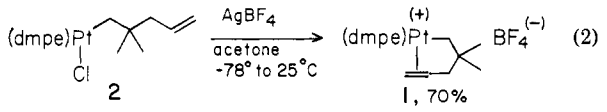
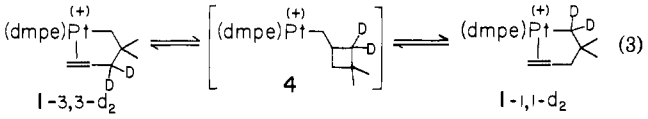


2 1, 70% (2)

of **1** with KI in acetone generates PtI(dmpe)($CH_2C(Me)_2CH_2CH{=}CH_2$) (**3**), and with KCN in ethanol Pt(CN)(dmpe)($CH_2C(Me)_2CH_2CH{=}CH_2$) is formed. Complex **1** has the unusual property (compared to [Pt(diars)($CH_2{=}CH_2$)Et]$^+$, for example[1g]) that it is rather stable at higher temperature; heating of **1** at 125 °C in CD_3NO_2 for 14 h results in only ca. 15% decomposition with no deuterium incorporation from solvent.[9]

Of most interest to us was the potential for observation of reversible formal β-alkyl insertion-elimination in **1**. Formation of a (cyclopentyl)platinum intermediate by direct insertion in **1** is not geometrically possible, but (cyclobutylcarbinyl)platinum **4** formation is.[10,11] One can test for the presence of this equilibrium by the labeling experiment shown in eq 3. Within 8 h



1-3,3-d_2 4 1-1,1-d_2 (3)

of heating **1**-*3,3*-d_2 at 125 °C in CD_3NO_2 a 50:50 mixture of **1**-*3,3*-d_2 and **1**-*1,1*-d_2 had formed. In a preliminary kinetics study, the rearrangement at 125 °C for about one half-life exhibited kinetics which were consistent with a reversible first-order reaction, with $k_{forward} = k_{reverse} = 3.5 \times 10^{-5}$ s^{-1}. The system behaves very cleanly with regard to the position of the deuterium label; both ^{1}H and ^{2}H NMR of both **1** and the iodide **3** derived from **1** indicate that deuterium resides only in the 1- and 3-positions—none has been incorporated into the olefinic or methyl groups or into dmpe.

The overall reaction of eq 1 is anticipated to possess a heat of reaction of ca. −20 kcal/mol (C=C π-bond energy − C—C σ-bond energy) when L is alkene, but the first step will be less favorable by the amount of the M(alkene) bond strength. A partial explanation for the lack of examples of M(alkene)R insertions may lie in the relative strengths of M(alkene) bonding. If the bond is too strong, the first step of eq 1 is rendered unfavorable. In the present case, the M(alkene) bond in **1** is kinetically stabilized by chelation, and β-hydride elimination is not possible because of the two β-methyl groups. These attributes of the complex apparently inhibit other paths of reaction so that heating the sample leads to observable insertion–elimination. The ΔH for the insertion step in eq 3 would be ca. −20 + 26(ring strain) + ΔH(Pt(alkene)) kcal/mol. We are not aware of any data on Pt(alkene) bond energies; however, our observation of rapidly reversible insertion suggests that the inherent barrier to alkene insertion may be low for **1**.

This observation of the reversible formal β-alkyl insertion in a M(alkene)R complex is, to our knowledge, the best-defined extant example for a transition metal. Detailed kinetic, activation parameter, conformational, and other mechanistic investigations are under way. Most important, we are in a position to thoroughly probe for substituent and electronic effects on the reaction in other metal and ancillary ligand systems. We are particularly interested in those systems that exhibit Ziegler polymerization activity in the presence of aluminum reagents.

Acknowledgment. This reaction was supported by National Science Foundation Grant CHE 8016573.

Registry No. 1, 91898-44-1; **1**-*1,1*-d_2, 91898-48-5; **1**-*3,3*-d_2, 91898-46-3; **2**, 91898-49-6; **2**-*3,3*-d_2, 91898-50-9; **3**, 91898-51-0; **3**-*1,1*-d_2, 91898-52-1; **3**-*3,3*-d_2, 91898-53-2; Pt(CN)(dmpe)($CH_2C(Me)_2CH_2CH{=}CH_2$), 91898-54-3; 4,4-dimethyl-1-pentene, 762-62-9.

(5) The preparations of close analogues of **1** have been reported[6] and are based on the HCl cleavage (Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1959**, *705–716*) of $Pt(PR_3)_2R_2$ complexes prepared as previously reported (ref 7 and Bockmann et al.: Bochmann, M.; Wilkinson, G.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1980**, 1879–1887). The synthesis of the organic ligands is based on the alkylation of the anion of the *tert*-butyl imine of isobutyraldehyde (House, H. O.; Liang, W. C.; Weeks, P. D. *J. Org. Chem.* **1974**, *39*, 3102–3107).

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(8) Complex **2**: ^{1}H NMR (CD_3NO_2, 270 MHz) δ 1.16 (s, CCH_3), 1.24 (s, CCH_3), 1.68 (dtd, $\Delta\delta$ = 38, J_{PtH} = 16, J_{PH} = 10 Hz, $P(CH_3)_2$), 1.77 (dtd, $\Delta\delta$ = 16, J_{PtH} = 18, J_{PH} = 13 Hz, $P(CH_3)_2$), 2.08 (br, PCH_2CH_2P), 2.63 (br td, J_{PtH} = 50, J_{PH} = 11 Hz, one allylic CH), 4.05 (br td, J_{PtH} = 42, J_{HH} = 16 Hz, C=CH_2, cis H), 5.39 (tdddd, J_{PtH} = 42, J_{PH} = 12, J_{PH} = 3, $J_{HH_{cis}}$ = 9, $J_{HH_{gem}}$ = 3 Hz, C=CH_2, trans H), 5.72 (m, =CH), $PtCH_2$ and the second allylic H are obscured by dmpe resonances. partial $^{13}C\{^1H\}$ NMR (acetone-d_6, 67.9 MHz) δ 84 (td, J_{PtC} = 50, J_{PC} = 12 Hz, =CH_2), 121 (td, J_{PtC} = 50, J_{PC} = 10 Hz =CH). $^2H\{^1H\}$ NMR of **2**-*3,3*-d_2 (CH_3NO_2, 41.4 MHz) δ 1.83 (br), 2.56 (br), small intensity at ca. 4.0 and 5.4 (small % of $CH_2CH{=}CD_2$ from preparative route).

(9) The reaction is carried out in a sealed NMR tube, and monitored by ^{1}H and ^{2}H NMR. There is considerable darkening and loss of clarity of the solution, but the resonances of **2** remain sharp and diminish only slightly in intensity. The only obvious side product detected by ^{1}H NMR is 4,4-dimethyl-1-pentene, formed in ca. 15% yield in 14 hrs.

(10) The reported [Atkins, M. P.; Golding, B. T.; Bury, A.; Johnson, M. D.; Sellars, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 3630–3632] reversible acid-catalyzed rearrangement of (3-buten-1-yl)[Co] to (cyclopropylcarbinyl)[Co] ([Co] = (dimethylglyoximato)$_2$(pyridine)cobalt(III)) is formally similar to the rearrangement reported herein, which may be regarded as a pent-4-enyl/cyclobutylcarbinyl rearrangement.

(11) Confidence in the intermediacy of **4** is enhanced by our extensive direct study of [(1-methylcyclobutyl)methyl]PtCl(PMe_3)$_2$ and {[(1-methylcyclobutyl)methyl]Pt(PMe_3)$_2$(acetone)}$^+$ which indicates that the barrier to ring opening is indeed low.[6] Thus, an unsaturated (cyclobutylcarbinyl)platinum species is a "kinetically competent" intermediate.

Automated Solid-Phase Synthesis, Separation, and Stereochemistry of Phosphorothioate Analogues of Oligodeoxyribonucleotides

Wojciech J. Stec,*[1] Gerald Zon,* William Egan, and Bożena Stec[1]

Division of Biochemistry and Biophysics
Office of Biologics Research and Review
Food and Drug Administration
Bethesda, Maryland 20205

Received April 10, 1984

Phosphorothioate (PS) analogues of nucleotides are useful substrates for studying phosphorolytic and phosphoryl-transfer enzymes.[2] These analogues are also employed in the stereospecific synthesis of P-chiral nucleoside phosphates in which chirality at phosphorus exists by virtue of the isotopes of oxygen.[3,4] Chemical methods for the synthesis of PS analogues of oligonucleotides have dealt primarily with dimers;[5-9] however, their elaboration to longer

(1) W.J.S.: FDA International Visiting Scientist; permanent address: Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Department of Bioorganic Chemistry, 90362 Lodz, Poland. B.S.: FDA Guest Worker.

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Scheme I

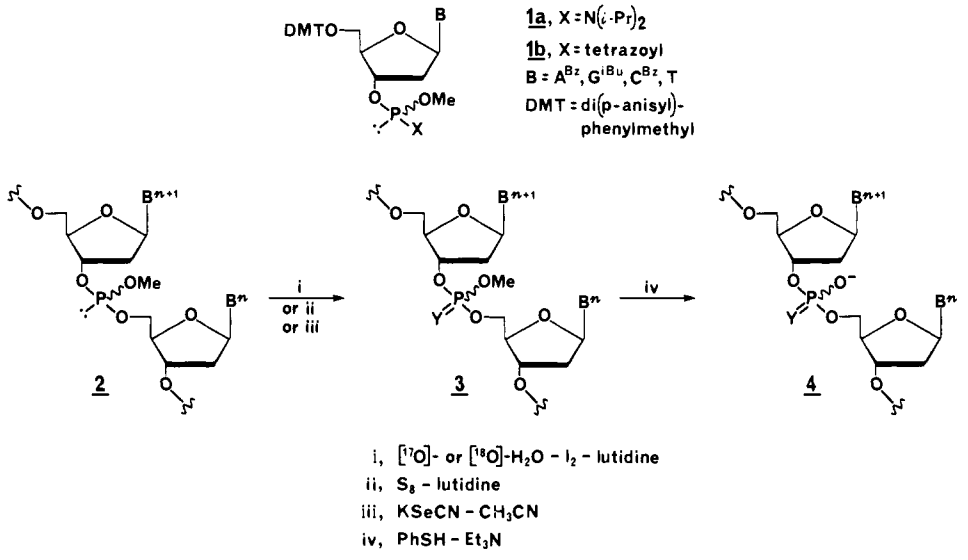

Table I. Numbering of Analogues of Oligonucleotides and Analytical Data

compd	formula[a] 5′→3′	elution time, min 5′-DMT[b]	elution time, min 5′-HO[c,d]	^{31}P, ppm 5′→3′[e]
5	T_P[^{18}O]T	10.2[f]	11.0 (*R* + *S*)[g]	1.40, 1.37
6	GGAA$_P$[^{17}O]TTCC	12.7	11.6 (*R* + *S*)	*f*
7–9[g]	$N_{PSe}R$	11–23	13–24[g]	**8**: 50.43, *786*,[h] 49.32, *796*[h]
10–19[i]	$N_{PS}N'$	10–22	10–18[i]	**10**: 55.97 (*R*), 55.61 (*S*)
20–28[j]	$R_{PS}R'$	10–22	12–30[j]	**20**: 56.47 (*R*), 55.38 (*S*) **25**: 55.19 (*R*), 55.09 (*S*)
29–36[k]	$R_{PS}N_{PS}R'$	13–25	11–34[k]	**29**: 55.51–55.27[l]
37–40[m]	$N_{PS}R_{PS}N'$	15–17	16–25[m]	
41	T[(pT)$_{48}$]$_{PS}$T	10.9	15.9 (*R* + *S*)	
42	GGAATTC$_{PS}$C	11.9	17.1 (*R*) 17.6 (*S*)	55.37, −1.26 to −1.53 54.39, −1.26 to −1.53
43	GGAATT$_{PS}$CC	11.2	16.9 (*R*) 17.7 (*S*)	
44	GGAAT$_{PS}$TCC	10.9	17.4 (*R*) 17.9 (*S*)	
45	GGAA$_{PS}$TTCC	11.2	18.2 (*R* + *S*)	54.65, 54.41, −1.69 to −2.03[n]
46	GGA$_{PS}$ATTCC	11.4	17.7 (*R* + *S*)	
47	GG$_{PS}$AATTCC	19.2 21.8	14.7 (*R*) 14.7 (*S*)	54.89, −1.19 to −1.73[n] 54.55, −1.14 to −1.70[n]
48	G$_{PS}$GAATTCC	18.4 19.8	18.9 (*S*) 18.1 (*R*)	53.65, −1.17 to −1.70[n] 54.65, −1.17 to −1.70[n]

[a] ^{17}O, ^{18}O, S, and Se refer to the internucleotide linkage as derived from **3**. [b] HPLC of the 5′-DMT compound on a μBONDAPAK C_{18} column with 0.1 M triethylammonium acetate buffer (TEAA, pH 7) and gradients of 0.5–3% per min of CH_3CN, starting at 20% CH_3CN; flow rates = 4–5 mL/min. [c] HPLC of the 5′-HO compound as indicated in *b* using 5:95 CH_3CN:TEAA at injection and gradients of 0.16–2% per min of CH_3CN. [d] Absolute configurations at P given in parentheses and assigned as described earlier.[4,14] [e] Chemical shifts, relative to external 25% H_3PO_4 in D_2O, measured at 121.51 MHz for the 5′-HO compound in 0.1 M Tris, pH 7.6, 20 °C, with 5 mM EDTA, except for **5** and **8**, which were analyzed as the 5′-DMT compound. [f] ^{17}O chemical shift, relative to internal [^{17}O]H_2O, measured at 33.95 MHz, was ~92 ppm ($w_{1/2}$ ~ 750 Hz) at pH 6.7, 85 °C. [g] N, R, elution times: **7**, T, T, 12.9, 13.4; **8**, T, TT, 24.1, 23.7; **9**, G, C, 14.1, 15.4. [h] Italicized value refers to ^1J (PSe), Hz. [i] N, N′, respective elution times for *R* and *S* compound: **10**, T, T, 13.4, 14.2; **11**, T, A, 12.3, 13.1; **12**, T, G, 10.6, 11.3; **13**, A, T, 13.3, 14.1; **14**, A, A, 16.5, 18.3; **15**, G, G, 12.5, 14.0; **16**, G, C, 12.7, 13.9; **17**, G, A, 10.8, 11.6; **18**, C, C, 9.9, 11.6; **19**, C, G, 11.0, 12.0. [j] R, R′, respective elution times for *R* and *S* compound: **20**, TT, T, 17.8, 19.4; **21**, T, TT, 19.1, 19.4; **22**, TTT, T, 27.2, 29.3; **23**, TTT, TTT, 14.1, 14.4; **24**, TAT, A, 19.0, 19.8; **25**, T, ATA, 19.9, 20.4; **26**, AT, T, 14.8, 16.2; **27**, GC, GCGC, 20.7, 21.5; **28**, C, CTTAAGG, 12.3, 12.8. [k] R, N, R′, respective elution times for (*S*,*R*, *S*,*S*, *R*,*R*, and *R*,*S* compound: **29**, T, T, T, 21.5, 22.5, 20.0, 22.2; **30**, TTT, T, T, 33.3, 34.5, 32.1, 33.6; **31**, TTT, T, TTT, 33.2, 34.6, 32.5, 33.7; **32**, A, A, A, 31.7, 33.3, 29.5, 31.3; **33**, G, G, G, 22.2, 23.9, 20.4, 22.5; **34**, G, G, A, 13.2, 13.6, 12.6, 13.1; **35**, C, C, C, 12.0, 14.2, 10.7, 13.1; **36**, G, G, AATTCC, 15.6, 15.8, 15.3, 15.6. [l] Seven of eight signals resolved. [m] N, R, N′, respective elution times for *S*,*R*, *S*,*S*, *R*,*R*, and *R*,*S* compound: **37**, T, TT, T, 24.1, 24.9, 23.7, 24.6; **38**, T, AT, A, 22.0, 22.8, 21.5, 22.3; **39**, T, ATA, T, 20.9, 22.0, 20.2, 21.3; **40**, G, GC, C, 17.0, 18.1, 16.0, 17.5. [n] PO:PS = 6:1.

sequences is possible.[10] In this communication we report modifications of the methodology used in the automated synthesis of oligodeoxyribonucleotides in order to introduce isotopes of either oxygen, sulfur, or selenium at any phosphate moiety within the oligonucleotide.

The cycle for synthesis (1–10 μmol) with our Applied Biosystems synthesizer has been described elsewhere[11] and features 1*H*-tetrazole-catalyzed coupling of phosphoramidites **1a** to give phosphite intermediates **2** for conversion to phosphates **3** (Y =

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O) by oxidation with I_2–H_2O (Scheme I). The latter step can be performed with either [^{17}O]- or [^{18}O]H_2O to obtain specifically labeled phosphate moieties **3** (Y = ^{17}O or ^{18}O),[12] as exemplied by compounds **6** and **5** in Table I. Reaction of **2** with either sulfur (S_8) in 2,6-lutidine (0.4 M, 15 min, 60 °C) or KSeCN in CH_3CN (0.1 M, 1 h, 60 °C) gives **3** with either Y = S or Se, respectively. The PS moiety in **3** survived a relatively large number of subsequent cycles of synthesis, as demonstrated by isolation of T-[(pT)$_{48}$]$_{PS}$T (**41**). The variety of products listed in Table I indicated that "thioylation" can be achieved regardless of the nature of the bases in **2** and the value of *n*.

Although use of an ~10-fold molar excess of ~1:1 (R_p)- and (S_p)-**1a** could lead to highly diastereoselective formation of PS linkages, this was not found, even with diastereomerically enriched **1a**, which was attributed to epimerization at phosphorus in the tetrazoyl intermediate **1b**. In any event, most of the diastereomeric oligonucleotides (up to ~5 mg) were separable with more or less ease, depending on chain length, the position of the PS moiety in a given sequence, and the number of PS centers. A two-stage chromatographic procedure was used, starting with elution on a reverse-phase (C_{18}) HPLC column to separate "5′-dimethoxytrityl" (DMT) product(s) from relatively fast-eluting fully deprotected failure sequences and 5′-DMT oxo byproduct (5–10% of the desired oligomer). The second stage of isolation involved detritylation[11c] and HPLC of the resultant 5′-HO-DNA. The presence of PS linkages was established by ^{31}P NMR spectroscopy, in selected cases, and in all cases by treatment with either snake venom phosphodiesterase (SVPDE, type II) or nuclease P1 followed, if necessary, by addition of alkaline phosphatase and then HPLC identification of the undigested dinucleoside phosphorothioate. The action of SVPDE, which is R_p selective,[13] was not sufficient for the assignment of absolute configuration at phosphorus in oligonucleotides having *two adjacent* PS centers, as this 3′-exonuclease did not hydrolyze R_P,S_P and S_P,S_P diastereomers. Parallel digestions with SVPDE and nuclease P1, which is S_P selective,[4] were therefore used to obtain complementary results that revealed the absolute configurations in question.

The self-complementary octamers **47** and **48** were tested as substrates for EcoRI endonuclease, which cleaves between G and A in duplex DNA having the sequence GAATTC.[14] Interestingly, it was found that neither of the two separated diastereomers of **47** was a good substrate for this enzyme, relative to oxo-**47**[15] and that (R_P)-**48** but not (S_P)-**48** was cleaved. The resistance of **47** toward hydrolysis by EcoRI implies that it may be possible to selectively "protect" restriction sites. Since the diastereomers of **48** represent modifications of internucleotide linkages with retention of ionic character, it appears that the recognition process may not involve a purely Coulombic interaction between the protein and phosphate groups that are not at the site of cleavage;[14] however, further structural and biochemical studies are now in progress to clarify this point.

The presently described procedures, which may be performed manually[16,17] and can be applied to ^{35}S labeling, have been used to prepare longer mono- and polyphosphorothioate analogues of oligonucleotides for studies that will be reported elsewhere.

Acknowledgment. We thank Drs. Frederick T. Gates, Blair A. Fraser, and R. Andrew Byrd and Kathleen A. Gallo for their assistance.

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Solid-State ^{13}C CPMAS Spectra of Rapidly Equilibrating Carbocations

P. C. Myhre,* J. D. Kruger, B. L. Hammond, and S. M. Lok

Department of Chemistry, Harvey Mudd College Claremont, California 91711

C. S. Yannoni,* V. Macho,† H. H. Limbach,‡ and H. M. Vieth†

IBM Research Laboratory San Jose, California 95193

Received May 16, 1984

We report studies of the variable-temperature solid-state CPMAS ^{13}C NMR spectra of four carbocations (**1**–**4**), all of which

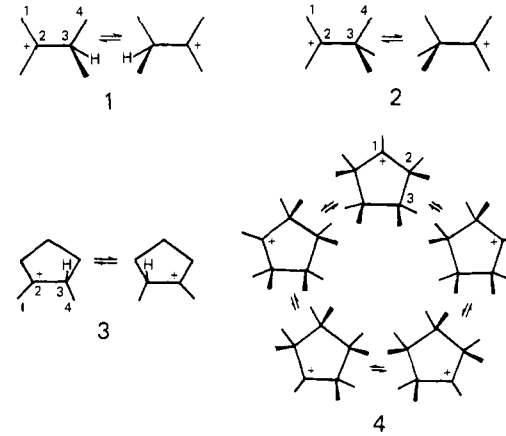

exhibit average spectra in solution owing to rapid degenerate rearrangements at all accessible temperatures.[1] In contrast, the solid-state CPMAS spectra show resonances expected for static classical ions at low temperatures. At higher temperatures (about 200 K), the spectra show these classical ions undergoing rapid degenerate rearrangement. Table I lists the chemical shift data observed at the upper and lower temperatures of this solid-state investigation,[2] together with comparisons of liquid-state values. The most interesting feature, however, is the appearance of the spectra at intermediate temperatures.

If the dynamics of these ions in the solid conformed to solution behavior, one would expect line broadening and coalescence as the system passes from the slow to the fast exchange regime. The spectra of the 2,3-dimethyl-2-butyl cation (**1**) in solid SbF_5 (Figure 1) do not show this. Instead, the spectra at temperatures between 193 and 128 K show *both* static and rapidly equilibrating classical ions in apparent coexistence, with decreasing amounts of static ion as the temperature increases. The spectral patterns found for the 2,3,3-trimethyl-2-butyl cation (**2**), 1,2-dimethylcyclopentyl cation (**3**), and cyclopentyl cation (**4**) are similar, although some evidence of line broadening and coalescence is observed, especially in the cases of **3** and **4**.

Cycling the sample temperature indicates that the relative populations of static and dynamic forms can be reproduced. Hence, the spectral observations do not appear to be due to transient phenomena; rather, they indicate an equilibrium property of the system at a given temperature. By changing the solid matrix

†Permanent address: Institute for Atomic and Solid State Physics, Free University of Berlin, D1000 Berlin 33, West Germany.
‡Permanent address: Institute for Physical Chemistry, Freiburg University, D7800 Freiburg, West Germany.

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