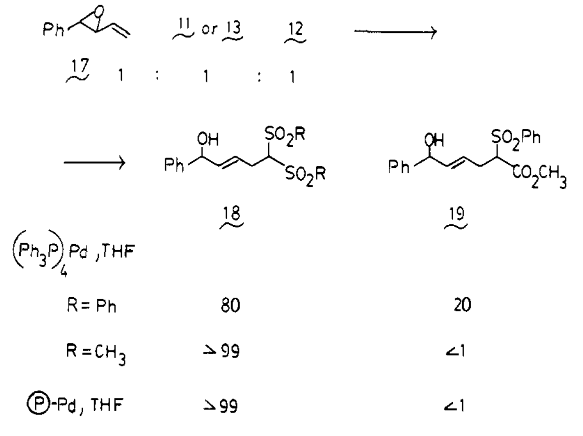
14 **15**

That the failure of **3** (R = CO_2CH_3) stemmed from the nature of the "active site" of the catalyst and not the thermodynamic pK_a was conclusively demonstrated by subjecting **3** (R = CO_2CH_3) to a homogeneous catalyst [5 mol % $(Ph_3P)_4Pd$, 10 mol % dppe][13] at 0.001 M (THF, reflux), which now indeed did cause it to cyclize. Due to the diastereomeric nature of **4** it was best characterized after oxidation[12a] to the homogeneous enone **16**.[10,11]



16

The dramatic sensitivity of the cyclization to the nature of the nucleophile appears to stem from the facility of absorption of the substrate on the polymer and a favorable competition for proton transfer and alkylation compared to alternative pathways of reaction for the initially ionized intermediate. To test the relative reactivity of **11**, **12**, and **13** with vinyl epoxides, **11** and **12** as well as **12** and **13** were allowed to compete for a limited amount of vinyl epoxide **17**. In the **11** vs. **12** competition with a homogeneous catalyst, a 4:1 ratio favoring alkylation of **11** was obtained. With the polymeric catalyst, exclusive alkylation of **11** occurred. Similarly, the **12** vs. **13** competition favored alkylation of the bis(sulfone) **13**. Thus, the bis(sulfone) system intrinsically is more reactive—a reactivity advantage that is enhanced by the polymer. The high reactivity of the bis(sulfonylalkane) unit toward the vinyl epoxides then accounts for its ability to competitively swamp any undesired reactions.[15] The delicate balance that must exist is highlighted by the total failure of the polymer-based reaction by simply substituting an ester for one sulfonyl group. While the range of pro-nucleophiles that can be used in this cyclization by isomerization remains to be elucidated, the excellent success of the bis(sulfone) combined with its tremendous versatility makes the current method a very useful one. The possible implications of the relative reactivity of the bis(sulfone) unit in other types of cyclizations would be interesting to explore.[16]



Acknowledgment. We thank the National Institutes of Health, General Medical Sciences, and the National Science Foundation for their generous support of our programs. Appreciation of Johnson Matthey Inc. and Englehardt Industries for generous supplies of palladium salts is heartily noted. Robert W. Warner would like to thank Artie G. Romero for his helpful insight and enthusiastic contributions in this work.

Registry No. 3 (R = $PhSO_2$), 86471-67-2; **3** (R = CO_2CH_3), 86471-68-3; **4**, 86471-69-4; **5**, 86471-70-7; **6**, 86471-71-8; **7**, 86471-72-9; **8**, 86471-73-0; **9**, 86471-74-1; **10**, 86471-75-2; **11**, 3406-02-8; **12**, 34097-60-4; **13**, 1750-62-5; **14**, 86471-76-3; **15**, 86471-77-4; **16**, 86471-78-5; **17**, 20248-57-1; **18** (R = Ph), 86471-79-6; **18** (R = CH_3), 86471-80-9; **19**, 86471-81-0.

Supplementary Material Available: Schemes of the preparation of **3** (R = CO_2CH_3, $PhSO_2$), **14**, and **8** and spectra data of these compounds (3 pages). Ordering information is given on any current masthead page.

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[15] This result contrasts with our earlier observation on the stereochemistry of the Pd-catalyzed intermolecular alkylation (Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4730) of allylic acetates. In the vinyl epoxide reaction, two stages determine the alkylation (1) rate of proton transfer and (2) rates of formation of the carbon–carbon bond. Since the allylic acetate reactions only depend upon the rate of carbon–carbon bond formation, the kinetic preference for **11** may relate to its rate of proton transfer. The fact that the thermodynamic pK_a's of **11** and **12** are virtually identical suggests that scrambling of anions after initial proton transfer does not occur.

[16] For reviews on sulfone chemistry see: Magnus, P. D. *Tetrahedron* **1977**, 33, 2019. Durst, T. *Compr. Org. Chem.* **1979**, *2*, 171.

α-Elimination of α-Acetoxysilanes Induced by Palladium: Evidence for the Intermediacy of a Vinylcarbene–Palladium Complex

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Modifying the behavior of reactive intermediates by complexing them to transition metals may offer the potential of adjusting their reactivity pattern. An interesting example is trimethylenemethane, whose complexation to transition metals permits variations running from selective cycloadditions to electron-deficient olefins[1-3] to forming stable unreactive complexes.[4] Use of palladium as the transition metal apparently alters its structure such that it behaves as a zwitterion rather than a diradical.[2] In order to probe the ability of palladium to impose polar properties on or to reverse such properties of reactive intermediates, we considered the case of vinylcarbenes.[5,6] If one considers a potential dipolar form for

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[1] Noyori, R.; Odagi, T.; Takaya, H. *J. Am. Chem. Soc.* **1970**, *92*, 5780. Noyori, R.; Ishigami, I.; Hayashi, N.; Takaya, H. *Ibid.* **1973**, *95*, 1674. Noyori, R.; Yamakawa, M.; Takaya, H. *Tetrahedron Lett.* **1978**, 4823.

[2] Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1979**, *101*, 6429, 6432; **1980**, *102*, 6359; **1981**, *103*, 5972; **1982**, *104*, 3733. Gordon, D. J.; Fenske, R. F.; Nanninga, T. N.; Trost, B. M. *Ibid.* **1981**, *103*, 5974. Trost, B. M.; Nanninga, T. N.; Chan, D. M. T. *Organometallics* **1982**, *1*, 1543. Albright, T. A. *J. Organomet. Chem.* **1980**, *198*, 159.

[3] Cf.: Binger, P.; Schuchardt, U. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 249; *Chem. Ber.* **1980**, *113*, 3334; **1981**, *114*, 3313. Binger, P.; Germer, A. *Ibid.* **1981**, *114*, 3325. Binger, P.; Bentz, P. *J. Organomet. Chem.* **1981**, *221*, C33.

[4] Barnes, S. G.; Green, M. *Chem. Commun.* **1980**, 267. Samuelson, A. G.; Carpenter, B. K. *Ibid.* **1981**, 354. Becker, Y.; Eisenstadt, A.; Shro, Y. *Tetrahedron* **1976**, *32*, 2123. Kritskaya, I. I.; Struchkov, Y. T. *J. Chem. Soc. D* **1970**, *85*. Noyori, R.; Nishimura, T.; Takaya, H. *Ibid.* **1969**, 89. Day, A. C.; Powell, J. T. *Chem. Commun.* **1968**, 1241. Ehrlich, K.; Emerson, G. F. *J. Am. Chem. Soc.* **1972**, *94*, 2464.

[5] Hartzler, H. D. In "Carbenes"; Moss, R. A., Jones, M., Jr., Eds.; Wiley-Interscience: New York, 1975; Chapter 2. Pincock, J. A.; Mathur, N. C. *J. Org. Chem.* **1982**, *47*, 3699 and earlier references cited therein.

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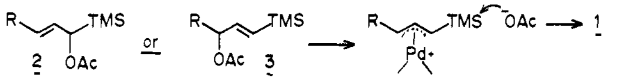
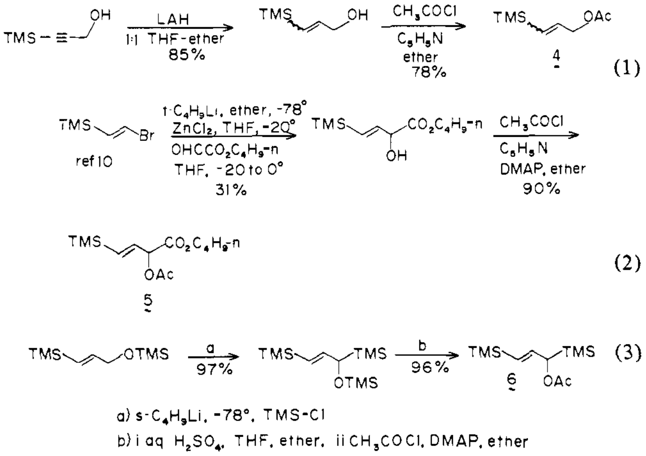
the singlet carbene, it would appear that complexation to palladium as represented in **1** would fix it in a dipolar form in which the

carbanion center would initiate reactions. Furthermore, such species could be envisioned to be generated from readily available acetoxysilanes such as **2** via a palladium-mediated α-elimination.[7]

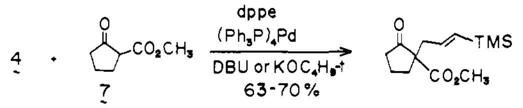


Three silyl acetates, **4**,[8] **5**,[9] and **6**,[9] were synthesized as summarized in eq 1–3. The silane **4** was available as an *E,Z* mixture;

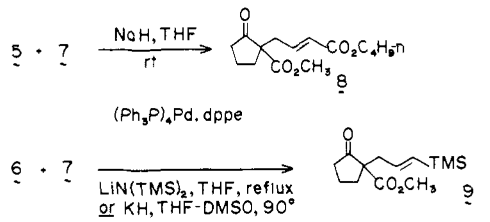


the stereochemistry derived from the variable stereochemistry in the reduction of the propargyl alcohol. The addition of an (*E*)-2-(trimethylsilyl)vinyl organometallic to *n*-butyl glyoxalate for the synthesis of **5** proved troublesome. Best results utilized in situ generation of the vinylzinc reagent to which *n*-butyl glyoxalate was added dropwise at −20 °C. In the first step of the preparation of **6** the silylation of the anion of the Me_3Si ether required about 2 h for maximum yields.

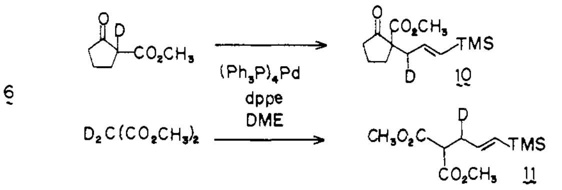
Palladium-catalyzed alkylation[12] of **4** with 2-(methoxycarbonyl)cyclopentanone led only to substitution with no desilylation.[8b] On the other hand, alkylation of **5** or **6** under similar



conditions led to desilylated products **8**[9] and **9**.[9] Since use of **5**

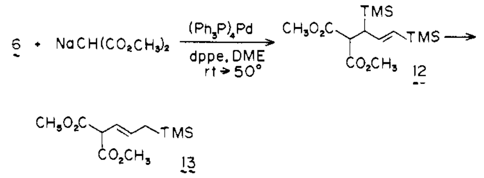


in such alkylations was accompanied by double-bond migration in this starting material, we probed the source of these products in the reactions of **6** with **7** and dimethyl malonate. Alkylation of 2-deuterio-2-(methoxycarbonyl)cyclopentanone with **6** even in the absence of any base led to a unique monodeuterated product **10**[9] as shown by the ^1H [δ 5.78 (dd, J = 18.4, 6.3 Hz, 1 H), 5.69



(d, J = 18.4 Hz, 1 H), 2.64 (d, J = 6.3 Hz, 1 H)] and proton-decoupled ^{13}C [δ 40.88 (1 C, t, J = 19.6 Hz)] NMR spectroscopy as well as mass spectrometry (*m/e* 255.1400). Similarly, alkylation of methyl dideuteriomalonate under identical conditions followed by back exchange of any deuterium α to the ester groups with aqueous sodium bicarbonate led to the monodeuterated product **11**[9] as a ~9:1 *E,Z* olefin mixture whose structure is defined by ^1H [δ 6.18 (dd, J = 14, 7, Hz) and 5.91 (dd, J = 18.4, 5.8 Hz), (total 1 H), 5.72 (dd, J = 18.4, 0.8 Hz) and 5.60 (dd, J = 14.0, 1.4 Hz) (total 1 H), 3.45 (d, J = 7 Hz, 1 H)] and proton decoupled ^{13}C [E isomer δ 35.4, t, J = 26.2 Hz] NMR spectroscopy and mass spectrometry (*m/e* 245.1193).

Use of dimethyl sodiomalonate with **6** led to the normal alkylation product **12**.[9,13] Suitable control experiments revealed that neither starting material nor product proto-desilylated under these reaction conditions. Further, deliberate proto-desilylation of **12** produces **13**, not the vinyl silane corresponding to **11**.



The fact that desilylation must occur in an intermediate as shown by the control experiments, that the normal π-allylpalladium species **14** is produced as shown by the formation of **12** with sodiomalonate, and that the deuteration occurs specifically at the carbon bonded to the incoming nucleophile point to the pathway outlined in eq 4. Depending on the nature of the nucleophile,

interception of **14** by the nucleophile can occur prior to desilylation as in the case of the more reactive malonate anion (pK_a of conjugate acid 16) but not with the more stable and less reactive 2-(methoxycarbonyl)cyclopentanone anion (pK_a of conjugate acid 14).[2] Such preferential trapping of the analogous initial intermediates from **4** even with the latter anion accounts for it giving only the normal alkylation product. While the protonation al-

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(6) For "nucleophilic" carbenes see: Jones, W. M.; Stowe, M. E.; Wells, E. E., Jr.; Lester, E. W. *J. Am. Chem. Soc.* **1968**, *90*, 1849. Jones, W. M.; Ennis, C. L. *Ibid.* **1969**, *91*, 6391. Lemal, D. M.; Grosselink, E. P.; McGregor, S. D. *Ibid.* **1966**, *88*, 582. Quast, H.; Hunig, S. *Chem. Ber.* **1966**, *99*, 2017. Brook, A. G.; Kucera, H. W.; Pearce, R. *Can. J. Chem.* **1971**, *49*, 1618.

(7) For thermal or halide initiated α-eliminations in silicon conjunctive reagents see: Motsarev, G. V.; Rozenberg, V. R. *Zh. Prikl. Khim. (Leningrad)* **1964**, *37*, 747; *Chem. Abstr.* **1964**, *61*, 4389. Mueller, R.; Mueller, W. *Chem. Ber.* **1965**, *98*, 2916. Fishwick, G.; Haszeldine, R. N.; Parkinson, C.; Robinson, P. J.; Simmons, R. F. *Chem. Commun.* **1965**, 382. Haszeldine, R. N.; Tipping, A. E.; Watts, R. O.'B. *Ibid.* **1969**, 1364. Brook, A. G.; Dillon, P. J. *Can. J. Chem.* **1969**, *47*, 4347. Atwell, W. H.; Weyenburg, D. R.; Uhlmann, J. G. *J. Am. Chem. Soc.* **1969**, *91*, 2025.

(8) (a) Cf.: Stork, G.; Jung, M. E.; Colvin, E.; Noel, Y. *J. Am. Chem. Soc.* **1974**, *96*, 3684. (b) For an independent investigation of this compound see: Hirao, T.; Enda, J.; Ohshiro, Y.; Agawa, T. *Tetrahedron Lett.* **1981**, *22*, 3079. (c) Also See: Denmark, S. E.; Jones, T. K. *J. Org. Chem.* **1982**, *47*, 4595.

(9) This compound has been fully characterized by spectral means including high-resolution mass spectroscopy.

(10) Voronkov, M. G. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1976**, 1545.

(11) Cf.: Hosomi, A.; Hashimoto, H.; Sakurai, H. *J. Org. Chem.* **1978**, *43*, 2551.

(12) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. Trost, B. M.; Verhoeven, T. R. *Compr. Organomet. Chem.* **1982**, *8*, 779–983. Tsuji, J. "Organic Synthesis with Palladium Compounds"; Springer-Verlag: Berlin, 1980.

(13) Such alkylations uncomplicated by desilylation are best performed with molybdenum catalysts (Lautens, M., unpublished work in these laboratories). See: Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1982**, *104*, 5543.

kylation supports the zwitterion formalism for **15**, attempts to react **15** with aldehydes failed. This palladium-complexed vinyl carbene[14] also fails to give reactions typical of carbenes—a type of behavior reminiscent of some nucleophilic carbenes.[6] Nevertheless, the facility of this palladium initiated α-elimination of α-acetoxysilanes suggests a new route to metal-complexed carbenes and supports the notion that palladium complexation imparts substantial polarization to such reactive intermediates.

Acknowledgment. We thank the National Science Foundation for their generous support of our programs. C.R.S. gratefully acknowledges a SERC NATO postdoctoral fellowship during his stay in these laboratories. We thank Johnson-Matthey and Englehardt for generous supplies of palladium salts.

Registry No. (*E*)-**4**, 86422-21-1; (*Z*)-**4**, 86422-22-2; **5**, 86422-23-3; **6**, 86422-24-4; **7**, 10472-24-9; **8**, 86422-25-5; **9**, 86422-26-6; **10**, 86422-27-7; **11**, 86422-28-8; **12**, 86422-29-9; **13**, 86422-30-2; TMSC≡CCH$_2$OH, 5272-36-6; (*E*)-TMSCH=CHCH$_2$OH, 59376-64-6; (*Z*)-TMSCH=CHCH$_2$OH, 62861-80-7; (*E*)-TMSCH=CHBr, 41309-43-7; (*E*)-TMSCH=CHCH(OH)CO$_2$C$_4$H$_9$-*n*, 86422-31-3; (*E*)-TMSCH=CHCH$_2$OTMS, 86422-32-4; (*E*)-TMSCH=CHCH(OTMS)TMS, 86422-33-5; (Ph$_3$P)$_4$Pd, 14221-01-3; D$_2$C(CO$_2$CH$_3$)$_2$, 36647-07-1; *n*-butyl glyoxalate, 6295-06-3; methyl 2-oxo-1-(3-trimethylsilyl-2-propenyl)cyclopentanecarboxylate, 86422-34-6; dimethyl malonate, 108-59-8; methyl 1-deuterio-2-oxocyclopentanecarboxylate, 86422-35-7.

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[14] For palladium-initiated cyclopropanation of olefins by diazo compounds that may involve carbene-palladium complexes as intermediates see: Kottwitz, J.; Vorbruggen, H. *Synthesis* **1975**, 636. Anciaux, A. J.; Hubert, A. J.; Noals, A. F.; Petinot, N.; Teyssie, P. *J. Org. Chem.* **1980**, *45*, 695. Nakamura, A.; Koyama, T.; Otsuka, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 593. Bien, S.; Segal, Y. *J. Org. Chem.* **1977**, *42*, 1685.

Syntheses and Structures of the $[Fe^{III}(SPh)_4]^-$ and $[Fe^{III}(SEt)_4]^-$ Anions. A General Route to Iron(III) Tetrathiolate Complexes

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Since the first report of the X-ray crystal structure of oxidized rubredoxin in 1969,[1] there has been a recognized need for iron(III) tetrathiolate complexes to serve as synthetic analogues for the $[Fe^{III}(S\text{-}cys)_4]$ unit of this protein. Although one example of this type of complex was achieved using a bidentate ligand,[2] attempts by several groups to obtain stable $[Fe^{III}(SR)_4]^-$ complexes with monodentate thiolate ligands or with other polydentate ligands have all resulted in failure.[3] This lack of success has been ascribed to the tendency of $[Fe^{III}(SR)_4]^-$ complexes to oligomerize and/or to undergo autoredox reactions to Fe^{II} and RSSR. Our recent success using the sterically hindered thiolate ligand 2,3,5,6-tetramethylbenzenethiolate to stabilize the $[Fe^{III}(SR)_4]$ coordination unit[4] has prompted us to reexamine the problem of $[Fe^{III}(SR)_4]^-$ complexes with less sterically hindered ligands. We wish to report a new and general route to the synthesis of stable iron(III) tetrathiolate complexes.

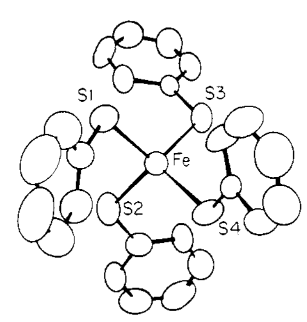

Figure 1. Anion of $[NEt_4][Fe^{III}(SPh)_4]$. Selected distances (Å) and bond angles (deg): Fe–S$_1$ 2.297 (3), Fe–S$_2$ 2.295 (3), Fe–S$_3$ 2.289 (3), Fe–S$_4$ 2.303 (3), Fe–S$_1$–C$_{11}$ 112.8 (4), Fe–S$_2$–C$_{21}$ 112.5 (4), Fe–S$_3$–C$_{31}$ 112.4 (5), Fe–S$_4$–C$_{41}$ 107.8 (5).

The reaction of $(NEt_4)[Fe(2,6\text{-dimethylphenolate})_4]$[5] with excess benzenethiol in DMF at 0 °C followed by the addition of diethyl ether gives black crystals of $(NEt_4)[Fe(SPh)_4]$ (**1**) in 60% yield.[6] Previously, this complex had been thought to be too unstable for isolation and characterization.[7,8] Its formulation and structure have been established by an X-ray diffraction study.[9] As the ORTEP view in Figure 1 indicates, the geometry of the entire $[Fe(SPh)_4]^-$ anion has idealized S_4 point group symmetry. Taken alone, the $[FeS_4]$ unit is distorted from T_d symmetry by a compression along the noncrystallographic S_4 axis to produce a $[FeS_4]$ unit with approximate D_{2d} symmetry. If the $[FeS_4]$ unit had exact D_{2d} symmetry, S$_1$–Fe–S$_4$ (114.3 (1)°) and S$_2$–Fe–S$_3$ (115.2 (1)°) would be equal and the four remaining S–Fe–S angles would be equal; rather they are 106.0 (1)° (S$_1$–Fe–S$_2$), 107.1 (1)° (S$_1$–Fe–S$_3$), 110.7 (1)° (S$_2$–Fe–S$_4$), and 103.7 (1)° (S$_3$–Fe–S$_4$). The average Fe–S distance of 2.296 (6) Å is about 0.06 Å shorter than the corresponding distance in the previously reported iron(II) complex $(PPh_4)_2[Fe(SPh)_4]$ (**2**).[7]

For each Fe–S–Ph group, the Fe–S bond lies in the plane determined by the phenyl ring; this plane is perpendicular to and approximately bisects a triangular face of the FeS$_4$ tetrahedron. The occurrence of this basic Fe–S–Ph conformation has been previously recognized by Coucouvanis[7,10] and it has been discussed by him in detail for the structure of $(PPh_4)_2[Fe^{II}(SPh)_4]$.[7,11] We add to this discussion by noting that if one assumes this basic conformation of the individual Fe–S–Ph groups, the overall geometry of the $[Fe(SPh)_4]$ unit can have only two possible types

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[1] Watenpaugh, K. D.; Sieker, L. C.; Jensen, L. H. *J. Mol. Biol.* **1980**, *138*, 615.

[2] Lane, R. W.; Ibers, J. A.; Frankel, R. B.; Holm, R. H. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 2868. Lane, R. W.; Ibers, J. A.; Frankel, R. B.; Papaefthymiou, G. C.; Holm, R. H. *J. Am. Chem. Soc.* **1977**, *99*, 84.

[3] Holm, R. H.; Ibers, J. A. In "Iron-Sulfur Proteins"; Lovenberg, W., Ed.; Academic Press: New York, 1977, Vol. III, Chapter 7, and references therein. Christou, G.; Ridge, B.; Rydon, H. N. *J. Chem. Soc., Chem. Commun.* **1977**, 908. Ueyama, N.; Nakata, M.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1727.

[4] Millar, M.; Lee, J. F.; Koch, S. A.; Fikar, R. *Inorg. Chem.* **1982**, *21*, 4105.

[5] Koch, S. A.; Millar, M. *J. Am. Chem. Soc.* **1982**, *104*, 5255.

[6] The electronic spectrum of **1** in DMF solution is as follows: λ = 556 nm (ϵ = 10 000), 387 nm (sh) (12 400), 342 nm (18 000). Anal. Calcd for $FeS_4C_{32}H_{40}N$: C, 61.72; H, 6.47; N, 2.25; S, 20.59. Found: C, 61.75; H, 6.46; N, 2.42; S, 21.51.

[7] Coucouvanis, D.; Swenson, D.; Baenziger, N. C.; Murphy, C.; Holah, D. G.; Sfarnas, N.; Simopoulos, A.; Kostikas, A. *J. Am. Chem. Soc.* **1981**, *103*, 3350.

[8] Hagen, K. S.; Reynolds, J. G.; Holm, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 4054.

[9] $(NEt_4)[Fe(SPh)_4]$ crystallizes in the monoclinic space group $P2_1/n$ with a = 9.194 (2) Å, b = 8.892 (2) Å, c = 40.779 (8) Å, β = 92.69 (1)°, V = 3330 (2) Å^3, and Z = 4. Diffraction data were collected at room temperature using an Enraf-Nonius CAD4 diffractometer. The structure was solved using direct methods and Fourier methods. The positions of the phenyl hydrogens were calculated and used in the structure factor calculations but were not refined. Final least-squares refinement with the nonhydrogen atoms of the anion anisotropic gave R = 0.060, R_w = 0.075 using 1291 unique reflections $I > 3\sigma(I)$.

[10] Coucouvanis, D.; Stremple, P.; Simhon, E. D.; Swenson, D.; Baenziger, N. C.; Draganjac, M.; Chan, L. T.; Simopoulos, A.; Papaefthymiou, V.; Kostikas, A.; Petrouleas, V. *Inorg. Chem.* **1983**, *22*, 293.

[11] The structural parameters described in ref 7 and applied to compound **1** are as follows: α_{av} = 124 (2)°, β_{av} = 117 (2)°, γ_{av} = 111 (2)°, δ_{av} = 107 (3)°, ϵ_{av} = 111 (5)°, ϵ_{av}' = 111 (5)°.

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