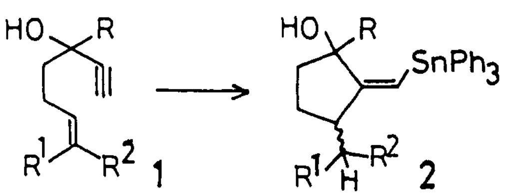
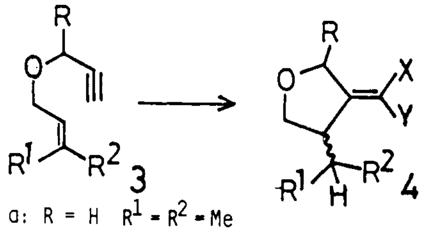


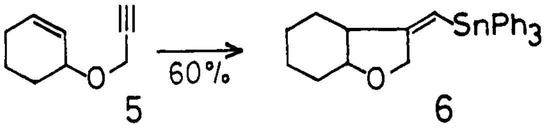
(1)

a: R = Me R1 = R2 = Me 75% (78/22)
b: R = Me R1 = R2 = H 50% (80/20)
c: R = Me R1 = Me R2 = CH2CH2CH=CMe2 78% (79/21)
d: R = nC5H11 R1 = H R2 = Ph 87% (63/37)

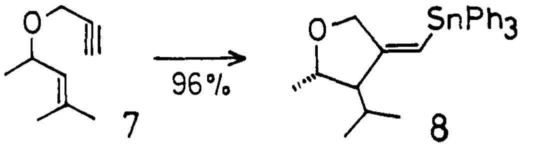


(2)

a: R = H R1 = R2 = Me
X = SnPh3 Y = H (Y. 78%)
b: R = H R1 = H R2 = nC3H7
X = SnPh3 Y = H (Y. 85%)
c: R = nBu R1 = R2 = Me
X = SnPh3 Y = H (Y. 69%, 64/36)
d: R = H R1 = R2 = Me X = Ha Y = Hb
e: R = H R1 = R2 = Me X = SnPh3 Y = D
f: R = H R1 = R2 = Me X = H Y = D



(3)



(4)

stannylation (n-BuLi/THF, H_2O)[12] showed ^1H NMR signals at δ 5.00 (m, Ha) and 4.95 (m, Hb). Treatment of the deuteriated acetylene **3a** ($DC{\equiv}CCH_2OCH_2CH{=}CMe_2$) with Ph_3SnH followed by destannylation provided **4f**, whose ^1H NMR spectrum showed only one signal in the olefinic region at δ 4.99. The complete disappearance of the higher field signal is consistent with a formation of single stereoisomer **4e**.[13] The compounds **1a–d** and **3c** provided cis–trans stereoisomeric mixtures concerning the substituents on a five-membered ring. In contrast, the compound **7** gave trans isomer **8**[14] as a single product.

Scheme I illustrates the synthesis of dehydroiridodiol and isodehydroiridodiol. The triethylborane-induced triphenyltin radical addition–cyclization process provided vinylstannane **11** (84%) starting from readily available propargylic alcohol **10**. Collins oxidation of **11** gave **12** (54%).[15] Diisobutylaluminum hydride reduction followed by treatment with p-TsOH provided a mixture of dehydroiridodiol ($3R^*,8S^*$) and isodehydroiridodiol ($3R^*,8R^*$) (26/74, 58% overall yield from **12**),[16] which was easily separated by preparative TLC on silica gel.

The reaction was not so effective for the formation of a six-membered ring. For instance, treatment of $HC{\equiv}CCH_2OCH_2CH_2CH{=}CMe_2$ gave the desired cyclized product in only 28% yield along with uncyclized vinylstannane (49%). An addition of galvinoxyl to a reaction mixture of 1-dodecyne, Ph_3SnH, and Et_3B resulted in a recovery of the acetylene (73%).[17,18]

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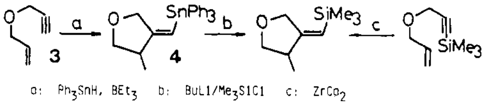
[12] (Triphenylstannyl)alkenes were easily transformed into alkenyllithium as (trialkylstannyl)alkenes following the procedure described in ref 5.

[13] The structure of the cyclized product was also confirmed as follows. Treatment of **3** ($R = R^1 = R^2 = H$) with our new method provided **4** (32% yield) along with six-membered-ring product 3-(triphenylstannyl)methylenetetrahydropyran (45%). The vinylstannane **4** was converted into vinylsilane by treatment with n-BuLi and Me_3SiCl, which was identical with the sample prepared from allyl (trimethylsilyl)propargyl ether following Negishi's procedure (Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2827. Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568).



a: Ph_3SnH, BEt_3 b: $BuLi/Me_3SiCl$ c: $ZrCp_2$

[14] **8**: bp 170 °C (bath temp, 0.1 torr); IR (neat) 3062, 2958, 1619, 1429, 1075, 727, 697 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.98 (d, J = 7.0 Hz, 3 H), 1.02 (d, J = 7.0 Hz, 3 H), 1.25 (d, J = 6.0 Hz, 3 H), 2.02 (m, 1 H), 2.30 (m, 1 H), 3.95–4.25 (m, 3 H), 6.08 (m, 1 H), 7.3–7.8 (m, 15 H); ^{119}Sn NMR δ −142.6. Anal. Calcd for $C_{27}H_{30}OSn$: C, 66.29; H, 6.18. Found: C, 66.43; H, 6.29.

[15] **12**: ^1H NMR ($CDCl_3$, 200 MHz) δ 0.67 (d, J = 7.0 Hz), 0.72 (d, J = 7.0 Hz), 0.94 (d, J = 2.5 Hz), 0.97 (d, J = 2.5 Hz, total 3 H), 1.4–2.0 (m, 8 H), 2.14 (brs, 3 H), 2.2–2.7 (m, 3 H), 3.0–4.0 (m, 5 H), 4.5–4.7 (m, 1 H), 10.0 (s, 1 H).

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[18] After this work was completed we were informed by Professor G. Stork that he has reached a similar cyclization reaction. We thank Prof. G. Stork for giving us information prior to publication.

Synthesis and Characterization of Five-Coordinate High-Spin Iron(II) Porphyrin Complexes with Unusually Large Quadrupole Splittings. Models for the P460 Center of Hydroxylamine Oxidoreductase from *Nitrosomonas*

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Hydroxylamine oxidoreductase from *Nitrosomonas europeae* catalyses the oxidative conversion of NH_2OH to NO_2^-.[2] The enzyme, which has an $(\alpha,\beta)_3$ subunit containing seven–eight c-type hemes contains also an unusual prosthetic group, termed P460. This P460 center is also found in a $M_r \simeq 17\,000$ protein fragment. Mössbauer spectra of the reduced P460 groups in hydroxylamine oxidoreductase and the fragment exhibit nearly identical quad-

Table I. Electronic Spectra of Complexes **1**, **2**, and **3** at 25 °C in Chlorobenzene

	λ_m (log ϵ), nm
$[Fe(OCH_3)TP_{piv}P]^-$ **1**	456 (4.83), 580 (3.86), 622 (3.71)
$[Fe(O_2CCH_3)TP_{piv}P]^-$ **2**	448 (5.32), 572 (4.22), 611 (3.81)
$[Fe(OC_6H_5)TP_{piv}P]^-$ **3**	450 (5.02), 576 (4.09), 616 (3.89)

Table II. Mössbauer Parameters of Complexes: δ (mm s^{-1}) ±0.02 Relative To α-Fe; ΔE_q (mm s^{-1}) ±0.03; Γ (mm s^{-1}) ± 0.02

	4.2 K			77 K			150 K			215 K		
	ΔE_q	δ	Γ	ΔE_q	δ	Γ	ΔE_q	δ	Γ	ΔE_q	δ	Γ
$\|Fe(OCH_3)TP_{piv}P\|^-$ **1**	3.67	1.03	0.40	3.64	1.00	1.29	3.62	0.98	0.29	3.56	0.94	0.26
$\|Fe(O_2CCH_3)TP_{piv}P\|^-$ **2**	4.25	1.05	0.30	4.19	1.03	0.29	4.13	1.01	0.29	4.01	0.97	0.28
$\|Fe(OC_6H_5)TP_{piv}P\|^-$ **3**	3.90	1.06	0.38	3.86	1.04	0.35	3.82	1.02	0.36	3.75	0.97	0.34

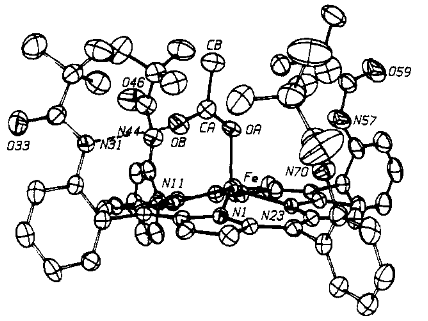

Figure 1. ORTEP drawing of the $|Fe^{II}(O_2CCH_3)TP_{piv}P|^-$ anion present in **2**. Vibrational ellipsoids are contoured to enclose 50% of the electron density. The N(H)31---O=C hydrogen bond occurring in the molecular cavity between the pivalamide N(H)31 and the carbonyl group of the acetate ligand is displayed.

rupole doublets with an unusually large splitting, $\Delta E_q = 4.21$ mm s^{-1} and an isomer shift $\delta = 0.96$ mm s^{-1} at 4.2 K. The spectroscopic and chemical evidence published so far indicate that the ferrous iron present in P460 resides in a heme-like macrocycle, although no other ferrous heme protein is, so far, known with a Mössbauer quadrupole splitting larger than 2.75 mm s^{-1}.

We have shown recently that a five-coordinate chloro-iron(II)-porphyrin complex presents a Mössbauer spectrum with a quadrupole splitting as large as 4.32 mm s^{-1} at 4.2 K.[3] More recently, it was also shown that iron(II) protoporphyrin IX solutions prepared at pH 12, 14, and >14 without and with additional ligands contain species exhibiting unusually large quadrupole splittings.[4] We have now synthesized and characterized five-coordinate, high-spin iron(II) "picket-fence" porphyrin derivatives with oxygen donor anions, CH_3O^-, $CH_3CO_2^-$, and $C_6H_5O^-$ as axial ligands. As shown below the zero-field Mössbauer spectra of all three compounds consist of quadrupole doublets with unusually large splittings.

The five-coordinate, high-spin iron(II) picket fence porphyrin anions $|Fe(X)TP_{piv}P|^-$ [X = CH_3O^- (**1**), $CH_3CO_2^-$ (**2**), and $C_6H_5O^-$ (**3**)] were synthesized by the following procedures: (i) stirring under argon for 1 h of a mixture of zinc amalgam (1 mL) and iron(III) (triflate) picket-fence porphyrin[5] (220 mg, 0.013 mmol) in chlorobenzene (10 mL); (ii) filtration and addition of chlorobenzene solutions (10 mL) of either $|K^+\subset 222(CH_3O^-)|$ (223 mg, 0.52 mmol), $|Na^+\subset 222(CH_3CO_2^-)|$ (59 mg, 0.13 mmol), or $|K^+\subset 222(C_6H_5O^-)|$ (66 mg, 0.13 mmol). Precipitation of the iron(II) complexes occurred by addition of an excess of pentane (**1**) or by leaving the solutions in the cold (−10 °C) (**2**, **3**). Single crystals suitable for X-ray studies were obtained for **2** and **3** by slow diffusion of pentane into chloro- or fluorobenzene solutions of the complexes. All these complexes present in chlorobenzene similar visible spectra with red-shifted Soret bands[6] (Table I).

Table III. Bond Parameters for the Coordination Geometry of Iron in **2** and **3** $P_N = 4N_p$ Mean Plane; P_c = 24-Atom Core Mean Plane; C_t Center of the $4N_p$ Mean Plane

	Fe–N_p, Å	Fe–L_{ax}, Å	Fe---P_N, Å	Fe---P_c, Å	C_t–N_p, Å
$\|Fe(O_2CCH_3)$-$TP_{piv}P\|^-$ **2**	2.107 (2)	2.034 (3)	0.554 (1)	0.637 (1)	2.033
$\|Fe(OC_6H_5)$-$TP_{piv}P\|^-$ **3**	2.114 (2)	1.937 (4)	0.565 (1)	0.620 (1)	2.037

The Mössbauer spectra[7] were obtained in the absence of applied magnetic fields between 4.2 and 215 K. They consist of quadrupole doublets centered at δ 1.00 (**1**), 1.03 (**2**), and 1.04 (**3**) at 77 K. The Mössbauer parameters obtained at 4.2, 77, 150, and 215 K are given in Table II. These parameters show that all three complexes are high-spin iron(II) species. The observed quadrupole splittings which range from 3.8 to 4.25 mm s^{-1} at 4.2 K are large and lie close to the value of 4.21 mm s^{-1} found for the P460 center.[2] The X-ray structures of **2** and **3** have been studied.[8] The molecular stereochemistry of the porphyrin present in **2** is displayed in Figure 1. The bond parameters for the coordination environment of iron in **2** and **3** are given in Table III. In both compounds, the iron is five-coordinate, bonded to the four Np nitrogens and an oxygen atom of the axial ligand. Despite the presence of only moderate doming (Table III), the displacements of the iron atoms with respect to the 4Np mean planes of 0.55 and 0.57 Å respectively for **2** and **3** are clearly larger than the average value of 0.47 Å found in a number of iron(III) complexes[9] and also larger than in the five-coordinate iron(II) halide "picket-fence" porphyrin derivatives $|Fe^{II}(X)TP_{piv}P|^-$ (X = F^-, Cl^-, Br^-, and I^-).[10] The displacement of the metal from the 4Np mean plane is related to the bonding strength of the axial ligand. Thus, despite a difference of ≃0.1 Å in the Fe–O bond distances of **2** (2.034 (3) Å) and **3** (1.937 (4) Å) the Fe–O bond with the acetato ligand is probably almost as strong as that with the phenolate. The carbonyl group of this ligand is involved in a hydrogen bond with an N–H group of one pivalamide "picket". The corresponding N(H)---O=C— distance is 3.027 (7) Å.

Supplementary Material Available: Tables of fractional atomic coordinates, anisotropic thermal parameters, and isotropic thermal parameters for the hydrogen atoms for **2** and **3** (30 pages). Ordering information is given on any current masthead page.

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(5) $Fe^{III}(CF_3SO_3)TP_{piv}P$ was prepared by reaction of $AgSO_3CF_3$ and $|Fe^{III}ClTP_{piv}P|$ in THF under inert atmosphere (λ_m = 409, 543, 652 nm). Nasri, H.; Doppelt, P.; Weiss, R., unpublished results.

(6) See also: Mincey, T.; Traylor, T. G. *J. Am. Chem. Soc.* **1979**, *101*, 764–765.

(7) Mössbauer spectra were accumulated with a standard apparatus in the constant acceleration mode with Co/Rh (ca. 50 mCi) source. Isomeric shifts are given with respect to α-Fe at room temperature.

(8) $|Fe(CH_3CO_2^-)TP_{piv}P||Na\subset 222|\cdot C_6H_5Cl$ (**2**); $C_{90}H_{108}N_{10}O_{12}NaClFe$: MW = 1636.21; monoclinic, $P2_1/n$; a = 18.040 (6), b = 21.521 (6), c = 22.605 (6) Å; β = 100.37 (2)°, V = 8632.8 Å^3, Z = 4, d_c = 1.259 g cm^{-3}, Cu Kα radiation; t = −100 °C; deep-blue crystal (0.36 × 0.22 × 0.20 mm); experimental absorption corrections; 12111 independent ±*hkl* reflections measured on a Philips PW1100 diffractometer; 7337 with $I > 3\sigma(I)$, R_F = 0.077, R_{WF} = 0.098. $|Fe(C_6H_5O^-)TP_{piv}P||K\subset 222|\cdot C_6H_5F$ (**3**); $C_{94}H_{110}N_{10}O_{11}FKFe$: MW = 1669.93, monoclinic, $P2_1/n$; a = 17.990 (6), b = 20.741 (6), c = 24.064 (6) Å; β = 94.90 (2)°, V = 8946.2 Å, Z = 4, d_c = 1.240 g cm^{-3}, Cu Kα radiation; t = −100 °C; deep blue crystal (0.32 × 0.26 × 0.20 mm); experimental absorption corrections; 12558 independent ±*hkl* reflections measured on a Philips PW1100 diffractometer, 6514 with $I > 3\sigma(I)$ R_F = 0.066, R_{WF} = 0.086. Refinements were conducted for both compounds by using anisotropic temperature factors for all non hydrogen atoms and isotropic factors for the hydrogen atoms which were introduced by their computed coordinates.

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