Table I. Photophysical and Photochemical Behavior of Styryl Amines

amine	τ_s,[a] ns	Φ_f[b]	**2**/**3**[c]	(**2** + **3**)/isom[d]	yield,[e] %
trans-*N*-methyl-3-phenyl-2-propen-1-amine ($\mathbf{1}_1$)	<0.1	<0.005	>20	0.1	15
trans-*N*-methyl-4-phenyl-3-buten-1-amine ($\mathbf{1}_2$)	0.73	0.046	14 (3.0)	>10	63
trans-*N*-methyl-5-phenyl-4-penten-1-amine ($\mathbf{1}_3$)	0.51	0.021	2.4 (1.0)	3.0	57
trans-*N*-methyl-6-phenyl-5-hexen-1-amine ($\mathbf{1}_4$)	1.6	0.070	0.15 (0.8)	>10	82
trans-*N*-methyl-7-phenyl-6-hepten-1-amine ($\mathbf{1}_5$)		0.13	>8	1.0	30
cis-*N*-methyl-5-phenyl-4-penten-1-amine	0.35	0.015	2.4	>10	62
trans-5-phenyl-4-penten-1-amine	3.7	0.19	1.5	0.4	

[a] Fluorescence lifetime of 6×10^{-5} M styryl amine in nitrogen-purged cyclohexane solution at 300 K. Samples were excited at 308 nm with the frequency-doubled output of a synchronously pumped mode-locked dye laser, and fluorescence was selected with a prism monochromator and analyzed by means of a standard single-photon-timing apparatus using multiexponential least-squares fitting. The short-lived monomer emission accounted for >96% of the total fluorescence in all cases. [b] Fluorescence quantum yield determined under conditions of footnote *a* relative to styrene ($\Phi_f = 0.24$[8a]). [c] Ratio of cyclic adducts from 0.005–0.01 M styryl amine in nitrogen-purged acetonitrile solution. Values in parentheses are for cyclohexane solution. [d] Ratio of total adduct to isomerization. [e] Yield of the major adduct (**2** or **3**) determined by GC analysis at moderate to high conversion (>50%).

previously observed for fluorescent arene–tertiary amine intramolecular exciplexes.[5,11] Adduct formation quantum yields are largest for the styryl amines that form the most stable intramolecular exciplexes. The similar values of k_f for $\mathbf{1}_2$–$\mathbf{1}_5$ and 1-phenylpropene ($k_f = \Phi\tau_s \sim (5 \pm 1) \times 10^7\ \mathrm{s}^{-1}$) indicate that there is no significant ground-state interaction between the chromophores except in the case of the nonfluorescent allylamine $\mathbf{1}_1$.[12] It is interesting to note that the photophysical properties of *cis*- and *trans*-$\mathbf{1}_3$ are similar, while those of the primary amine analogues of $\mathbf{1}_3$ are more like those of 1-phenylpropene, indicative of inefficient intramolecular singlet quenching by the primary amino group. Primary amines are known to be much poorer electron-transfer quenchers than secondary or tertiary amines as a consequence of their higher ionization potentials.[10]

Following exciplex formation, transfer of the N–H hydrogen to the styrene β- or α-carbon yields the singlet biradical precursors of **2** and **3**, respectively (eq 2). The absence of intersystem crossing in the locally excited styrene or singlet exciplex is indicated by the nearly complete intramolecular quenching of styrene trans,cis isomerization in $\mathbf{1}_2$ and $\mathbf{1}_3$ and the ability of a triplet sensitizer (Michler's ketone) to affect trans,cis isomerization but not cyclization of *trans*- or *cis*-$\mathbf{1}_3$. Evidence for the singlet multiplicity of the biradical intermediate is provided by the stereospecific formation of the syn adduct $\mathbf{2}_3$-*d*, from $\mathbf{1}_3$-*N*-*d*, and the absence of D–H exchange of the vinyl hydrogens in recovered $\mathbf{1}_3$.[13] While cage escape accounts for over half of the 1-phenylpropyl radicals formed in the intramolecular reaction (eq 1), the biradicals formed in the intramolecular reaction either cyclize or revert to starting material, resulting in improved preparative yields for the intra- vs intermolecular reaction.

An intriguing feature of the intramolecular styrene–amine addition reaction is the formation of α-benzyl amines (**3**) as the major product from $\mathbf{1}_4$ and as a minor product from some of the other styryl amines. On the basis of biradical stabilities (eq 2) and the regioselectivity of the intramolecular reaction (eq 1), we had anticipated the regioselective formation of the α-phenyl amines (**2**). Among the factors that may influence the regioselectivity of intramolecular addition are (a) the conformational energy of the polymethylene chain, (b) N–H···C hydrogen bond formation in the exciplex,[14] (c) biradical stabilities, and (d) partitioning of the biradical intermediate between product and reactants. The increase in cyclization regioselectivity with increasing solvent polarity (Table I) indicates that solvation of the exciplex may also be an important factor. In the case of $\mathbf{1}_3$ the **2**/**3** ratio is also temperature dependent, decreasing from 2.4 at 30 °C to 6.2 at −40 °C in acetonitrile solution. Thus cycloaddition regioselectivity can be controlled by the appropriate choice of solvent and temperature. As noted by Aoyama et al.,[3b] hydrogen transfer in styryl amines is not limited to five- and six-membered transition states but has now been observed for four- to eight-membered transition states. In reactions such as these, where intramolecular exciplex formation precedes hydrogen transfer, extension to even larger ring sizes is limited only by the requirement that intramolecular exciplex formation compete with decay of the styrene singlet.

Acknowledgment. Financial support for this research has been provided by the National Science Foundation and the Deutsche Forchungsgemeinschaft and travel expenses by a NATO Research Grant.

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3-Oxaplatinacyclobutanes. Synthesis and Intramolecular Cyclization of the First Bis(hydroxymethyl) Transition-Metal Complex

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The relevance of metallacyclic transition-metal complexes to organic synthesis is well documented.[2,3] While most investigations have focused on all-carbon metallacycles, recently effort has been directed toward metallacycles substituted with synthetically interesting heteroatoms such as oxygen and nitrogen. In these cases, involving early[3b,4] and late[5] transition metals, the heteroatom is invariably bonded directly to the metal. In contrast, metallacyclic complexes substituted with oxygen or nitrogen on ring positions away from the metal center have not been investigated, despite the potential for using such systems in organic heterocycle syn-

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(1) Du Pont Young Faculty Awardee, 1988–1989. Union Carbide Innovation Recognition Program Awardee, 1989.

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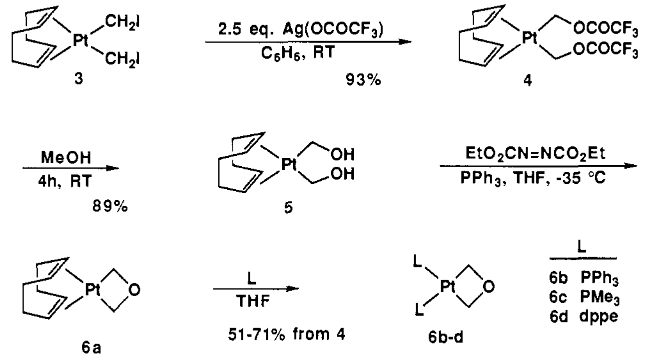
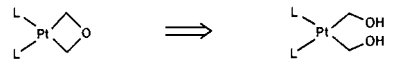
Scheme I



thesis. In such ring systems, the heteroatom may influence structure and reactivity indirectly through electronic effects or, depending on the coordination environment, directly through a transannular dative interaction.

We are developing synthetic pathways to oxygen- and nitrogen-substituted metallacycles, concentrating initially on 3-oxametallacyclobutane complexes, an unprecedented organometallic ring system.[6,7] While development of novel synthetically interesting reactions is the ultimate goal of this research, stable representative examples of this structural class must be prepared and comparisons drawn to the reactivity of analogous all-carbon metallacycles. For this reason, platinacyclobutane complexes (**1**)



1 2

constitute the initial targets of this investigation. Corresponding all-carbon platinacyclobutanes have been prepared and characterized spectroscopically and crystallographically, and the reactivity of these complexes has been established.[8,9] Additionally, in this system, no donor interaction from the oxygen to the platinum center is anticipated, decoupling assessment of the heteroatom electronic effect from complicating dative bonding.

Among the many strategies for rational synthesis of the 3-oxaplatinacyclobutane complexes, an intramolecular dehydration of the bis(hydroxymethyl) complex **2** was considered most interesting. Bis(hydroxymethyl) complexes are unprecedented[10,11] and constitute significant synthetic targets well beyond the present context.[12] The starting material for this investigation is the bis(iodomethyl) complex (COD)Pt$(CH_2I)_2$ (**3**) (COD = 1,5-cyclooctadiene), quantitatively prepared by diazomethane insertion into (COD)PtI_2.[13] Conversion of the bis(iodomethyl) complex to the bis(hydroxymethyl) complex requires suppression of reactivity typically observed in similar systems: attack by nucleophiles on the coordinated olefin[14] and solvolytic ionization of the carbon-halide bond, ultimately yielding ethylene.[15] Thus, use of strongly acidic or basic conditions in the manipulation of bis(iodomethyl) complex **3** is precluded.

Replacement of iodide with oxygenated functionality was accomplished by using AgO_2CCF_3 in benzene, affording bis(trifluoroacetate) complex **4** in 93% yield after recrystallization from pentane (Scheme I).[16] The trifluoroacetates were removed under essentially neutral conditions by methanolysis[17] at high dilution (~0.001 M), giving the bis(hydroxymethyl) complex **5** in 89% yield after recrystallization from THF/hexane.[18] This reaction may be catalyzed by trace water or acid in the methanol (0.004% H_2O, stored over 3-Å molecular sieves); no conversion was observed in methanol dried with $Mg(OMe)_2$. Bis(hydroxymethyl) complex **5** is air sensitive and somewhat thermally labile, decomposing at room temperature over several days. The ^1H NMR spectrum of **5** (300 MHz, acetone-d_6) is characteristic, giving a doublet at δ 4.33 (J_{HH} = 4.7 Hz, J_{PtH} = 71.9 Hz, 4 H) for the equivalent hydroxymethyl methylene groups and a triplet at δ 3.35 (J_{HH} = 4.7 Hz, J_{PtH} = 40.6 Hz, 2 H) for the alcohol protons. The latter exchange with D_2O, and resolution of the proton coupling is concentration dependent. A detailed investigation of the chemistry of this unique complex is anticipated.[12]

For synthetic purposes, the bis(hydroxymethyl) complex **5** obtained on methanol evaporation is used without further purification. Intramolecular dehydrative cyclization to oxametallacyclobutane complex **6a** was accomplished under similarly neutral, nonnucleophilic conditions using triphenylphosphine/diethyl azodicarboxylate, technology adapted from organic synthesis (Scheme I).[19] To avoid displacement of the cyclooctadiene ligand, the phosphine and azo compound are premixed in THF prior to addition of **5**. The product cyclooctadiene complex **6a** was also slightly thermally sensitive; however, stable derivatives can be prepared in high overall yield (51–71% from **4**) by replacement of the olefin with phosphine in situ after cyclization. The robust phosphine derivatives **6b–d** have been fully characterized, bis(triphenylphosphine) complex **6b** by X-ray crystallography (Figure 1).[20] In contrast to many structurally characterized platinacyclobutanes,[6c,8,9] the metallacyclic ring of **6b** is completely planar in the solid state.

In summary, the rational synthesis of a novel class of metal-

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(15) McCrindle, R.; Arsenault, G. J.; Farwaha, R.; Hampden-Smith, M. J.; McAlees, A. J. *J. Chem. Soc., Chem. Commun.* **1986**, 943.

(16) Spectroscopic data for complex **4**: mp 61–63 °C (open tube, no dec); IR (KBr) 2920, 1770, 1140, 860, 770 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.19 (br s, J_{PtH} = 41.4 Hz, 4 H), 5.06 (s, J_{PtH} = 67.2 Hz, 4 H), 2.46 (br s, 8 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 158.2 (q, J_{FC} = 39.1 Hz), 114.7 (q, J_{FC} = 287 Hz), 103.6 (s, J_{PtC} = 63.4 Hz), 67.9 (s, J_{PtC} = 984 Hz), 29.4 (s). Anal. Calcd for $C_{14}H_{16}F_6O_4Pt$: C, 30.17; H, 2.89. Found: C, 30.11; H, 2.98.

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(20) Spectroscopic data for complex **6b**: mp 127–129 °C (open tube, no dec); IR (KBr) 3080, 3060, 2900, 2880, 2810, 1485, 1440, 1100, 920, 745, 695 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39–7.13 (m, 30 H), 3.55 (s, J_{PtH} = 73.5 Hz, 4 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 134.0 (m), 133.3 (d, J_{PC} = 43.5 Hz), 129.6 (s), 127.8 (m), 31.6 (d, J_{PC} = 86.0 Hz, J_{PtC} = 471 Hz). $^{31}P\{^1H\}$ NMR (146 MHz, $CDCl_3$) δ 25.3 (s, J_{PtP} = 1797 Hz). Anal. Calcd for $C_{38}H_{34}OP_2Pt$: C, 59.76; H, 4.49. Found: C, 59.72; H, 4.51.

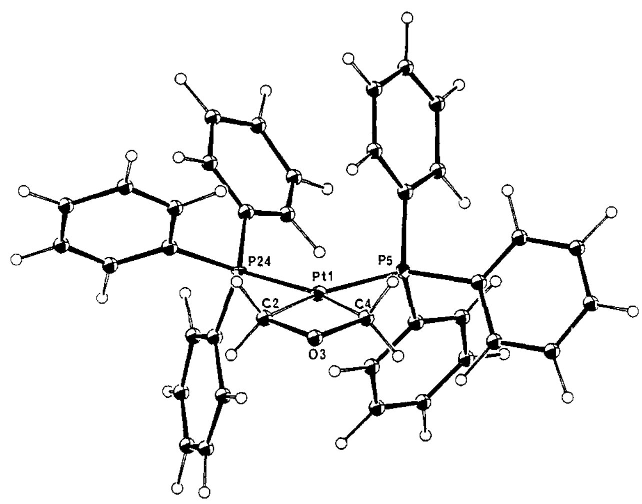

Figure 1. ORTEP drawing of complex **6b**. Selected bond distances (Å): Pt(1)-C(2), 2.061 (22); Pt(1)-C(4), 2.037 (20); O(3)-C(2), 1.434 (26); O(3)-C(4), 1.467 (24); Pt(1)-P(5), 2.302 (5); Pt(1)-P(24), 2.315 (5). Selected bond angles (deg): C(2)-Pt(1)-C(4), 65.1 (8); Pt(1)-C(2)-O(3), 97.9 (13); Pt(1)-C(4)-O(3), 97.9 (12); C(2)-O(3)-C(4), 99.0 (14); P(5)-Pt(1)-P(24), 102.85 (18); P(5)-Pt(1)-C(4), 94.6 (6); P(24)-Pt(1)-C(2), 97.5 (6). Final residuals: $R(F) = 0.087$ and $R_w(F) = 0.088$.

lacyclobutane complexes has been accomplished through the controlled manipulation of organometallic precursors possessing multiple reactive sites. The reactivity of these compositionally unique metallacycles toward migratory insertion and oxidative addition is currently being explored.

Acknowledgment. We thank Dr. John Huffman for the X-ray crystal structure determination. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Supplementary Material Available: Spectroscopic and analytical data for complexes **6a**, **6c**, and **6d**, details of the X-ray data collection and structure solution (**6b**), atomic positional and thermal parameters, and complete bond distance and angle data (17 pages); a listing of F_o vs F_c (20 pages). Ordering information is given on any current masthead page.

Long-Range {Fe^{2+}(heme) → (M(porphyrin))$^+$} Electron Transfer within [M, Fe] (M = Mg, Zn) Hemoglobin Hybrids

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We report the spectroscopic observation of long-range $\mathrm{Fe}^{2+}\mathrm{P} \rightarrow (\mathrm{MP})^+$ electron transfer (eq 1) within the charge-transfer

$$(\mathrm{MP})^+ + \mathrm{Fe}^{2+}\mathrm{P} \xrightarrow{k_b} \mathrm{MP} + \mathrm{Fe}^{3+}\mathrm{P} \tag{1}$$

intermediate of the mixed-metal [β(MP), α(FeP)] (M = Mg, Zn) hemoglobin (Hb) hybrids.[1] We[2,3] and others[4-7] have shown that proteins modified to contain closed-shell metalloporphyrins can be used to study photoinitiated electron transfer from the triplet state (eq 2). In general, however, it is difficult to observe the

$$^3(\mathrm{MP}) + \mathrm{Fe}^{3+}\mathrm{P} \xrightarrow{k_t} (\mathrm{MP})^+ + \mathrm{Fe}^{2+}\mathrm{P} \tag{2}$$

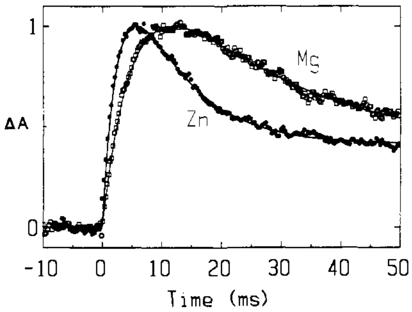
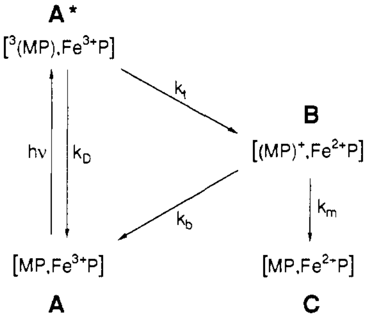


Figure 1. Normalized kinetic progress curves at 5 °C for mixed-metal Hb hybrids: [β(Mg), α(Fe)] (□, λ = 432 nm); [β(Zn), α(Fe)] (•, λ = 435 nm). Solid lines are nonlinear least-squares fits to the equations in ref 20 and 21. For [Mg, Fe], $k_b = 155\ (15)\ \mathrm{s}^{-1}$, $k_p = 47\ (5)\ \mathrm{s}^{-1}$, and $k_m = 20\ (5)\ \mathrm{s}^{-1}$; for [Zn, Fe], $k_b = 350\ (35)\ \mathrm{s}^{-1}$, $k_p = 112\ (10)\ \mathrm{s}^{-1}$, and $k_m = 40\ (8)\ \mathrm{s}^{-1}$. Buffer: 0.01 M $\mathrm{KP_i}$, pH 7.0.

Scheme I



charge-separated state and the charge-return reaction, eq 1, the major success to date being with [cytochrome *c*, cytochrome *c* peroxidase] complexes.[3] This report shows that [Zn, Fe] and [Mg, Fe] Hb hybrids are excellent systems for studying the electron transfer reaction of eq 1 as well as that of eq 2. Furthermore, comparison of Mg and Zn hybrids provides a powerful probe of mechanistic, energetic, and electronic aspects of long-range electron transfer in protein complexes.[2-14]

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(1) All experiments here refer to the [β(MP), α(FeP)] hybrid where P = protoporphyrin IX and the symbol in brackets for the hybrid represents an [α_2, β_2] T-state tetramer of hemoglobin (Hb) in which the iron ions in the two β-chains are replaced by M = Mg or Zn; Cc, cytochrome *c*; CcP, cytochrome *c* peroxidase.

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