Table I. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for **1**[a]

	x	y	z	U^a
Pt	1732 (1)	1122 (1)	2032 (1)	32 (1)
Te(1)	459 (1)	1270 (1)	3152 (1)	52 (1)
Te(2)	302 (1)	1705 (1)	742 (1)	56 (1)
P(1)	2915 (2)	561 (1)	3191 (2)	35 (1)
P(2)	2799 (2)	1133 (1)	955 (2)	35 (1)
C(1)	-893 (8)	1761 (5)	2341 (7)	53 (4)
C(2)	-1768 (10)	1908 (7)	2741 (9)	80 (6)
C(3)	-2627 (10)	2230 (7)	2223 (9)	84 (6)
C(4)	-2668 (11)	2446 (8)	1326 (12)	102 (7)
C(5)	-1835 (10)	2304 (6)	910 (10)	79 (6)
C(6)	-926 (8)	1950 (5)	1433 (8)	56 (4)
C(11)	1788 (5)	-16 (3)	4408 (4)	54 (4)
C(12)	1492	-98	5257	64 (5)
C(13)	1969	290	6026	78 (6)
C(14)	2743	761	5946	77 (6)
C(15)	3039	843	5098	57 (4)
C(16)	2561	455	4329	38 (3)
C(21)	4084 (4)	1699 (3)	3438 (5)	47 (4)
C(22)	4987	2101	3729	64 (5)
C(23)	5989	1817	4104	70 (5)
C(24)	6087	1129	4187	75 (5)
C(25)	5184	727	3895	66 (5)
C(26)	4183	1012	3521	43 (4)
C(31)	3921 (5)	-708 (4)	3370 (5)	72 (5)
C(32)	4015	-1360	3084	86 (7)
C(33)	3279	-1610	2308	89 (7)
C(34)	2450	-1209	1818	81 (6)
C(35)	2356	-557	2104	60 (5)
C(36)	3091	-306	2880	44 (4)
C(41)	3124 (5)	2496 (3)	1295 (4)	46 (4)
C(42)	3591	3109	1196	65 (5)
C(43)	4312	3170	619	71 (5)
C(44)	4567	2617	142	64 (5)
C(45)	4100	2004	241	52 (4)
C(46)	3379	1944	818	40 (3)
C(51)	1947 (5)	1334 (3)	-988 (4)	43 (3)
C(52)	1305	1160	-1858	62 (5)
C(53)	714	573	-1959	66 (5)
C(54)	766	158	-1190	72 (5)
C(55)	1408	332	-320	61 (4)
C(56)	1999	920	-220	40 (3)
C(61)	3908 (6)	-58 (3)	832 (5)	63 (5)
C(62)	4812	-467	1002	91 (7)
C(63)	5807	-221	1477	93 (7)
C(64)	5900	463	1783	88 (6)
C(65)	4996	846	1614	64 (5)
C(66)	4000	599	1138	46 (4)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table II. Selected Bond Distances (Å) and Angles (deg) for **1**

		Distances	
Pt-Te(1)	2.586 (1)	Pt-Te(2)	2.592 (1)
Pt-P(1)	2.298 (2)	Pt-P(2)	2.317 (3)
Te(1)-C(1)	2.106 (10)	Te(2)-C(6)	2.117 (12)
C(1)-C(2)	1.411 (18)	C(1)-C(6)	1.379 (16)
C(2)-C(3)	1.350 (17)	C(3)-C(4)	1.377 (23)
C(4)-C(5)	1.375 (22)	C(5)-C(6)	1.427 (16)
		Angles	
Te(1)-Pt-Te(2)	88.4 (1)	P(1)-Pt-P(2)	97 (1)
Te(1)-Pt-P(1)	89.3 (1)	Pe(2)-Pt-P(2)	85.6 (1)
Te(1)-Pt-P(2)	172.2 (1)	Te(2)-Pt-P(1)	176.4 (1)
Te(1)-C(1)-C(2)	119.2 (8)	Te(1)-C(1)-C(6)	121.1 (8)
Te(2)-C(6)-C(5)	117.4 (9)	Te(2)-C(6)-C(1)	122.6 (7)
C(1)-C(6)-C(5)	119.9 (11)	C(2)-C(1)-C(6)	119.7 (10)
C(4)-C(5)-C(6)	118.8 (13)	C(1)-C(2)-C(3)	119.0 (13)
C(3)-C(4)-C(5)	119.9 (13)	C(2)-C(3)-C(4)	122.6 (14)
		Dihedral Angles	
C(1)-C(6)/Te(1), C(1), C(6), Te(2)			2.9 (3)
Te(1), C(1), C(6), Te(2)/Te(1), Pt, Te(2)			1.3 (2)
Te(1), C(1), C(6), Te(2)/P(1), P(2), Pt, Te(1), Te(2)			1.3 (2)

CH_2Cl_2 solution of **1**. The crystal belonged to the monoclinic space group $P2_1/n$ (295 K): a = 12.782 (2) Å, b = 20.174 (3) Å, c = 14.704 (3) Å, β = 103.36 (1)°, V = 3688.9 (10) Å^3, Z = 4, D(calcd) = 1.892 g cm^{-3}, μ(Mo Kα) = 57.2 cm^{-1}. By the use of a Nicolet R3 diffractometer with a graphite monochromator and ω scans ($4° \le 2\theta \le 48°$), 6274 reflections were collected. A total of 5732 data were unique (R_{int} = 1.12%), and 4241 data with $F_o \ge 5\sigma(F_o)$ were considered observed. An empirical absorption correction (T_{max} = 0.237, T_{min} = 0.163) and a 4% linear decay correction were applied. The structure was solved by direct methods (Pt and two Te atoms) and refined by subsequent difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically while the phosphine phenyl rings were constrained as rigid bodies and hydrogen atoms were constrained as idealized, updated isotropic contributions. R_F = 0.0397, R_{wF} = 0.0424, GOF = 1.008. In the final refinement cycle the maximum shift/σ was 0.018 and the maximum nonassigned electron density in the difference map was 0.64 e/Å^3 (0.84 Å from Pt). The data/parameter ratio was 12.0. The atomic coordinates and isotropic thermal parameters are collected in Table I. Selected bond angles and bond distances are in Table II.

Acknowledgment. This research was supported by the National Science Foundation through Grant DMR 83-16981. We thank Johnson Matthey for the loan of the platinum. T.B.R. is a Camille and Henry Dreyfus Teacher-Scholar. We thank Professor Fred Wudl for helpful comments on the preparation of $C_5H_6(TeLi)_2$.

Registry No. **1**, 107494-87-1; **2**, 107494-88-2; $Pt(STeC_6H_4)(PPh_3)_2$, 107494-89-3; $Pt(SeTeC_6H_4)(PPh_3)_2$, 107494-90-6; $(HgC_6H_6)_6$, 256-24-6; Li, 7439-93-2; Te, 13494-80-9; *cis*-$PtCl_2(PPh_3)_2$, 15604-36-1; $Pt(S_2C_6H_4)(PPh_3)_2$, 107494-91-7; *t*-BuLi, 594-19-4; *n*-BuLi, 109-72-8; Ph_2Se_2, 1666-13-3; 1,2-dibromocyclopentene, 75415-78-0; benzenethiol, 108-98-5.

Supplementary Material Available: A table of anisotropic thermal parameters (1 page); a table of structure factors (25 pages). Ordering information is given on any current masthead page.

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A New Synthetic Route to Cyclic Polyarsines

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Cyclic polyarsines have been of continued interest[1-7] owing to the extreme adaptability of arsenic as a bridging element in metal clusters and their unique coordinating modes in transition-metal complexes. A variety of reactions have been reported for the synthesis of polyarsines.[8-13] Typically, low yields of the cyclic polyarsines are obtained. Furthermore, the products are often contaminated with difficult to remove byproducts. In this paper, we report a new and convenient synthetic pathway to high yields of pure cyclic polyarsines.

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In our recently reported synthetic route to diarsines,[14] we noted that the lability of the As–N, As–As, and As–H bonds leads to several exchange reactions that involve H–, Me_2As–, and Me_2N– moieties. These exchange reactions were shown to influence the rate of the overall reaction. Thus, a variable-temperature NMR study of the reaction of $(MeAs)_5$ with $PhAsH_2$ was carried out to determine the mechanism of the reaction and the importance of possible exchange reactions in influencing the product yields.

Results and Discussion

Reactions of $(MeAs)_5$ with the appropriate mole ratio of $RAsH_2$ in benzene solution produce highly pure cyclic polyarsines, $(RAs)_n$ (R = Et, *n*-Pr, $n = 5$; R = Ph, *p*-Tol, $n = 6$), in good yields (80–85%).

$$n(MeAs)_5 + 5nRAsH_2 \rightarrow 5(RAs)_n + 5nMeAsH_2$$

The polyarsines are easily isolable from the other product, $MeAsH_2$, due to its high volatility. Separation of $MeAsH_2$ from the reaction mixture is essential. Otherwise, an equilibrium distribution of reactants, products, and intermediate As–As-bonded oligomers results (see discussion below). The $MeAsH_2$ obtained from these reactions can be converted quantitatively to highly pure starting material, $(MeAs)_5$.[10]

Previously described synthetic routes to cyclic polyarsines require reagents or produce byproducts that have been found to cause polymerization.[5,15] Removal of byproduct/starting material impurities by repetitive distillation produces irreversible effects. The general method for preparing polyarsines[9] by reducing the appropriate arsonic acid with aqueous hypophosphorus acid is very sensitive to the presence of trace level, water-soluble impurities. These impurities catalyze the polymerization of polyarsines to give red-brown As–As ladder polymers,[9,15,16] which significantly lower the product yields. Since no side products are observed in the present synthesis, such undesirable side reactions do not occur and the pure polyarsines are obtained in high yields. Thus, the $(MeAs)_5/RAsH_2$ reaction is a very convenient synthetic pathway for the preparation of cyclic polyarsines.

NMR Study of the $(MeAs)_5/PhAsH_2$ Reaction. The ^1H and ^{13}C NMR spectra of a mixture of $(MeAs)_5$ and $PhAsH_2$ in toluene-d_8 solution showed no reaction from −80 to −20 °C. After 15 min at 0 °C, low-intensity ^1H NMR peaks were observed due to $MeAsH_2$ and linear As–As-bonded oligomers. The NMR spectra indicated a slow consumption with time of $(MeAs)_5$ and $PhAsH_2$ and the concomitant production of $MeAsH_2$ and As–As-bonded oligomers. After 12 h, the ^1H NMR spectra indicated that all $(MeAs)_5$ had undergone ring opening. The observation of no significant change in peak intensities of the reactants and products after 18 h at 0 °C indicated the establishment of equilibrium. The NMR spectra showed no formation of $(PhAs)_6$. Even at 24 °C, after reestablishment of equilibrium, there was no detectable formation of $(PhAs)_6$.

The ^1H NMR spectrum of the reaction mixture at 0 °C showed additional minor peaks in the ranges 0.69–1.71, 3.49–4.25 and 6.65–7.95 ppm. These resonances are attributed to the MeAs<, Ph(*H*)As–, and PhAs< moieties, respectively, which are present in the uncharacterized As–As-bonded oligomers. Very weak intensity resonances, which are due to Me(*H*)As– units were observed in the range 2.17–2.91 ppm. As discussed below, specific sets of resonances in the ^1H spectra could be assigned to two stereoisomeric forms of Me(H)AsAs(H)Ph. The corresponding ^{13}C NMR peaks were noted in the regions −2.63–0.44, 3.12–7.44 and 133.2–135.4 ppm.

The NMR tube was then opened inside the drybox and was warmed to approximately 40 °C for 20 min to facilitate the escape of the low-boiling $MeAsH_2$ from the reaction mixture. The subsequent ^1H NMR spectrum indicated a decrease in $MeAsH_2$ concentration. After the solution was kept at room temperature for 12 h, $(PhAs)_6$ precipitated.

The above results suggest that the overall reaction of cyclic $(MeAs)_5$ with $PhAsH_2$ to give $(PhAs)_6$ is complex. Following ring opening of $(MeAs)_5$, an equilibrium mixture of linear, H-terminated mixed polyarsines of the type $Me(H)As(AsMe)_x(AsPh)_yAs(H)Ph$ probably occurs in solution. The formation of such linear As–As-bonded intermediates is analogous to that of $Me(X)As(AsMe)_zAs(H)Me$, $Me(X)As(AsMe)_zAs(X)Me$, and $Me(H)As(AsMe)_zAs(H)Me$ as proposed in the $MeAsH_2/MeAsI_2$,[16] $(MeAs)_5/MeAsX_2$,[5,17] and $Me_2AsNMe_2/MeAsH_2$[18] systems, respectively. Several competing exchange equilibria that involve reactants, different intermediates, and products appear to influence the relative rates of consumption of different species at various stages of the reaction. These reactions could not be investigated independently, since there is insufficient spectroscopic information to characterize the individual intermediate oligomers in the mixture. Furthermore, they cannot be isolated by conventional separation methods due to the multiple temperature-dependent equilibria involved. An appreciable amount of $(PhAs)_6$ forms only upon lowering the $MeAsH_2$ concentration in solution.

^1H NMR Evidence for the Existence of Me(H)AsAs(H)Ph. The ^1H NMR spectra (δ; referenced to Me_4Si) indicated the presence of equimolar amounts of two stereoisomeric forms of Me(H)AsAs(H)Ph in solution [form I, 0.80 (d, *Me*As, 2.58 (pentet, MeAs*H*), 3.62 (d, PhAs*H*); form II, 0.92 (d, *Me*As), 2.50 (pentet, MeAs*H*), 3.49 (d, PhAs*H*)]. The peaks corresponding to the phenyl group could not be assigned because of overlapping signals in the phenyl region. The assignments for the ^1H NMR peaks of Me(H)AsAs(H)Ph were substantiated by homonuclear ^1H decoupling experiments. To our knowledge, this is the first example of the existence of an unsymmetrical diarsine possessing two chiral centers and one of the few examples of a diarsine containing an As–H bond. The symmetrical diarsine, $CF_3(H)AsAs(H)CF_3$,[19] has been reported previously. The analogous diphosphines of the type R(H)PP(H)R (R = CF_3, Me, Et, and Ph) are known.[20,21]

Experimental Section

Standard high-vacuum vacuum-line techniques and a Vacuum Atmospheres Model HE-43 Dri-lab equipped with a Model HE-493 Dri-Train were used for storing and handling of all compounds. Benzene was freshly distilled over CaH_2 prior to use. Phenylarsonic acid and *p*-tolylarsonic acid were purchased from Strem Chemicals. $(MeAs)_5$ (bp 178 °C (15 Torr)),[22] $PhAsH_2$ (bp 105 °C (107 Torr)),[23] *p*-$TolAsH_2$ (bp 114 °C (44 Torr)),[23] ethylarsonic acid (bp 100 °C)[24] and *n*-propylarsonic acid (bp 135 °C)[24,25] were synthesized by previously reported methods. $EtAsH_2$ (bp 36 °C) and *n*-$PrAsH_2$ (bp 61 °C) were prepared by reducing the corresponding alkylarsonic acid.[26] The purity of all compounds was checked by NMR spectroscopy prior to use. Microanalytical data were obtained from the Schwarzkopf Microanalytical Laboratory, New York. Note: $(MeAs)_5$ is pyrophoric, toxic, and acutely skin corrosive.

^1H and ^{13}C NMR spectra were recorded on a Nicolet 300-MHz multinuclear FT NMR spectrometer operating at 300.1 and 75.4 MHz, respectively. The chemical shifts were measured with respect to tetramethylsilane as an internal reference. See spectral data below for all NMR assignments.

General Procedure for the Synthesis of Cyclic Polyarsines, $(RAs)_n$ (R = Et, *n*-Pr, $n = 5$; R = Ph, *p*-Tol, $n = 6$). The appropriate molar amount of $RAsH_2$ was condensed onto approximately 25 mL of a degassed benzene solution containing $(MeAs)_5$ at −196 °C by using standard

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vacuum-line techniques. The reaction mixture was slowly warmed to approximately 10 °C and stirred until formation of $MeAsH_2$ was noted. The $MeAsH_2$ was separated and collected at −196 °C by trap-to-trap distillation. After the reaction was complete, all volatile materials were removed from the reaction mixture at reduced pressure. The product was purified by distillation at reduced pressure or by recrystallization in a chloroform/n-pentane mixture to give 80–85% product yield. Satisfactory C and H elemental analyses were obtained for all synthesized polyarsines. $(EtAs)_5$ and $(n\text{-}PrAs)_5$ boiled at 190 °C (1.0 Torr)[9] and 144 °C (0.05 Torr),[9] respectively, and $(PhAs)_6$ and $(p\text{-}TolAs)_6$ melted at 195 °C[27] and 216 °C,[5,28] respectively.

NMR Study of the $(MeAs)_5/PhAsH_2$ Reaction. A 0.60-mmol sample of $(MeAs)_5$, dissolved in toluene-d_8, and a drop of Me_4Si were added to a NMR tube (10 mm × 22.5 cm, Pyrex) equipped with a greaseless vacuum stopcock. The tube was degassed by using standard vacuum-line techniques. At −196 °C, 3.0 mmol of $PhAsH_2$ was condensed into the NMR tube. The total volume of the solution was maintained at 4.0 mL. The tube was sealed, agitated gently at −95 °C (toluene slush) and inserted into the precooled (−90 °C) probe of the NMR spectrometer. The reaction was then followed over the temperature range of −80 to 24 °C by recording the ^1H and ^{13}C NMR spectra as a function of time.

NMR Data. The following is a list of ^1H and ^{13}C NMR spectral data (δ; referenced to Me_4Si) determined independently in this laboratory on the synthesized compounds at 24 °C in toluene-d_8 solution except for $(PhAs)_6$ and $(p\text{-}TolAs)_6$ where $CDCl_3$ was used as solvent. The ^1H and ^{13}C NMR spectra of the cyclic polyarsines, except for $(MeAs)_5$, are complex, indicating the possibility of different solution conformations.[9] Only minor broadening, due to residual ^{75}As quadrupolar coupling, was noted in the ^1H NMR spectra of the As–H signals. References to previously reported NMR data are noted.

^1H NMR Data. $MeAsH_2$:[29] 0.65 (*Me*As, t, $^3J_{HH}$ = 7.2 Hz), 1.96 (AsH_2, q). $EtAsH_2$: 1.11 (CH_3CH_2As, t), 1.28 (CH_3CH_2As, m), 2.13 (AsH_2, t). *n*-$PrAsH_2$: 0.80 [$CH_3(CH_2)_2As$, t], 1.23–1.46 [$CH_3(CH_2)_2As$, m], 2.01 (AsH_2, t). $PhAsH_2$:[30] 3.45 (AsH_2), 6.97 (C-4; m), 6.99 (C-3,5, m), 7.28 (C-2,6, m). *p*-$TolAsH_2$: 2.05 (Me), 3.44 (AsH_2), 6.84 (C-3,5, m), 7.36 (C-2,6, m). $(MeAs)_5$:[31] 1.46, 1.50, 1.53. $(EtAs)_5$:[9] 1.22–1.37 (CH_3CH_2As, m), 2.01–2.25 (CH_3CH_2As, m). $(n\text{-}PrAs)_5$:[9] 0.93 [$CH_3(CH_2)_2As$, m], 1.43–2.26 [$CH_3(CH_2)_2As$, m]. $(PhAs)_6$:[9] 7.00–7.45, 7.57–7.68, 7.73–7.86 (Ph, m). $(p\text{-}TolAs)_6$: 2.21–2.36 ($CH_3C_6H_4As$, m), 6.89–7.69 ($CH_3C_6H_4As$, m).

^{13}C NMR Data. $MeAsH_2$: −9.09 ($^1J_{CH}$ = 134.4 Hz). $EtAsH_2$: 5.90 (CH_3CH_2As, $^1J_{CH}$ = 134.1 Hz), 18.14 (CH_3CH_2As, $^1J_{CH}$ = 128.5 Hz). *n*-$PrAsH_2$: 14.63 ($CH_3CH_2CH_2As$, $^1J_{CH}$ = 134.0 Hz), 15.95 ($CH_3CH_2CH_2As$, $^1J_{CH}$ = 125.0 Hz), 26.46 ($CH_3CH_2CH_2As$, $^1J_{CH}$ = 127.7 Hz). $PhAsH_2$:[30] 127.8 (C-4), 128.6 (C-3,5), 129.8 (C-1), 135.7 (C-2,6). *p*-$TolAsH_2$: 21.03 (Me), 125.9 (C-1), 129.6 (C-3,5), 135.9 (C-2,6), 137.5 (C-4). $(MeAs)_5$: 3.80, 5.32, 6.80 ($^1J_{CH}$ = 134.9 Hz). $(EtAs)_5$: 15.37, 15.44, 15.67, 16.50, 17.41, 17.94 (*Et*As). $(n\text{-}PrAs)_5$: 3.70–7.10, 16.34, 24.20–28.02 (*Pr*As, m). $(PhAs)_6$: 128.3 (C-4, m), 128.4 (C-3,5, m), 134.4 (C-2,6, m), 137.2 (C-1). $(p\text{-}TolAs)_6$: 21.23 (Me), 129.2 (C-3,5, m), 134.3 (C-2,6, m), 138.0 (C-4, m).

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Additions and Corrections

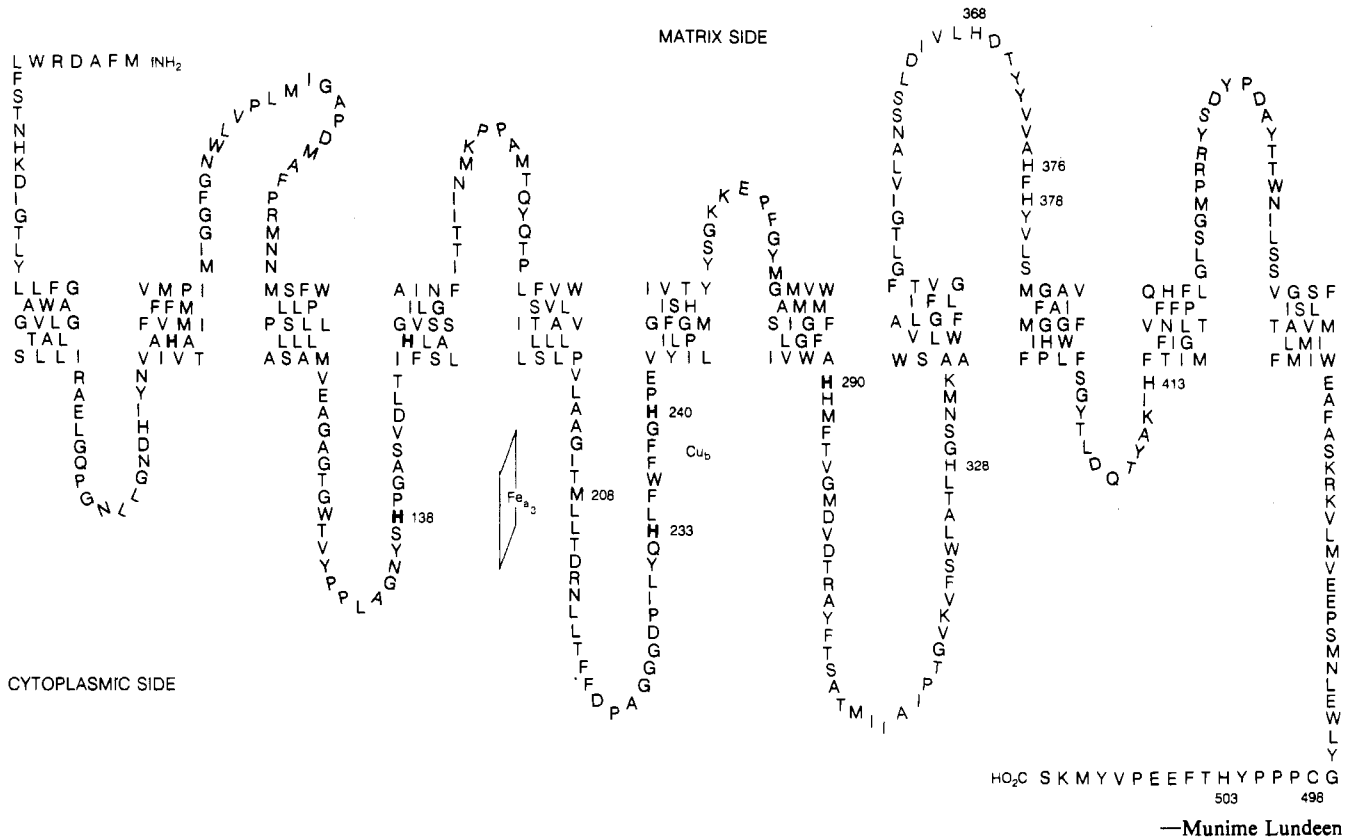
1986, Volume 25

Munime Lundeen: Where Is the Oxygen Binding Site of Cytochrome *c* Oxidase? Transmembrane Helices of Subunits I and II.

Page 4854. The residues of the eighth transmembrane helix in Figure 1 are WSAAVLWALGFIFLFTVG. The first residue of the fourth transmembrane helix is I and not T. The corrected Figure 1 is shown below.

Page 4855. The title to Table II should read as follows: Predicted Transmembrane (tm) Segments in Subunit I of CCO from Placental[16] and Yeast[42a] Enzymes and Subunit II of CCO from Beef Heart[30a] and Yeast[45] Enzymes.

Page 4856. Reference 45 was left out of the paper: (45) (a) Fox, T. D. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 6534. (b) Coruzzi, G.; Tzagoloff, A. *J. Biol. Chem.* **1979**, *254*, 9324.



—Munime Lundeen