Prepared in this manner, poly(dimethylphosphazene) bears a superficial resemblance to some lower molecular weight (3500–12 500) products reported by Sisler et al.[7] Their compounds were not characterized by NMR and were obtained only in low yields after a tedious purification process from the thermolysis of $Me_2P(NH_2)_2Cl$. By contrast, our method affords excellent yields and utilizes a conveniently prepared starting material.

The elimination of $Me_3SiOCH_2CF_3$ from N-silylphosphinimines is not unprecedented. Flindt and Rose[8] have reported that the symmetrically substituted phosphinimine $Me_3SiN=P(OCH_2CF_3)_3$ decomposes at 200 °C to form $[(CF_3CH_2O)_2PN]_n$ of relatively low molecular weight ($\bar{M}_n$ ~10 000).

Interestingly, when the P-bromophosphinimine **1** was heated under the same conditions as described for **2**, the product was not a polymer. Instead, a nearly quantitative yield of the cyclic tetramer $(Me_2PN)_4$ was obtained. This marked difference in reactivity probably has important mechanistic implications and, certainly, this aspect of the polymer formation process merits further investigation. As our results demonstrate, however, the elimination of silanes from N-silylphosphinimines is an important alternate synthesis of polyphosphazenes, especially those containing P–C-bonded substituents.

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Preparation, Disproportionation, and Reactions of Two Semi-Met Forms of Hemerythrin

Sir:

The respiratory protein hemerythrin occurs in the erythrocytes of certain marine worms as an octamer of mol wt 107 000. Each subunit contains two linked nonheme irons but there is still a question whether amino acids or oxy bridging is involved.[1-4] The deoxy form has both irons in the oxidation state +2. It is easily oxidized to the met form containing irons only in the +3 oxidation state. We have recently prepared a half-reduced form, in which one of the binuclear irons is +3 and the other +2, by one-electron reduction of methemerythrin with dithionite.[5] An identical species which we designate (semi-met)$_R$ can also be prepared by light irradiation of the met for a short period (1–2 min) in the presence of EDTA and catalytic amounts of a flavin, a method which has been generally effective for the reduction of a number of proteins.[6] Longer irradiation (30 min) leads to near-quantitative production of the deoxy form. We report here some interesting properties of (semi-met)$_R$ and of another form, (semi-met)$_O$,
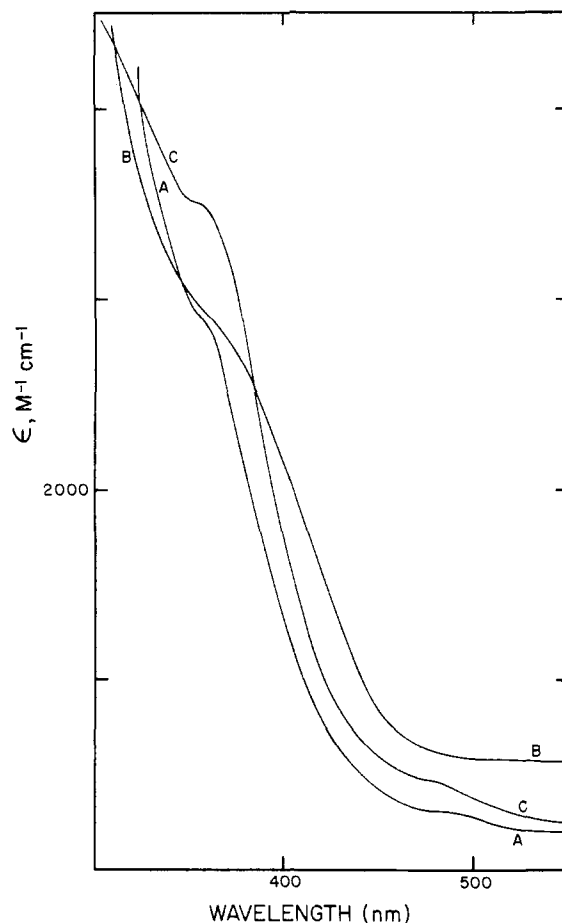

Figure 1. Spectra of (semi-met)$_R$ (A), (semi-met)$_O$ (B), and a common spectrum (C) of disproportionated products from (semi-met)$_O$ and (semi-met)$_R$, as well as an equimolar mixture of deoxyhemerythrin and methemerythrin. (Semi-met)$_R$ was prepared by either addition of 1.3 equiv of $S_2O_4{}^{2-}$ (per Fe–Fe unit) to met, or by irradiation of methemerythrin (0.1 mM), riboflavin (3–5 μM), and EDTA (5 mM) for 90 s by light from a 300-W projector lamp, 20 cm from the solution. (Semi-met)$_O$ was prepared by addition of 1 equiv of $Fe(CN)_6{}^{3-}$ to deoxyhemerythrin. Experiments were carried out at pH 8.2, $I = 0.15$ M and 10 °C.

reached from the other direction, namely by one-electron oxidation of the deoxy form by $Fe(CN)_6{}^{3-}$. The two semi-met forms have quite distinct spectra (Figure 1). Both slowly change to an identical spectrum [allowing for $Fe(CN)_6{}^{4-}$ present with (semi-met)$_O$] which is close to that of a mixture of equal amounts of met- and deoxyhemerythrin (Figure 1). This is the result of a remarkable spontaneous *first-order* disproportionation ($\geq$85% complete) which occurs within the octamer and leads to four [$Fe^{II}Fe^{II}$] and four [$Fe^{III}Fe^{III}$] units in each octamer (Table I). This mixed species behaves like a equimolar mixture of met and deoxy spectrally and kinetically toward O_2 and SCN^-. The disproportionation controls the rate of reaction of the semi-met forms with a number of reagents (see below). Both forms have an EPR spectrum (at liquid He temperatures) with g values of 1.95 and 1.71 (semi-met)$_O$ and 1.93, 1.86 and 1.68 (semi-met)$_R$.[7] The disproportionation in solution is accompanied by a decrease in the amplitude of the EPR signal, with an approximate $t_{1/2} = 8$ min for (semi-met)$_R$[7] at room temperature, consistent with the disproportionation rate constant measured spectrally (Table I). After both semi-met forms have been left for 30 min no EPR signal remains. This would be expected since the met and deoxy forms are EPR inactive,[8,9] even at liquid He temperature.[7] Both semi-met forms react with $N_3{}^-$ ion to give a single semi-met–azide adduct, with the same electronic and EPR spectrum ($g = 1.91$, 1.83). This semi-met azide complex is stable toward disproportionation, as shown by a constant spectrum and EPR

Table I. Rate Constants for Reaction of (Semi-Met)$_R$ and (Semi-Met)$_O$ from *Themiste zostericola* at pH 8.2 and 25 °C

reactant	product	(semi-met)$_R$, s^{-1} (M^{-1} s^{-1})	(semi-met)$_O$, s^{-1} (M^{-1} s^{-1})
spontaneous	(½ met + ½ deoxy)^a	2.1 × 10^{-3} ^{b}	2.6 × 10^{-3} ^{c}
Fe(CN)$_6$$^{3-}$	met	(4.0 × 10^5)^d	1.2 × 10^{-3} ^{e}
S$_2$O$_4$$^{2-}$	deoxy	0.9 × 10^{-3} ^{e,f}	(7 × 10^5)^g
O$_2$	(½ met + ½ oxy)^a	2.1 × 10^{-3} ^{e}	h
SCN$^-$	(½ met SCN$^-$ + ½ deoxy)^a	1.8 × 10^{-3} ^{e}	h
N$_3$$^-$	semi-met N$_3$$^-$ adduct	(45)	(87)

^{a} Composition of octamer (see text). ^{b} $\Delta H^\ddagger$ = 20.8 kcal mol^{-1}, $\Delta S^\ddagger$ = −1 eu. ^{c} $\Delta H^\ddagger$ = 22.4 kcal mol^{-1}, $\Delta S^\ddagger$ = +6 eu. ^{d} pH 8.0. ^{e} Via disproportionation, rate independent of reactant concentration. ^{f} Basis of second phase.[5] ^{g} Reaction with SO$_2$$^-$; cf. rate constant with met = 4.7 × 10^5 M^{-1} s^{-1}.[5] ^{h} Under investigation.
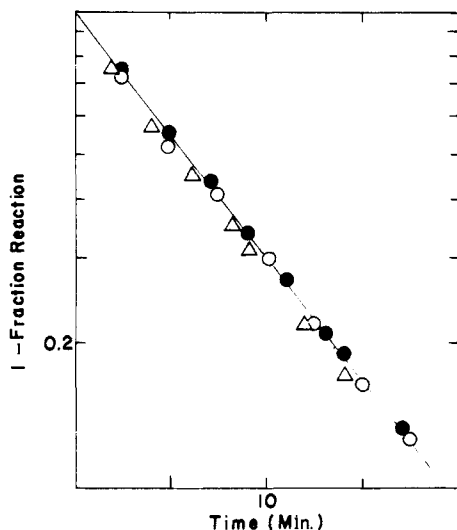

Figure 2. Semilog plots for reaction of (semi-met)$_R$ with O$_2$ (△) and SCN$^-$ (●) and for spontaneous disproportionation (○). Conditions: 0.2 mM protein, 4 μM riboflavin, 5 mM EDTA, 11 mM SCN$^-$, 0.5 mM O$_2$. Reducing concentrations of protein, riboflavin, EDTA, SCN$^-$, or O$_2$ by 3–4-fold (separately) had no effect on the plots: λ 500 (O$_2$), 450 (SCN$^-$), and 420 nm (spontaneous).

signal over many hours.[7]

The two forms differ significantly in their reactions with Fe(CN)$_6$$^{3-}$ and S$_2$O$_4$$^{2-}$ ions. (Semi-met)$_R$ is oxidized rapidly by Fe(CN)$_6$$^{3-}$ to give the met form (Table I). However, its reactions with S$_2$O$_4$$^{2-}$, O$_2$, and SCN$^-$ (Figure 2) to give the products indicated in Table I, are controlled by disproportionation. Conversely, (semi-met)$_O$ is reduced by S$_2$O$_4$$^{2-}$ rapidly and quantitatively to deoxyhemerythrin, but is not oxidized directly by Fe(CN)$_6$$^{3-}$ to met but only via disproportionation. The rate constants for reaction of (semi-met)$_R$ with dithionite and of (semi-met)$_O$ with Fe(CN)$_6$$^{3-}$ are approximately one half the corresponding disproportionation rate constants (Table I), since in each case one [Fe^{III}Fe^{II}] unit will be regenerated for every two lost by disproportionation. The disproportionation probably explains the results of Brunori et al.[9] who found only fully reduced and fully oxidized protein when deoxyhemerythrin (*Sipunculus nudus*) was allowed to stand for "10 to 30 min" with incomplete amounts of ferricyanide.

The oligomer contains eight identical subunits packed as a square donut with four subunits in each of two layers.[1-4,10,11] For *Themiste dyscritum* protein any iron pair within a subunit is ~30 Å from an adjacent one in the same layer and about the same distance from a pair in a different layer.[11] These are large distances over which the internal electron transfer must occur, although in solution these distances may be modified by protein flexibility. It must also be considered that the rate constant is some 11 or so orders of magnitude smaller than that for dif-

fusion controlled and some 10^5–10^8 less in value than electron transfer rate constants involving redox proteins, for which reaction distances of 15 Å appear feasible.[13]

Since it is believed that the detailed geometry, and even the nature of the ligands attached to the irons, in the binuclear site is quite different in the deoxy and met forms,[1] we believe that (semi-met)$_O$ reflects a "deoxy type" site and that (semi-met)$_R$ is more likely to mirror that of the met. This could begin to explain the differences in the ease of their *direct* oxidation and reduction.[14] Although the reduction of anionic adducts of methemerythrin by dithionite occurs via the met fragment, resulting from anion dissociation, it is much faster and simpler than reduction of methemerythrin itself.[15] This puzzling observation can now be explained if anion binding to methemerythrin promotes a "deoxy-type" iron site. This will then lead to a dissociated fragment which is reduced rapidly and cleanly through (semi-met)$_O$ rather than (semi-met)$_R$. Thus our results suggest that anion binding modifies the character of the binuclear site both in the met and semi-met form. This may explain the different X-ray structural results found for methemerythrin and the metmyohemerythrin–azide adduct,[1-4] although differences between the azide and thiocyanate derivatives of methemerythrin and native methemerythrin were not discerned at 4 and 3.5 Å resolution, respectively.[16]

All of the results reported are for protein from *Themiste zostericola*[17] at a pH 8.2. Two semi-met forms from *Phascolopsis gouldii* hemerythrin can also be obtained by similar methods but these disproportionate only slightly in solution, a process which however can be promoted by oxidizing and reducing agents.

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