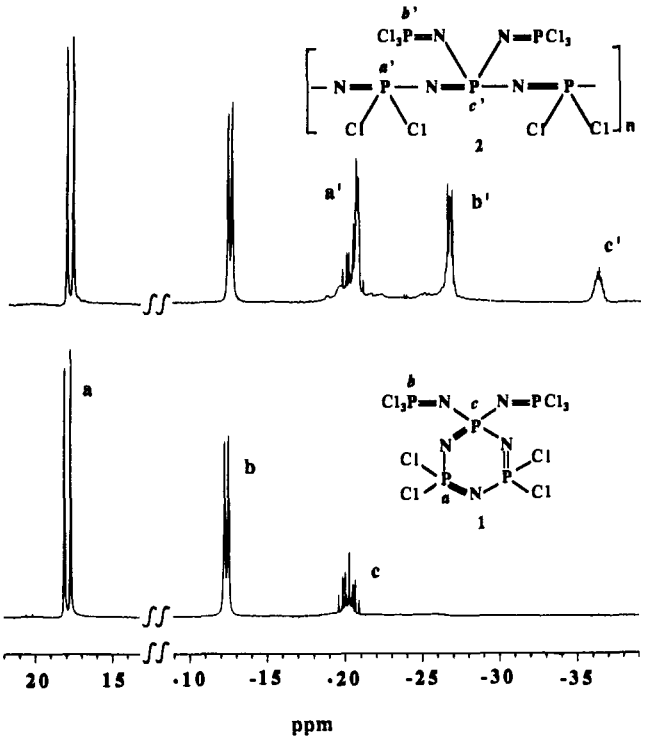

Figure 1. ^{31}P NMR spectra of compounds **1** and **2**.

spectroscopy and elemental analysis.[6] Films of **4** were significantly less flexible than films of classical poly[bis(phenoxy)phosphazene], $[NP(OC_6H_5)_2]_n$, which contains no branching. The small-molecule analogues **5**[5] and **6**[7] were also prepared as model compounds.

Treatment of model compound **1** with excess sodium trifluoroethoxide in dioxane at 102 °C resulted in complete replacement of the chlorine atoms by trifluoroethoxy side groups to form *gem*-$N_3P_3(OCH_2CF_3)_4[NP(OCH_2CF_3)_3]_2$ (**7**).[8] The corresponding high polymeric reaction of **2** with sodium trifluoroethoxide yielded the fully substituted polymer **8**.[9] Polymer **8** was isolated as a white, film-forming, fibrous material.

Gel permeation chromatograph (GPC) analysis of the hydrolytically stable polymers **3** ($M_n = 6 \times 10^4$, $M_w = 9 \times 10^5$), **4** ($M_n = 1 \times 10^5$, $M_w = 7 \times 10^5$), and **8** ($M_n = 4 \times 10^4$, $M_w = 1 \times 10^5$) indicated that high molecular weight materials were formed by the polymerization of **1** at a relatively low temperature, and that the polymers can be prepared without extensive chain cleavage. The glass transition temperatures (T_g) of these polymers are as follows: **3**, $T_g = -6$ °C; **4**, $T_g = 28$ °C; and **8**, $T_g = -69$ °C.

We are currently exploring the polymerization of **1** and $N_3P_3Cl_5(N{=}PCl_3)$ in detail and their copolymerization with unbranched cyclotriphosphazenes. The reaction of **2** with other nucleophiles to yield poly(organophosphazophosphazenes) is also under investigation.

Acknowledgment. This work was supported by the U.S. Army Research Office.

(6) Characterization data for **4**: ^{31}P NMR (A_2B_2C spin system, $\delta_A = -7$ ppm, $\delta_B = -19$ ppm, $\delta_C = -36$ ppm); ^{13}C NMR (122 (d), 127 (d), 131 (d), 152 (d) ppm); ^1H NMR (m, δ 6.9-7.5 ppm). Elemental anal. Calcd: C, 62.34; N, 6.06; H, 4.33; Cl, 0.00. Found: C, 59.97; N, 7.08; H, 4.14; Cl, 0.75.

(7) Characterization data for **6**: ^{31}P NMR (A_2BC_2 spin system, $\delta_A = 11$ ppm, $\delta_B = -4$ ppm, $\delta_C = -25$ ppm); ^{13}C and ^1H NMR same as for **4**; mass spectrum (calcd 1155, found 1155). Elemental anal. Calcd: C, 62.34; H, 4.33; N, 6.06. Found: C, 62.35; H, 4.31; N, 5.92.

(8) Characterization data for **7**: ^{31}P NMR (A_2BC_2 spin system, $\delta_A = 18$ ppm, $\delta_B = -5$ ppm, $\delta_C = -8$ ppm); ^1H NMR (multiplets, $\delta = 4.5$ ppm, $\delta = 4.8$ ppm); ^{13}C NMR (quartets, $\delta = 64$, 124 ppm); mass spectrum (calcd 1215, found 1215). Elemental anal. Calcd: C, 19.77; H, 1.66; N, 5.76. Found: C, 19.94; H, 1.66; N, 5.89.

(9) Characterization data for **8**: ^{31}P NMR (br resonances, $\delta = -3$ ppm (br) to -9 ppm (multiplets)); ^{13}C NMR (quartets, $\delta = 64$, 124 ppm); ^1H NMR (unresolved multiplets $\delta = 4.5$ ppm, $\delta = 4.8$ ppm). Elemental anal. Calcd: C, 19.77; H, 1.66; N, 5.76; Cl, 0.00. Found: C, 19.49; H, 1.59; N, 5.96; Cl, 0.094.

Template-Directed Diastereoselectivity. Cyclizations to Contrathermodynamic Products

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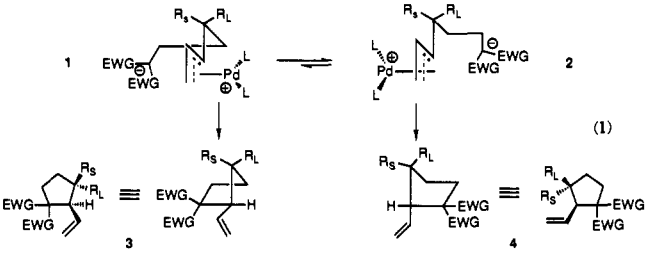
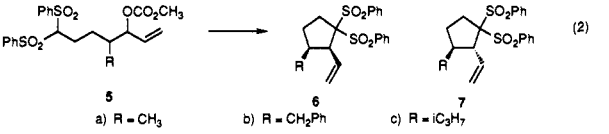
A major concern of synthetic chemistry during the past decade focused on diastereoselectivity. In cyclization reactions wherein stereochemistry is developed at one of the termini, intrinsic factors such as nonbonded interactions generally favoring 1,2-trans isomers normally dominate.[1] Developing approaches to force such groups to favor a thermodynamically less favorable cis orientation would be an important adjunct to existing methodology. Introduction of extrinsic factors that may dominate over such intrinsic ones provides a strategy to achieve this goal. Transition metal template directed reactions may offer one approach, as outlined in eq 1, provided the rates of the various steps depicted are appropriate to allow differential steric interaction between R_S and R_L and the metal template to dominate.[2] Further, the problem is complicated



by the question of regioselectivity in metal-catalyzed reactions which could lead to formation of the terminal substituted product **6**.[3-7]

Cyclization of the methyl substrate **5a** was explored in depth to examine the effect of catalyst and solvent (see Table I).



Gratifyingly, the cyclization generated the cyclopentyl products **6a**[8] and **7a**[8] in excellent yields with most catalysts. Somewhat surprisingly, electron-rich ligands that frequently prove ineffectual in promoting allyl alkylation, like trialkylphosphines and especially TTMPP, are very effective in promoting cyclization.[9,10]

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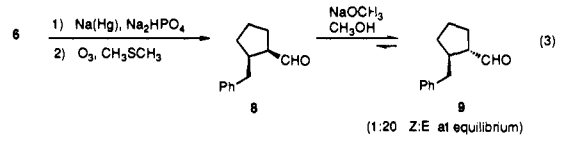
Table I. Dependence of Cyclization of **5a** on Experimental Parameters with $(dba)_3Pd_2{\cdot}CHCl_3$ as Catalyst

entry	ligand (mol %)	solvent	time, h	yield, %	Z	E
1[c]	$(iC_3H_7O)_3P$ (20)	THF	2.5	87	1	1.4
2[b,c]	$(iC_3H_7O)_3P$ (20)	THF	3.0	85	1	1.8
3	$(iC_3H_7O)_3P$ (15)	DMSO	5.0	91	6.9	1.0
4	$(iC_3H_7O)_3P$ (30)	DMSO	4.0	93	5.9	1.0
5[c]	Ph_3P (20)	THF	1.5	83	1.0	1.0
6	Ph_3P (30)	DMSO	2.0	89	5.5	1.0
7	$(o\text{-}CH_3C_6H_5)_3P$ (20)	THF	4.0	50	1.0	1.7
8	TTMPP[e] (30)	$PhCH_3$	0.3	89	1.0	1.1
9	TTMPP[e] (30)	THF	0.08	98	1.3	1.0
10	TTMPP[e] (30)	CH_3CN	0.4	91	1.2	1.0
11	TTMPP[e] (30)	DMSO	0.08	93	3.7	1.0
12	TTMPP[e] (10)	DMSO	0.3	87	4.5	1.0
13[d]	TTMPP[e] (5)	DMSO	1.0	73	4.5	1.0
14	$(C_4H_9)_3P$ (20)	THF	1.0	98	1.7	1.0
15	$(C_4H_9)_3P$ (20)	DMSO	1.0	97	2.7	1.0
16	$(iC_3H_7)_3P$ (30)	THF[f]	17.0	0		
17	$(iC_3H_7)_3P$ (30)	DMSO	1.0	93	3.0	1.0
18	none	DMSO[g]	12.0	44	2.3	1.0

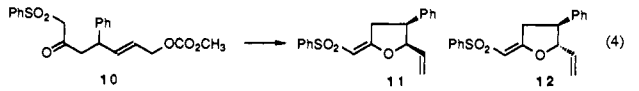
[a] Reactions were performed at approximately 0.1 M in the indicated solvent by using 1.25 mol % of $(dba)_3Pd_2{\cdot}CHCl_3$ and the indicated ligand at room temperature unless stated otherwise. [b] For this run, $Pd(OAc)_2$ was employed as the palladium source. [c] For this run, 2.5 mol % of $(dba)_3Pd_2{\cdot}CHCl_3$ was employed. [d] For this run, 0.125 mol % of $(dba)_3Pd_2{\cdot}CHCl_3$ was employed. [e] TTMPP = tris(2,4,6-trimethoxyphenyl)phosphine. [f] Reaction temperature = 70 °C. [g] Reaction temperature = 100 °C.

Most importantly, ring geometry proved sensitive to the reaction parameters. For the phosphite and triphenylphosphine ligands, solvent played a domineering role. The highest selectivities for the *Z* isomer were obtained with triisopropyl phosphite and TTMPP, two ligands that are diametrically opposite both in terms of electronic factors and steric bulk (cone angles of 130° and 184°, respectively).[11] The stereochemistry of **6a** and **7a** was established by an observed NOE between the methyl group and vinyl proton in **6** but between the methyl group and allylic methine proton in **7**.

The benzyl substrate **5b**[8] allowed dominance of either the *E* or *Z* isomers depending upon solvent with TTMPP as ligand. In dioxane, a 71% yield of a 1:3.1 *Z*:*E* ratio of **6b**:**7b**[8] was observed, whereas, in DMSO, an 82% yield of a 6.7:1 ratio of *Z*:*E* is observed with 10 mol % ligand. Triisopropyl phosphite was somewhat less *Z* selective (4.5:1 *Z*:*E*, 84% yield). Chemical equilibration of the aldehydes **8** and **9**[8] obtained as illustrated in eq 3 establishes the major cyclization product as *Z*.



Increasing the effective steric bulk of the substituent to isopropyl as in substrate **5c** enhances the *Z* selectivity of the cyclopentanes **6c** and **7c**[8] to 7.2:1 (94% yield) when TTMPP is used as ligand in DMSO at room temperature. Changing the nucleophile to the β-keto sulfone as in **10** generated the cyclization products derived from preferential O-alkylation, **11** and **12** (eq 4).[8,12] Under all



conditions studied, the *Z* isomer **11** dominated, the highest selectivity being observed with triphenylphosphine (20 mol %) in THF at 70 °C (*Z*:*E*, 6.2:1, 76% yield). Assignment of the *Z* stereochemistry derives from extensive NMR studies: NOE, solvent-induced shifts, and relative chemical shifts.[4]

Contrary to the general expectation to favor the thermodynamically favored *E* isomers in cyclizations, palladium-catalyzed cyclizations of the type generalized in eq 1 favor the *Z* product both for carbon and oxygen nucleophiles, regardless of the regioisomer or stereochemistry of the substrate. These results are in accord with the model presented in eq 1, wherein the steric demands associated with docking the substrate on the "template" dominate in spite of the generation of the product having the larger nonbonded interactions.

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health, General Medical Sciences, for their generous support of our programs. We are grateful for mass spectra kindly provided by the Mass Spectrometry Facility, University of California—San Francisco, supported by the NIH Division of Research Resources.

Supplementary Material Available: Characterization data for **5a–c**, **6a–c**, **7a–c**, and **10–12** (4 pages). Ordering information is given on any current masthead page.

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Efficient, Complementary Binding of Nucleic Acid Bases to Diaminotriazine-Functionalized Monolayers on Water

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Intensive effort has been made recently to develop organic host molecules that specifically bind substrates by complementary hydrogen bonding.[1-5] The hydrogen bonding involved in these host–guest interactions is most effective in aprotic organic solvents, and it is usually supressed in aqueous environments.[6] Realization

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