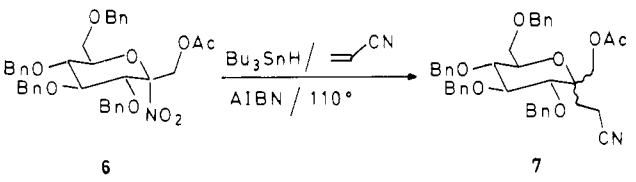
Scheme II



6 7

Bu_3SnD. In an analogous procedure the glucose derivative **6** gives the product of the C–C bond-forming reaction in 45% yield (Scheme II).[13,14] Compounds **5** and **7** are C-glycosides with a tertiary carbon atom at C-1.[15] This class of compounds can be, therefore, easily synthesized from the nitro sugars via a radical chain reaction.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinsschaft and the Fonds der Chemischen Industrie for financial support of this research and to Professor A. Vasella for helpful comments.

Registry No. 1, 85398-22-7; **2**, 96481-44-6; **3**, 96455-41-3; **4**, 96455-42-4; **5**, 96455-43-5; **6**, 89023-65-4; **7**, 96455-44-6; Bu_3SnH, 688-73-3; acrylonitrile, 107-13-1.

(14) The addition is stereoselective, but the NMR spectra do not show unambiguously whether the new C–C bond is axial or equatorial. From the reduction experiments of **6** with Bu_3SnH one expects the formation of an axial bond.[6]

(15) These are the C-glycosides of keto sugars: Tam, T. F.; Fraser-Reid, B. *J. Org. Chem.* **1980**, *45*, 1344.

Insertion and Oxidative Addition Reactions of Rhodium Porphyrin Complexes. Novel Free Radical Chain Mechanisms

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We have found that styrene and certain other olefins (including propylene and substituted styrenes) undergo facile insertion reactions into the Rh–Rh and Rh–H bonds of $Rh_2(OEP)_2$ and (OEP)RhH, respectively, in accord with eq 1 and 2 (OEP = octaethylporphyrin).[1]

$$Rh_2(OEP)_2 + PhCH{=}CH_2 \rightarrow (OEP)RhCH_2CH(Ph)Rh(OEP) \quad (1)$$

$$(OEP)RhH + PhCH{=}CH_2 \rightarrow (OEP)RhCH_2CH_2Ph \quad (2)$$

The facile occurrence of reaction 2 was somewhat unexpected since it is not apparent that (OEP)RhH possesses an accessible vacant cis-coordination site that is generally considered to be necessary for olefin migratory insertion.[4]

(1) $Rh_2(OEP)_2$ and (OEP)RhH have previously been prepared and characterized by Ogoshi[2] and by Wayland.[3]

(2) Ogoshi, H.; Setsume, J.; Yoshida, Z. *J. Am. Chem. Soc.* **1977**, *99*, 3869.

(3) (a) Wayland, B. B.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1981**, 475. (b) Wayland, B. B., Woods, B. A. *J. Chem. Soc.* **1981**, 700. (c) Wayland, B. B.; Woods, B. A.; Pierce, R. *J. Am. Chem. Soc.* **1982**, *104*, 302. (d) Wayland, B. B.; Del Rossi, K. J. *J. Organomet. Chem.* **1984**, *276*, C27.

(4) (a) An alternative mechanism of olefin insertion that also does not require an accessible cis-coordination site involves a nonchain free radical sequence, initiated by H atom transfer from the metal hydride to the olefin, i.e., $L_nM\text{-}H + PhCH{=}CH_2 \rightarrow L_nM\cdot + CH_3\dot{C}HPh \rightarrow L_nMCH(CH_3)Ph$. While such a mechanism has previously been demonstrated for certain cobalt hydrides[4b] it does not appear to contribute significantly to the reaction of (OEP)RhH with $PhCH{=}CH_2$ (eq 2) which yields exclusively the β- rather than α-phenylethyl adduct. (b) Halpern, J. *Pure Appl. Chem.* **1979**, *51*, 2171 and references therein.

In this paper we report results of our preliminary studies on the kinetics of reactions 1 and 2 which reveal that these reactions proceed through free radical chain mechanisms some features of which are without direct precedent in transition-metal chemistry.[5] Such mechanisms also would appear to have relevance to the related insertion reactions of CO and acetylenes reported by Ogoshi[2] and Wayland,[3b,c] as well as to certain oxidative addition reactions of $Rh_2(OEP)_2$.

Reaction 1 proceeds readily in C_6D_6 at ambient temperatures and attains a measurable equilibrium defined by $K_1^{eq}(25\ °C) = 8.5 \times 10^4\ M^{-1}$, $\Delta H_1^0 = -11.2 \pm 2.5$ kcal/mol, and $\Delta S_1^0 = -15 \pm 8$ cal/(mol K).[7] Kinetic measurements[7] at 30°C yielded the rate law eq 3, which is interpreted in terms of the free radical chain mechanism of eq 4–6.

$$-d[Rh_2(OEP)_2]/dt = k_3^{obsd}[Rh_2(OEP)_2]^{3/2}[PhCH{=}CH_2] \quad (3)$$

$$\text{initiation/termination:}\quad Rh_2(OEP)_2 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} 2(OEP)Rh\cdot \quad (4)$$

$$\text{propagation:}\quad (OEP)Rh\cdot + PhCH{=}CH_2 \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} (OEP)RhCH_2\dot{C}HPh \quad (5)$$

$$(OEP)RhCH_2\dot{C}HPh + Rh_2(OEP)_2 \xrightarrow{k_6} (OEP)RhCH_2CH(Ph)Rh(OEP) + (OEP)Rh\cdot \quad (6)$$

Under the conditions where reactions 4 and 5 effectively attain equilibrium and reaction 6 is rate limiting, the rate law for this mechanism reduces to eq 3, with $k_3^{obsd} = (k_4/k_{-4})^{1/2}(k_5/k_{-5})k_6 = (1.35 \pm 0.1) \times 10^2\ M^{-3/2}\ s^{-1}$ at 30 °C.

Further evidence for this mechanism and, particularly, for the intermediacy of the $(OEP)RhCH_2\dot{C}HPh$ radical was provided by trapping of the latter. Efficient trapping by (OEP)RhH was manifested in catalysis by $Rh_2(OEP)_2$ of reaction 2 in accord with the mechanistic scheme of eq 4, 5, and 7.[8,9]

$$\text{initiation/termination:}\quad Rh_2(OEP)_2 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} 2(OEP)Rh\cdot$$

$$\text{propagation:}\quad (OEP)Rh\cdot + PhCH{=}CH_2 \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} (OEP)RhCH_2\dot{C}HPh$$

$$(OEP)RhCH_2\dot{C}HPh + (OEP)RhH \xrightarrow{k_7} (OEP)RhCH_2CH_2Ph + (OEP)Rh\cdot \quad (7)$$

Under the conditions of our kinetic measurements on reaction 2 (42 °C; initial concentrations, 5.8×10^{-4} to 1.9×10^{-3} M (OEP)RhH, 3.8×10^{-4} to 2.4×10^{-3} M $Rh_2(OEP)_2$, 0.036–0.36 M styrene),[10] the equilibrium corresponding to eq 1 is rapidly

(5) Reference has previously been made to free radical like reactivity of Rh(OEP) and nonchain radical mechanisms have been suggested for some of its reactions.[3] At the same time, free radical chain mechanisms related to those identified in the present study have been proposed for the addition of trialkyltin hydrides to olefins.[6] However, certain features of the present mechanisms, notably the chain propagation sequences involving addition of metal free radicals to olefins and S_H2 displacement of metal radicals at metal–metal bonds (eq 5, 6) are, to our knowledge, without direct precedent in *transition-metal* chemistry.

(6) Kuivila, H. G. *Acc. Chem. Res.* **1968**, *1*, 299.

(7) The equilibrium measurements were made by ^1H NMR. The kinetic measurements encompassed the initial concentration ranges (2.9×10^{-5} to 4.7×10^{-4} M $Rh_2(OEP)_2$ and 1.9×10^{-3} to 1.6×10^{-1} M styrene); the disappearance of $Rh_2(OEP)_2$ was monitored spectrophotometrically at 600 nm and the products were identified by NMR. [(OEP)$RhCH_2CH$(Ph)Rh(OEP)]: ^1H NMR (C_6D_6, 12 °C, 500 MHz) δ 9.183 (s, 4 H, meso H), 9.223 (s, 4 H, meso H), 3.94, 3.76 (overlapping m, 32 H, CH_2CH_3), 1.779 (overlapping t, 48 H, CH_2CH_3), −8.870, −9.855, −11.269 (m, 1 H, m, 1 H, m, 1 H, $CHH'CH$Ph), 0.5556 (d, 1 H, J_{HH} = 7.5 Hz, ortho H); 0.788 (d, 1 H, J_{HH} = 7.5 H, ortho′ H), 4.948 (dd, 1 H, meta H); 5.486 (dd, 1 H, meta′ H), 6.232 (dd, 1 H, para H).

(8) A reaction paralleling eq 5 has been proposed by Ogoshi[2] as a step in a *nonchain* radical mechanism for the reaction of $Rh_2(OEP)_2$ with $CH_2{=}CHCH_2R$ (R = Ph, CN, n-C_3H_7) to yield $(OEP)RhCH_2CH{=}CHR$, i.e., $(OEP)Rh\cdot + CH_2{=}CHCH_2R \rightarrow (OEP)RhCH_2\dot{C}HCH_2R \xrightarrow{-H\cdot\,(?)} RhCH_2CH{=}CHR$.

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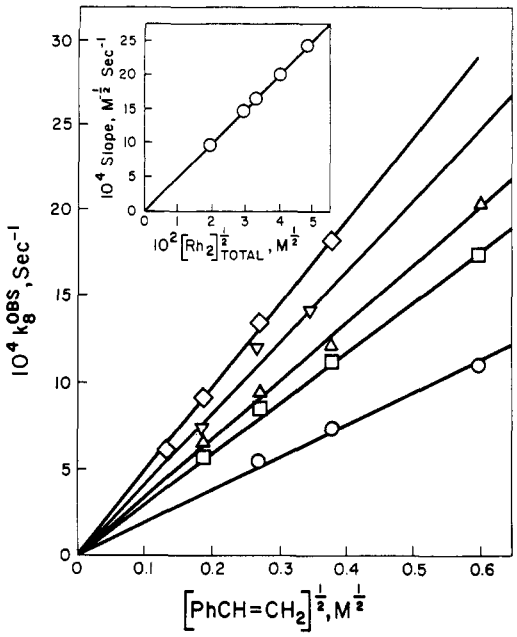

Figure 1. $Rh_2(OEP)_2$-catalyzed reaction of (OEP)RhH with $PhCH{=}CH_2$ in C_6D_6 at 42 °C (eq 2). $10^4[Rh_2]_{total}$: (○) 3.74; (□) 8.85; (△) 11.4; (▽) 16.4; (◇) 24.0 M. (Inset: slope vs. $[Rh_2]_{total}^{1/2}$).

established and lies far to the right, i.e., $[(OEP)RhCH_2CH(Ph)Rh(OEP)] = [Rh_2]_{total} - [Rh_2(OEP)_2] \approx [Rh_2]_{total}$. Thus, $[Rh_2(OEP)_2] = [(OEP)RhCH_2CH(Ph)Rh(OEP)]/K_1^{eq}[PhCH{=}CH_2] \approx [Rh_2]_{total}/K_1^{eq}[PhCH{=}CH_2]$. In the limit, when reaction 5 also effectively attains equilibrium and reaction 7 becomes rate limiting, the rate law for reaction 2 reduces to

$$-\text{d ln } [(OEP)RhH]/dt = k_8^{obsd} = k_7(k_5/k_{-5})(k_4/k_{-4})^{1/2}(K_1^{eq})^{-1/2}[Rh_2]_{total}^{1/2}[PhCH{=}CH_2]^{1/2} \quad (8)$$

The linear plots of k_8^{obsd} vs. $[PhCH{=}CH_2]^{1/2}$ and $[Rh_2]_{total}^{1/2}$ in Figure 1 are in accord with eq 8 and provide convincing evidence for the above mechanism. These plots yield $k_7(k_5/k_{-5})(k_4/k_{-4})^{1/2}(K_1^{eq})^{-1/2} = 9.8 \times 10^{-2}$ s^{-1}.[11]

A free radical chain mechanism, analogous to that of eq 4, 5, and 7, also accommodates the previously reported insertion of CO into the Rh–H bond of (OEP)RhH (eq 9).

$$(OEP)RhH + CO \rightleftarrows (OEP)RhC(=O)H \quad (9)$$

In accord with this, reaction 9 was found to be catalyzed by $Rh_2(OEP)_2$. Kinetic measurements at 36 °C (encompassing the initial concentration ranges, 3.1×10^{-5} to 5.5×10^{-4} M $Rh_2(OEP)_2$ and 1.7×10^{-3} to 2.2×10^{-2} M (0.2–2.5 atm) CO) yielded (after correction for the back reaction, since reaction 9 attains a measurable equilibrium corresponding to $K_9^{eq} = 5.5 \times 10^2$ M^{-1}) the rate law eq. 10, with $k_{10}^{obsd} = (k_4/k_{-4})^{1/2}(k_{11}/k_{-11})k_{12} = 0.28$ M$^{-3/2}$ s^{-1}.[12]

$$-\text{d}[(OEP)RhH]/dt = k_{10}^{obsd}[Rh_2(OEP)_2]^{1/2}[(OEP)RhH][CO] \quad (10)$$

initiation/termination: $Rh_2(OEP)_2 \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} 2(OEP)Rh\cdot$

propagation: $(OEP)Rh\cdot + CO \underset{k_{-11}}{\overset{k_{11}}{\rightleftarrows}} (OEP)Rh\dot{C}O$ (11)

$$(OEP)Rh\dot{C}O + (OEP)RhH \xrightarrow{k_{12}} (OEP)RhCHO + (OEP)Rh\cdot \quad (12)$$

This mechanism parallels the microscopic reverse of mechanisms previously postulated for the decarbonylation of metal formyl complexes.[13] Reaction 12 also finds a parallel in the mechanism recently proposed for the generation of metal formyl complexes by H-atom transfer to electrochemically generated metal carbonyl radicals.[14]

The oxidative addition of benzyl bromide to $Rh_2(OEP)_2$ (eq 13)[2] also can be accommodated by a free radical chain mechanism, depicted by eq 4, 14, and 15, which yields the rate law eq 16, in

$$Rh_2(OEP)_2 + C_6H_5CH_2Br \rightarrow (OEP)RhCH_2C_6H_5 + (OEP)RhBr \quad (13)$$

initiation/termination: $Rh_2(OEP)_2 \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} 2(OEP)Rh\cdot$

propagation: $(OEP)Rh\cdot + C_6H_5CH_2Br \xrightarrow{k_{14}} (OEP)RhBr + C_6H_5CH_2\cdot$ (14)

$$C_6H_5CH_2\cdot + Rh_2(OEP)_2 \xrightarrow{fast} (OEP)RhCH_2C_6H_5 + (OEP)Rh\cdot \quad (15)$$

$$-\text{d}[Rh_2(OEP)_2]/dt = (k_4/k_{-4})^{1/2}k_{14}[Rh_2(OEP)_2]^{1/2}[C_6H_5CH_2Br] \quad (16)$$

accord with the experimentally observed rate law $-\text{d}[Rh_2(OEP)_2]/dt = k_{16}^{obsd}[Rh_2(OEP)_2]^{1/2}[C_6H_5CH_2Br]$ where $k_{16}^{obsd} = 8.5 \times 10^{-4}$ M$^{-1/2}$ s^{-1} in toluene at 26 °C.[15]

We have found that $Rh_2(OEP)_2$ also undergoes oxidative addition reactions with $HSnBu_3$ and with 9,10-dihydroanthracene (AH_2) (eq 17 and 18). While analogous free radical chain

$$Rh_2(OEP)_2 + HSnBu_3 \rightarrow (OEP)RhH + (OEP)RhSnBu_3 \quad (17)$$

$$Rh_2(OEP)_2 + AH_2 \rightarrow (OEP)RhH + (OEP)Rh\text{–}AH \quad (18)$$

mechanisms seem likely for these reactions their kinetics remain to be elucidated.[16]

Two factors may be identified as contributing to the distinctive free radical chain processes that we have identified in these systems, namely, (a) unusually strong (OEP)Rh–C bonds which contribute to the driving force for the chain-propagating steps (5) and (11)[3] and (b) the absence of axial ligands in $Rh_2(OEP)_2$, which renders feasible the homolytic displacement steps (6) and (15).

We are continuing and extending our studies on these and related systems with a view to elaborating further details of their mechanisms and to exploring the scope of such free radical chain processes in other contexts of organometallic chemistry and homogeneous catalysis.

Acknowledgment. We thank the National Science Foundation for a grant in support of this research, the Monsanto Co. for a

(9) In further support of this mechanism, it was found that the corresponding reaction of (OEP)RhH with *cis*-stilbene was accompanied by cis–trans isomerization of the unreacted stilbene, presumably by a reversible addition–elimination step analogous to eq 5.

(10) The reaction was monitored and the products were identified by ^{1}H NMR. [(OEP)RhCH$_2$CH$_2$Ph, C_6D_6, 30 °C, 500 MHz] δ 10.188 (s, 4 H, meso H), 4.02 (m, 8 H, C*H*H′CH$_3$), 3.95 (m, 8 H, CHH′CH$_3$), 1.917 (t, 24 H, J_{HH} = 7.6 Hz, CH$_2$C*H*$_3$), −4.973 (2 H, dt, J_{RhH} = 3, J_{HH} = 8.4 Hz, RhC*H*$_2$), −3.428 (2 H, t, RhCH$_2$C*H*$_2$), 4.500 (d, 2 H, J_{HH} = 7.5 Hz, ortho H), 5.888 (dd, 2 H, meta H), 6.110 (1 H, t, J_{HH} = 7.5 Hz, para H).

(11) Reaction 2 does proceed *slowly* in the absence of added $Rh_2(OEP)_2$, apparently due to catalysis by small amounts of $Rh_2(OEP)_2$ generated in situ by the slow decomposition of (OEP)RhH, i.e., $2(OEP)RhH \rightleftarrows Rh_2(OEP)_2 + H_2$.[2,3] The latter reaction apparently is promoted by styrene since it does not proceed at a measurable rate under our reaction conditions in the absence of styrene. We have found that the dehydrogenation of (OEP)RhH also is promoted by certain other olefins such as 1,1-diphenylethylene.

(12) $Rh_2(OEP)_2$ also undergoes a much slower reaction with CO (monitored by NMR) to form a 1:1 adduct, tentatively assigned the symmetrical insertion structure (OEP)RhC(=O)Rh(OEP).

(13) (a) Narayanan, B. A.; Amatore, C.; Casey, C. P.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 6351. (b) Sumner, C. E.; Nelson, G. O. *J. Am. Chem. Soc.* **1984**, *106*, 432.

(14) Narayanan, B. A.; Kochi, J. K. *J. Organomet. Chem.* **1984**, *272*, C49.

(15) The reaction was followed by monitoring the disappearance of $Rh_2(OEP)_2$ spectrophotometrically at 543 nm and the products were identified by ^{1}H NMR.

(16) The occurrence of reactions 17 and 18 precludes the use of $HSnBu_3$, 9,10-dihydroanthracene, and related free radical traps to intercept the intermediate (OEP)RhCH$_2$C*H*Ph radical in reaction 2 (eq 4, 5, 7).

Postdoctoral Fellowship (to R.S.P.), and Johnson Matthey, Inc., for a generous loan of rhodium. The NMR facilities were supported in part through the University of Chicago Cancer Center Grant NIH-CA-14599.

Registry No. 1, 63439-10-1; **2**, 63372-77-0; **3**, 96502-52-2; **4**, 96502-53-3; (OEP)RhCH$_2$C$_6$H$_5$, 57650-51-8; (OEP)RhBr, 63372-78-1; PhCH=CH$_2$, 100-42-5; C$_6$H$_5$CH$_2$Br, 100-39-0.

On the Reported High Barrier to Nitrogen Inversion in Azetidine (Trimethylenimine)

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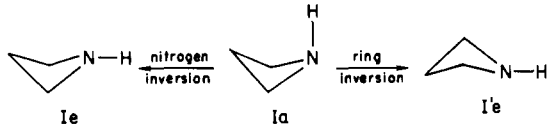
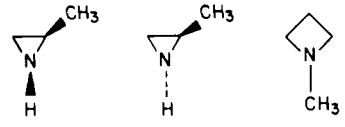
A paper by Friedman, Chauvel, and True (FCT) states that two separate (chemically shifted) NH resonances with unequal areas (ca. 3:1) are observed in the ^{1}H NMR spectrum of azetidine (I) at room temperature and that the free energy barrier to nitrogen inversion is about 17.9 kcal/mol.[1] This would require that *both* ring inversion and nitrogen inversion in nonplanar I be slow on the dynamic NMR time scale under these conditions, since *either* of the above processes is sufficient to cause exchange of the NH proton between the quasi-axial and quasi-equatorial sites, as can be seen from the structures Ia, Ie, and I'e.[2] Thus, both



Ie Ia I'e

free energy barriers must be more than 17 kcal/mol. However, it is known from other investigations quoted by FCT that the barrier to ring inversion in azetidine is at best only a few kilocalories per mole. Furthermore, the methylene chemical shifts of I in CCl_4 are known[3] and are quite different from those reported by FCT.

A consideration of the data reported by FCT shows that the compound that they studied must be 2-methylaziridine (II). The



IIc IIt III

250-MHz ^{1}H NMR spectrum of this compound in CCl_4 has been measured and analyzed previously.[4] The chemical shifts and integration are consistent with those given by FCT, except for the NH proton signals whose chemical shifts are about 1–1.5 ppm to lower fields in CCl_4 than are those in the gas phase. These chemical shifts are expected to be influenced by hydrogen bonding and thus to depend on both concentration and solvent. The conformational ratio (IIt:IIc) is 2:1 in the liquid phase and the small difference from the gas-phase value (3:1) is again not unexpected.

The free energy barrier to nitrogen inversion found by FCT is very close to that in aziridine itself ($\Delta G^* = 17.2 \pm 0.1$ kcal/mol in either the gas[5] or the liquid phase[6]) and much higher than that in 1-methylazetidine (III) ($\Delta G^* = 10.0$ kcal/mol in the liquid phase[7]). At present, the barrier to nitrogen inversion in I remains unknown,[8] but its value should be similar to that in its *N*-methyl derivative, III.[9]

(1) Friedman, B. R.; Chauvel, J. P., Jr.; True, N. S. *J. Am. Chem. Soc.* **1984**, *106*, 7638–7639.

(2) FCT correctly point out that both fast ring and nitrogen inversions are required for the β-CH$_2$ protons in Ia and Ie to give a single averaged chemical shift. However, the four lines that they ascribe to the β-protons at room temperature collapse to two lines and not to one line at high temperatures. Thus, their conclusion that there is "complete exchange" of these protons is not borne out by their published spectra. The NH proton has only two possible sites which are shown in Ia and Ie, and thus its behavior is different from that of the β-protons.

(3) Higgins, R. H.; Cromwell, N. H.; Paudler, W. W. *J. Heterocycl. Chem.* **1971**, *8*, 961–966. The chemical shifts of the α- and β-protons in I in CCl_4 solution, with tetramethylsilane as the internal reference, are δ 3.53 and 2.33, respectively, whereas the chemical shifts reported by FCT for these protons are between δ 1 and 2. These latter high-field shifts point to unusual shielding, such as occurs in a three- but not in a four-membered ring.

(4) Lopez, A.; Gauthier, M. M.; Martino, R.; Lattes, A. *Org. Magn. Reson.* **1979**, *12*, 418–428. In the major conformer (IIt), the assignments are as follows: CH$_3$, δ 1.04, J = 5.5 Hz; CH$_2$, δ 0.96 and 1.66; CH, δ 1.89; NH, δ 0.61. In the minor conformer (IIc), the CH$_3$ and NH protons are at δ 1.23 and 0.08, respectively, and the other protons lie between δ 1.2 and 1.4.

(5) Carter, R. E.; Drakenberg, T.; Bergman, N.-Å. *J. Am. Chem. Soc.* **1975**, *97*, 6990–6996.

(6) Nakanishi, H.; Yamamoto, O. *Tetrahedron* **1974**, *30*, 2115–2121. Skaarup, S. *Acta Chem. Scand.* **1972**, *26*, 4190–4192.

(7) Lambert, J. B.; Oliver, W. L., Jr.; Packard, B. S. *J. Am. Chem. Soc.* **1971**, *93*, 933–937.

(8) The barrier to nitrogen inversion in piperidine can be observed in solution, but special care must be taken to prevent NH exchange: Anet, F. A. L.; Yavari, I. *J. Am. Chem. Soc.* **1977**, *99*, 2794–2796.

(9) Professor, N. S. True (personal communication) has informed me that the compound studied by them was indeed 2-methylaziridine (see Additions and Corrections; True, N. S. *J. Am. Chem. Soc.*, in press.)

A Diacridine Derivative That Binds by Bisintercalation at Two Contiguous Sites on DNA

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When two DNA-intercalating chromophores are joined by a linker chain, the nature of this chain becomes a major constraint upon bisintercalative binding.[1-3] Results for derivatives of 9-aminoacridine indicate that compounds with polymethylene or amide-containing linker chains as short as 8.8 Å undergo bisintercalative binding.[1-6] Such compounds (e.g., **1** and **2**) must intercalate at contiguous sites, with one chromophore on either side of the same base pair, in violation of the "excluded-site" principle proposed as a thermodynamic limitation in some theoretical models of the binding of monointercalators and observed in practice for such compounds.[5,7]

However, monointercalative binding of a related bis(acridine) hydrazine **3** was indicated in a recent study.[2] Also, NMR studies show that **1** and **2** bind to the oligodeoxyribonucleotide d(A-T)$_5$-d(A-T)$_5$ by monointercalation,[6] suggesting that bisintercalation of chromophores joined by flexible chains is condition dependent.

Molecules where the chromophores are held by a rigid framework in a suitable orientation can show an increased propensity for intercalative binding. The quinoxaline chromophores of triostin A are known to both intercalate DNA[8] (although not

(1) Wakelin, L. P. G.; Romanos, N.; Chen, T.-K.; Glaubiger, D.; Canellakis, E. S.; Waring, M. J. *Biochemistry* **1978**, *17*, 5057.

(2) King, H. D.; Wilson, W. D.; Gabbay, E. J. *Biochemistry* **1982**, *21*, 4982.

(3) Atwell, G. J; Leupin, W.; Twigden, S. J.; Denny, W. A. *J. Am. Chem. Soc.* **1983**, *105*, 2913.

(4) Wright, R. G. McR.; Wakelin, L. P. G.; Fieldes, A.; Acheson, R. M.; Waring, M. J. *Biochemistry* **1980**, *19*, 5825.

(5) Le Pecq, J.-B.; Le Bret, M.; Barbet, J.; Roques, P. B. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 2915.

(6) Assa-Munt, N.; Denny, W. A.; Leupin, W.; Kearns, D. R. *Biochemistry*, **1985**, *24*, 1441–1449, 1449–1460.

(7) Von Hippel, P. H.; McGhee, J. D. *Annu. Rev. Biochem.* **1972**, *41*, 231.

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