netic resonance spectra, physical constants, thin-layer chromatographic mobility, and elemental combustion analyses of compounds **2**–**6** and **8**–**15** and isolated intermediates (6 pages). Ordering information is given on any current masthead page.

Hydridometallacycloalkane Complexes of Iridium. Unassisted Intramolecular Distal C–H Bond Activation

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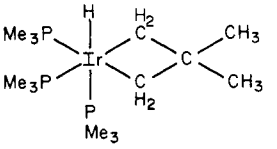
In recent years interest in transition-metal alkyl complexes has resulted in the preparation of complexes in which the well-known decomposition pathway, β-hydrogen abstraction, is obviated by substitution at the β-carbon atom.[1,2] Schrock and co-workers have demonstrated an alternative pathway, α-hydrogen transfer, in the preparation of alkylidene complexes of the early transition metals.[3] Quite recently γ- and δ-hydrogen abstractions have also been shown to be viable transformations for group 8 polyalkyl and organo f-element complexes.[4-11] Although cyclometallation involving coordinated ligands, such as $P(alkyl)_3$[12] and $P(C_6H_5)_3$ (orthometallation),[13] has long been recognized, its application to hydrocarbyl systems has been limited to a few examples. We believe that this reaction may represent a broadly applicable route to novel metallacyclic complexes and in this communication we report the facile preparation of an extensive series of hydridometallacycloalkane complexes of Ir(III) by γ- and δ-hydrogen-atom abstraction reactions of alkyl Ir(I) complexes.

A typical γ-H-atom abstraction reaction is represented by the heavy arrow in Scheme I. For group 8 complexes mechanism A, which involves initial oxidative addition to a distal C–H bond and subsequent reductive elimination of the R and H ligands, has been suggested.[7] In this reaction sequence the presence of a second alkyl or hydrido ligand may assist in driving the reaction. In the alternative mechanism B, which is related to that recently proposed for α-H abstraction,[3,14] the ligand R plays an even more fundamental role. Here an incipient radical actively abstracts a H atom in a four-centered transition state, and the metal center undergoes no formal change in oxidation state during the reaction. The reactions described below demonstrate that the oxidative addition portion of mechanism A occurs readily in Ir(I) alkyl complexes even in the absence of an "assisting" leaving group (e.g., alkyl or hydride ligand).

Reaction of $[Ir(PMe_3)_4]Cl$ (**1**)[15,16] with $LiCH_2CMe_3$ in hexane or toluene at room temperature smoothly produces *fac*-tris(trimethylphosphine)hydrido(2,2-dimethyl-1,3-propanediyl)iridium (**2**) in high yield. The complex has been characterized by IR



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and ^1H, ^{13}C, and ^{31}P NMR spectroscopies, the results of which are consistent with the structure shown.[17] Similar reactions with chloroiridium(I) complexes containing arsine ligands produce analogous products, e.g., *fac*-$IrH(CH_2CMe_2CH_2)(AsR_3)_3$, R = Me, Et,[18] and these have served to verify the spectroscopic assignments for complex **2**. Additional substantiation of the proposed formulation has been provided by an X-ray molecular structure determination of the trimethylarsine complex, details of which will be published separately. Complex **2** is remarkably stable; it is unaffected by air and moisture for short periods of time and is inert to CO and C_2H_4 at room temperature. Furthermore, a solution of complex **2** in benzene-d_6 was unchanged after 24 h at 90 °C.

We have not detected the presumed precursor to complex **2**, $Ir(CH_2CMe_3)(PMe_3)_3$, except as a transient orange solution.[19] The reaction of complex **1** with $LiCH_2SiMe_3$ does, however, yield the relatively stable initial product, $Ir(CH_2SiMe_3)(PMe_3)_3$ (**3**).[20] Only after standing for prolonged periods or upon heating does complex **3** transform into the Si congener of complex **2**, *fac*-$IrH(CH_2SiMe_2CH_2)(PMe_3)_3$ (**4**).[21] This reactivity difference may arise from the decreased steric demand of the (trimethylsilyl)methyl ligand as compared with that of the neopentyl group.[22,23] Experiments are in progress which utilize this slower

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(15) Abbreviations: Me, CH_3; Et, C_2H_5; Ph, C_6H_5; Cp, η^5-C_5H_5; THF, tetrahydrofuran.
(16) Herskovitz, T., submitted to *Inorg. Synth.*
(17) Complex **2**: IR (Nujol mull) ν_{Ir-H} 2018 (s) cm^{-1}; ^1H NMR (C_6D_6, 220 MHz) δ −9.81 (dt, $^2J_{HP_{trans}}$ = 167 Hz, $^2J_{HP_{cis}}$ = 21 Hz, IrH), 1.37 (18, d, $^2J_{HP}$ = 7 Hz, PCH_3 (basal)), 1.40 (dd, $^2J_{HP}$ = 7 Hz, $^4J_{Hhydride}$ = 1 Hz, PCH_3 (axial)), 1.46 (3, s, CCH_3), 1.77 (3, s, CCH_3); $^1H\{^{31}P\}$ NMR (C_6D_6, 100 MHz) (m), (s), (d), (s), (s), δ 0.55 (2, d, $^2J_{AB}$ = 8 Hz, $IrCH_2$), 1.02 (2, dd, $^2J_{AB}$, $^3J_{Hhydride}$ = 2 Hz, $IrCH_2$); $^{13}C\{^1H\}$ NMR (C_6D_6, 22.63 MHz) δ −17.87 (d, $^2J_{CP_{trans}}$ = 65 Hz, $IrCH_2$), 18.23 (d, $^1J_{CP}$ = 19 Hz, PCH_3 (axial)), 22.84 (d, $^1J_{CP}$ = 28 Hz, PCH_3 (basal)), 31.72 (s, CCH_3), 38.60 (s, CCH_3), 45.75 (s, CH_2CCH_3); $^{13}C\{^1H$ single-frequency off-resonance decoupled$\}$ NMR (dt plus long range J_{CH}), (dq), (dq), (q), (q), (s); $^{31}P\{^1H\}$ NMR C_6D_6, 29.94 MHz) AB_2 pattern, centered at −60.3 ppm relative to 85% H_3PO_4 (external). Anal. Calcd for $C_{14}H_{38}IrP_3$: C, 34.21; H, 7.79. Found: C, 34.30; H, 7.81.
(18) *fac*-$IrH(CH_2CMe_2CH_2)(AsR_3)_3$: R = Me; IR ν_{Ir-H} 2044 cm^{-1}; ^1H NMR δ −12.4 (1, s, IrH), 1.25 (18, s, $AsCH_3$(basal)), 1.30 (9, s, $AsCH_3$ (axial)), 1.38 (3, s, CCH_3), 1.70 (3, s, CCH_3), 0.92 (2, d, $^2J_{AB}$ = 8 Hz, $IrCH_2$), 1.45 (2, dd, $^2J_{AB}$, $J_{Hhydride}$ = 2 Hz); $^{13}C\{^1H\}$ NMR δ −20.96 ($IrCH_2$), 12.25 ($AsCH_3$ (axial)), 16.96 ($AsCH_3$ (basal)), 31.62 (CCH_3), 36.75 (CCH_3), 47.28 (CH_2CCH_3); $^{13}C\{^1H$ SFORD$\}$ NMR (t), (q), (q), (q), (q), (s). R = Et; IR ν_{Ir-H} 2010 cm^{-1}; ^1H NMR δ −13.3 (1, s, IrH), overlapping aliphatic region. Anal. Calcd for $C_{23}H_{56}As_3Ir$: C, 36.85; H, 7.53. Found: C, 37.01; H, 7.56.
(19) Note that under these conditions the analogous rhodium(I) neopentyl complex is isolated, unpublished results.
(20) Complex **3**: ^1H NMR δ 0.38 (9, s, $SiCH_3$), 0.65 (2, dt, $^3J_{HP_{trans}}$ = 8 Hz, $^3J_{HP_{cis}}$ = 13 Hz, $IrCH_2Si$), 1.24 (9, d, $^2J_{HP}$ = 8 Hz, PCH_3 (unique)), 1.31 (18, t (virtual), $^2J_{HP}$ + $^4J_{HP}$ = 6 Hz, PCH_3 (mutually trans)).
(21) Complex **4**: IR ν_{Ir-H} 2005 (m) cm^{-1}; ^1H NMR δ −10.93 (1, dt, $^2J_{HP_{trans}}$ = 168 Hz, $^2J_{HP_{cis}}$ = 22 Hz, IrH), −1.01 (2, br m, $IrCH_2Si$), −0.40 (2, br m, $IrCH_2Si$ (wings of AB quartet with superimposed J_{HP} and J_{HH})), 0.36 (3, s, $SiCH_3$), 0.63 (3, s, $SiCH_3$), 1.13 (9, d, $^2J_{HP}$ = 7 Hz, PCH_3 (axial)), 1.20 (18, d, $^2J_{HP}$ = 7 Hz, PCH_3 (basal)); $^{31}P\{^1H\}$ NMR AB_2 pattern centered at δ −58.35 and −60.72. Anal. Calcd for $C_{13}H_{38}IrP_3Si$: C, 30.76; H, 7.55. Found: C, 30.80; H, 7.71.
(22) Compare: the complex $(\eta^5$-$C_5Me_5)_2Zr(CH_2SiMe_3)_2$ is readily prepared whereas we have been unable to prepare the analogous bis(neopentyl) complex. Tulip, T. H., unpublished results.

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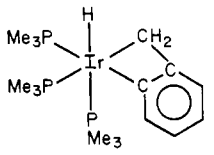
overall reaction to determine other factors, e.g., solvent, ancillary ligands, etc., which affect the oxidative cyclization.

Intramolecular oxidative additions to distal aryl C–H bonds also proceed readily. The reaction of $[Ir(PMe_3)_4]Cl$ with benzylmagnesium chloride in THF at room temperature yields the benzometallacyclobutene complex **5**.[24] The hydride hydrogen



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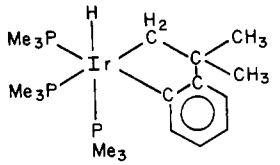
atom presumably is derived from the ortho position of a transient benzyliridium(I) complex. The preparation of the trimethyl phosphite analogue via the corresponding Ir(I) *o*-tolyl complex has been previously reported.[25] In both cases cyclization results from Ir insertion into a γ-C–H bond. We have also observed a facile insertion at the aryl δ (ortho) position of the neophyl (CH_2CMe_2Ph) ligand. Thus a 1:1 mixture of complex **1** and $LiCH_2CMe_2Ph$ in hexane rapidly yields the benzoiridacyclopentene complex **6**.[26] The spectral features of this complex are



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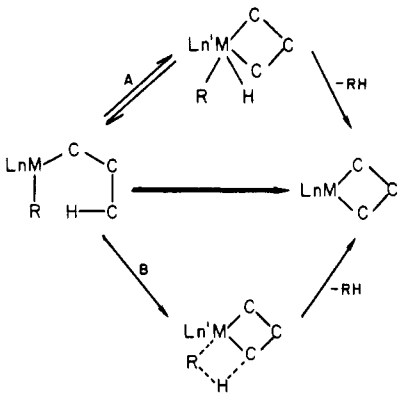
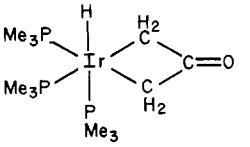
similar to those of a zirconacyclopentene complex, $Cp_2Zr(CH_2CH_2C_6H_4\text{-}o)$, recently prepared by an alternative route.[27] Furthermore, the formation of complex **6** is consistent with the initial step of the proposed mechanism for rearrangement of bis(*tert*-phosphine)neophylnickel(II) complexes to isomeric (*o*-*tert*-butylphenyl)nickel(II) species.[28] No iridium hydrocarbyl intermediates have been detected in the reactions which produce complexes **5** and **6**.

We have also observed rapid cyclization via oxidative addition to a distal C–H bond of functionalized alkyl groups. As one

Scheme I



example, the reaction of complex **1** with the enolate salt of acetone yields the iridacyclobutan-3-one complex **7**.[29] An analogous Pt



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complex was prepared by the reaction of $Pt(PPh_3)_2$(styrene) with dimethyl 3-oxoglutarate.[30] The enolate salts of other methyl ketones, e.g., pinacolone and acetophenone, react with complex **1** to yield the corresponding iridacycloalkanone complexes, details of which will be described separately.

Our attempts to prepare metallacyclic compounds containing other heteroatoms, e.g., O or N, by the above route have not been successful, owing to a competing reaction in which a trimethylphosphine ligand is metalated to give $Ir(CH_2P(CH_3)_2)(P(CH_3)_3)_3$.[31] Alternative routes to a variety of heterometallacycles as well as elucidation of the chemistry of complexes **2**–**7** are being actively pursued.

The syntheses described above derive from the propensity of Ir(I) centers to undergo facile oxidative addition reactions.[32] Here, as in a number of other cases,[33-39] this ability has been applied

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(24) Complex **5**: IR ν_{Ir-H} 1976 (vs) cm^{-1}; ^1H NMR δ −9.42 (1, dt, $^2J_{HP_{trans}}$ = 155 Hz, $^2J_{HP_{cis}}$ = 21 Hz, IrH), 0.93 (9, d, $^2J_{HP}$ = 7 Hz, PCH_3 (axial)), 1.16 (9, d, $^2J_{HP}$ = 7 Hz, PCH_3), 1.27 (9, d, $^2J_{HP}$ = 7 Hz, PCH_3), 2.16 (2, br d, $^2J_{AB}$ = 10 Hz, $IrCH_2$, one wing of AB quartet), 6.63 (1, d), 7.05 (1, t), 7.16 (1, t), 7.36 (1, br d, aromatic H, J_{HH} ~ 7 Hz); $^{13}C\{^1H\}$ NMR δ −7.15 (d, $^2J_{CP_{trans}}$ = 80.6 Hz, $IrCH_2$), 16.90 (d, $^1J_{CP}$ = 27 Hz), 18.36 (d, $^1J_{CP}$ = 39 Hz), 19.06 (d, $^1J_{CP}$ = 27 Hz, PCH_3), 121.07 (s), 123.82 (d, J_{CP} = 7 Hz), 125.90 (d, J_{CP} = 10 Hz), 126.14 (d, J_{CP} = 10 Hz), 130.78 (d, J_{CP} = 5 Hz), 164.00 (s, aromatic C); $^{31}P\{^1H\}$ NMR three pseudotriplets: δ −43.9, −53.6, −56.7 (J_{obsd} = 11 Hz). Anal. Calcd for $C_{16}H_{34}IrP_3$: C, 37.57; H, 6.70. Found: C, 37.59; H, 6.68.

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(26) Complex **6**: IR ν_{Ir-H} 2010 (s) cm^{-1}; ^1H NMR δ −10.87 (1, ddd, $^2J_{HP_{trans}}$ = 162 Hz, $^2J_{HP_{cis}}$ = 24, 15 Hz, IrH), 0.88 (9, d, $^2J_{HP}$ = 7 Hz, PCH_3 (axial)), 1.19 (9, d, $^2J_{HP}$ = 7 Hz), 1.32 (9, d, $^2J_{HP}$ = 8 Hz, PCH_3 (basal)), 1.59 (3, s, CCH_3), 1.73 (3, d, $J_{Hhydride}$ = 1 Hz, CCH_3), 1.55, 1.98 (2, m, partially obscured wings of AB quartet, $IrCH_2$), 6.89 (1, t), 7.02 (2, d), 7.32 (1, t, J_{HH} = 7 Hz, aromatic H); $^1H\{^{31}P\}$ NMR δ −10.9 (br m), 0.88 (d, $^4J_{Hhydride}$ = 1 Hz), 1.55 (1, dd, $^2J_{AB}$ = 10 Hz, $^3J_{Hhydride}$ = 3 Hz, $IrCH_2$), 1.98 (1, d, $IrCH_2$); $^{13}C\{^1H\}$ NMR δ −22.23 (d, $^2J_{CP_{trans}}$ = 55 Hz, $IrCH_2$), 17.38 (d, $^1J_{CP}$ = 22 Hz), 22.10 (d, $^1J_{CP}$ = 26 Hz), 24.40 (d, J_{CP} = 28 Hz, PCH_3), 31.07 (s), 33.40 (d, $^4J_{CP}$ = 6 Hz, CCH_3), 48.55 (d, $^3J_{CP}$ = 9 Hz, CH_2CCH_3), 120.69, 121.99, 123.03, 123.22, 141.42, 141.68 (aromatic C). $^{31}P\{^1H\}$ NMR complex second-order ABC pattern centered at δ −55.8 and −59.3. Anal. Calcd for $C_{19}H_{40}IrP_3$: C, 41.22; H, 7.28. Found: C, 41.23; H, 7.20.

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(29) Complex **7**: IR ν_{Ir-H} 2030 (s), $\nu_{C=O}$ 1560 (vs) cm^{-1}; ^1H NMR δ −12.8 (1, dt, $^2J_{HP_{trans}}$ = 157 Hz, $^2J_{HP_{cis}}$ = 22 Hz, IrH), 1.29 (9, dd, $^2J_{HP}$ = 8 Hz, $^4J_{Hhydride}$ = 1 Hz, PCH_3 (axial)), 1.31 (18, d, $^2J_{HP}$ = 8 Hz, PCH_3 (basal)), 2.20 (2, br m, $IrCH_2$), 3.10 (2, br m, $IrCH_2$); $^1H\{^1P\}$ NMR δ 2.20 (2, br d, $^2J_{AB}$ = 5 Hz, $IrCH_2$), 3.10 (2, br d, $IrCH_2$). Anal. Calcd for $C_{12}H_{32}IrOP_3$: C, 30.18; H, 6.76. Found: C, 29.86; H, 6.66. The analogous tris(trimethylarsine) complex has also been synthesized to facilitate spectroscopic analysis. IR ν_{Ir-H} 2060 (s), ν_{CO} 1572 (s) cm^{-1}; ^1H NMR δ −15.7 (s, IrH), 1.13 (18, s, $AsCH_3$ (basal)), 1.15 (9, s, $AsCH_3$ (axial)), 2.49 (2, d, $^2J_{AB}$ = 5 Hz, $IrCH_2$), 3.10 (2, d, $IrCH_2$); $^{13}C\{^1H\}$ δ 10.04, ($AsCH_3$ (axial)), 12.32 ($IrCH_2$), 18.36 ($AsCH_3$ (basal)), 185.06 ($CH_2C{=}O$); $^{13}C\{^1H$ SFORD} (q), (t), (q), (br m). Anal. Calcd for $C_{12}H_{32}As_3IrO$: C, 23.65; H, 5.29. Found: C, 23.44; H, 5.40.

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with particular success to C-H bond activation where the formation of stable Ir^{III}-H bonds acts as an additional driving force.[40] Much remains to be learned about the intimate mechanisms and scope of such reactions, and studies are ongoing in our laboratory which should clarify these questions.

(40) For a comprehensive review of C-H bond activation see: Parshall, G. W. *Catalysis (London)* **1977**, 1.

The "Pocket" Porphyrin: A Hemoprotein Model with Lowered CO Affinity

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The role of the heme cavity in causing discrimination in the binding of small ligands to hemoproteins is an area of active interest.[1,2] We report here the synthesis and preliminary binding studies of a new model compound, the "pocket" porphyrin H_2PocPivP (Ia). This compound has been specificially designed to investigate the effect of steric interaction on O_2 and CO binding in ferrous porphyrins. Our findings indicate that, compared with open-cavity models such as the "picket fence",[3,4] the added steric encumbrance of the pocket reduces the CO affinity without substantially changing that[5] of O_2.

Structural analyses in carbonylated hemoproteins reveal that the CO unit is bent and/or tilted from the perpendicular to the porphyrin plane owing to interaction with the distal residues[6] (histidine,[6a] valine,[6b] and leucine[6c] or isoleucine[6d]). In simple model compounds, the linear FeCO group is normal to the porphyrin plane.[7] We[4,5] and others[8a,9] have proposed that in hemoproteins distortion of the FeCO unit reduces the CO affinity without affecting the O_2 affinity of the intrinsically bent FeO_2 group.[2a,10,11]

Mutant hemoglobins such as HbZh (β63His→Arg), for which structural studies reveal a more open binding pocket,[8a] have been investigated as a means of assessing distal steric effects.[8,12] The CO affinities of this mutant apparently have not yet been directly determined; however, HbZh appears to bind CO more tenaciously than does normal HbA.[12b,13] Investigations in hemoproteins can be complemented by carefully designed model porphyrin systems which explore particular aspects of ligand-heme binding.[15,16]

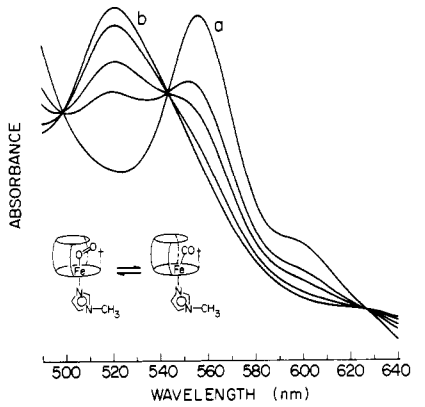
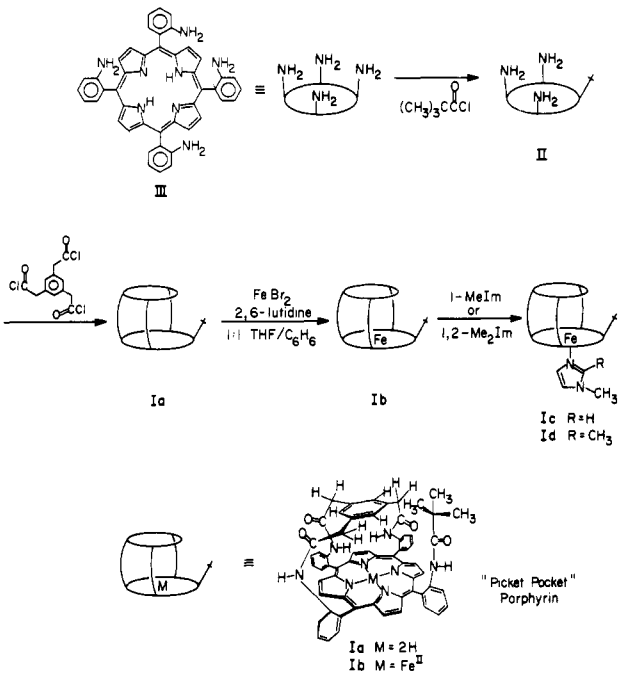


Figure 1. Determination of M value for Fe(PocPivP)(1-MeIm) (Ic). Ic; ca. 5×10^{-5} M in toluene, 1.0 M 1-methylimidazole, 25.0 ± 0.1 °C. Curve a; under 1 atm of O_2; curve b; under 1 atm of CO. Intermediate curves obtained by diluting O_2 with increased quantities of 4.95% CO/N_2.

Scheme I



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(3) Abbreviations: $P_{1/2}$ = partial pressure of gas at half-saturation; $M = P_{1/2}{}^{O_2}/P_{1/2}{}^{CO}$; K_B = equilibrium constant for the binding of a single axial ligand to the four-coordinate heme; 1-MeIm = 1-methylimidazole; 1,2-Me_2Im = 1,2-dimethylimidazole; TPivPP = picket-fence, *meso*-$\alpha,\alpha,\alpha,\alpha$-tetrakis[*o*-(pivalamido)phenyl]porphyrinato; Fe[Piv_3(5ClmP)Por] = *meso*-α,α,α-tris-[*o*-(β-pivalamido)phenyl]-β-[*o*-[5-(*N*-imidazoyl)valeramido]phenyl]prophyrinatoiron(II); Hb (R), Hb (T) = relaxed and tense hemoglobin (human), respectively; Mb = myoglobin (human); HbZh = hemoglobin Zurich.

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(13) The O_2 affinity and CO "on" rate have been kinetically determined for isolated mutant chains of HbZh (see ref 12d). An M value for the tetrameric form has also been reported[8] (Table I). It has been suggested[14] that the lower O_2 affinity could account for the higher M value of HbZh. However, studies with this mutant, in general, and comparisons between single chain and tetramer data, in particular, are complicated by cooperativity, its heterogeneity, and sensitivity toward oxidation. The 10-fold higher CO "on" rate for monomeric mutant chains[12d] may indicate a higher CO affinity for HbZh. Importantly, the blood of a "patient with HbZh disease was found to contain the abnormal β subunits saturated with CO under conditions where the α subunit and normal β subunits were only occupied to a normal extent by CO" (ref 12a, p 2).

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