Complex 7 was characterized by X-ray diffraction. It contains a planar central five-membered metallabicyclic ring system (Zr-C(14)-C(15)-Al-Cl) with very unusual bonding parameters. The plane of this ring system bisects the Cp–Zr–Cp angle, and the substituents at the carbon atoms C(14) and C(15) are oriented in the plane of the metallacycle. These features are evident from Figure 1, which gives geometric parameters of the central part of the molecule.

Carbon atom C(15) is planar and tetracoordinate. Its bonding situation is best described by forming four σ-bonds to its neighboring atoms. These bonds are oriented normal to the plane of the π-bond between atoms C(14) and C(15). The angle Cl–Zr–C(14) (119.5 (1)°) is about 20–30° larger than typically found in tetracoordinated bis(η-cyclopentadienyl)ZrX_2 complexes.[6] The bonding angles at C(14) deviate strongly from the expected values for a sp^2-hybridized carbon atom. The angle Zr–C(14)–C(15) (84.9 (2)°) is very small. As a consequence, the angles Zr–C(14)–Si and Si–C(14)–C(15) are larger than 120°. These structural features support a bonding interaction between atoms Zr and C(15).

The plane of the aromatic substituent at atom C(15) is oriented perpendicular to the mean plane of the metallabicycle. This completely eliminates any conjugation between the aromatic and olefinic π-systems present. It may be that this orientation is favored because it allows for a small stabilizing electronic interaction between the electron-rich aromatic π-system and the electron-deficient σ-system around the planar and tetracoordinate carbon atom C(15) or a weak bonding interaction between Al and C(16) (the distance is 2.602 (3) Å).[7]

The Zr–Cl bond (2.638 (1) Å) is quite long. This and an elongated Al–C(15) bond (2.121 (3) Å)—the Al–methyl distances (Al–C average, 1.96 (1) Å) are normal—support an alternative description of the bonding situation as a Cp_2Zr-alkyne ("metallacyclopropene") fragment stabilized by addition of R_2AlCl.

Controlled stoichiometric hydrolysis of 7 leads to the formation of the agostic alkenylmetallocene complex 5. With excess aqueous acid, *cis*-1-phenyl-2-(trimethylsilyl)ethene is formed. Exposure of 7 to molecular oxygen leads to the formation of phenyl(trimethylsilyl)acetylene. A regioisomeric complex (8), where the positions of the phenyl and trimethylsilyl substituents at the Zr,Al-bridging alkyne moiety are exchanged, is formed upon thermolysis of 7 (benzene solution, room temperature). Equilibrium ([7]:[8] = 0.7) is reached after 2 weeks at 25 °C. The isomerization reaction presumably proceeds via a ring-opened (η^2-alkyne)zirconocene–$ClAlMe_2$ adduct.[8] We are currently investigating whether the presence of a planar-tetracoordinate carbon in 7 gives rise to uncommon chemical behavior of such a metal complex.

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Registry No. 5, 119747-83-0; **7**, 129265-56-1; **7a**, 129265-58-3; **8**, 129265-57-2; **8a**, 129265-59-4; $AlMe_3$, 75-24-1; $AlEt_3$, 97-93-8; *cis*-1-phenyl-2-(trimethylsilyl)ethene, 19319-11-0; phenyl(trimethylsilyl)acetylene, 2170-06-1.

Supplementary Material Available: Tables of crystal structure and details of data collection, bond distances and angles, and atomic positional and thermal parameters of 7 (8 pages); listings of observed and calculated structure factors of 7 (17 pages). Ordering information is given on any current masthead page.

(5) **7**: 90% isolated; mp 140–142 °C dec; ^1H NMR (C_6D_6) δ –0.42 (s, 6 H, $AlMe_2$), –0.12 (s, 9 H, $SiMe_3$), 5.63 (s, 10 H, Cp), 6.60–7.12 (m, 5 H, Ph); ^{13}C NMR (C_6D_6) δ –5.9 ($AlMe_2$), 1.2 ($SiMe_3$), 110.4 (Cp), 126.4, 127.4, 130.5, 143.2 (Ph), 221.4 (Zr—C=), signal of =C—Al not observed. Anal. Calcd for $C_{23}H_{30}AlClSiZr$: C, 56.58; H, 6.19. Found: C, 56.61; H, 6.45. X-ray crystal structure analysis: space group $C2/c$; a = 18.146 (6), b = 9.731 (1), c = 27.218 (3) Å; β = 102.97 (2)°; V = 4683.5 Å^3; d_{calc} = 1.39 g cm^{-3}; μ = 6.69 cm^{-1}; Z = 8; λ = 0.71069 Å; measured reflections 5790 ($\pm h,+k,+l$); sin θ/λ_{max} = 0.65; independent reflections 5350, observed reflections 4703; refined parameters 244, R = 0.037, R_w = 0.049; residual electron density 0.56 e Å^{-3}; structure was solved by heavy atom method; hydrogen atom positions were calculated and kept fixed in the final refinement stages. **8**: ^1H NMR (C_6D_6) δ –0.12 (s, 6 H, $AlMe_2$), 0.12 (s, 9 H, $SiMe_3$), 5.47 (s, 10 H, Cp), 6.60–7.15 (m, 5 H, Ph); ^{13}C NMR (C_6D_6) δ –3.3 ($AlMe_2$), 4.6 ($SiMe_3$), 110.6 (Cp), 123.3, 124.7, 128.1, 150.5 (Ph), 231.4 (Zr—C=), =C—Al signal not observed. The reaction of **5** with triethylaluminum gave the analogous $Cp_2Zr(\mu\text{-}\eta^1,\eta^2\text{-}Me_3SiCCPh)(\mu\text{-}Cl)AlEt_2$ compounds (**7a**, **8a**). **7a**: 45% isolated; mp 104–106 °C dec; ^1H NMR (C_6D_6) δ –0.11 (s, 9 H, $SiMe_3$), 0.15 (q, 4 H) and 1.23 (t, 6 H, $AlEt_2$), 5.65 (s, 10 H, Cp), 6.70–7.12 (m, 5 H, Ph); ^{13}C NMR (C_6D_6) δ 1.3 ($SiMe_3$), 3.2 and 10.4 ($AlEt_2$), 110.3 (Cp), 126.5, 127.8, 129.6 143.7 (Ph), 221.0 (ZrC=), =CAl signal not observed. Anal. Calcd for $C_{25}H_{34}AlClSiZr$: C, 58.14; H, 6.64. Found: C, 57.86; H, 6.82. **8a**: ^1H NMR (C_6D_6) δ 0.11 (s, 9 H, $SiMe_3$), 0.30 (q, 4 H) and 1.45 (t, 6 H, $AlEt_2$), 5.49 (s, 10 H, Cp), 6.70–7.12 (m, 5 H, Ph); ^{13}C NMR (C_6D_6) δ 4.5 ($SiMe_3$), 5.6 and 10.6 ($AlEt_2$), 110.6 (Cp), 123.4, 124.7, 128.1, 141.7 (Ph), 232.8 (Zr—C=), =C—Al signal not observed. The [**7a**]:[**8a**] equilibrium ratio is 1.7 at room temperature.

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A Negative Catalytic Term Requires a Common Intermediate in the Imidazole Buffer Catalyzed Cleavage and Rearrangement of Ribodinucleotides

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We have described a detailed kinetic study of the reactions of 3′,5″-uridyluridine (UpU) catalyzed by imidazole buffer.[1] The cyclization/cleavage to form uridine 2′,3′-cyclic phosphate with cleavage of uridine was catalyzed by a sequential bifunctional mechanism in which a phosphorane monoanion is formed in one early step and then is cleaved to product in a later step. Imidazole (Im) catalyzes one of these steps, imidazolium ion (ImH^+) the other, but the sequence of their operation is kinetically ambiguous. By contrast, the rearrangement of 3′,5″-UpU to its 2′,5″-UpU isomer is catalyzed by ImH^+ alone. If this also proceeds through the same phosphorane monoanion, then the ambiguity is removed, and in the cleavage the first catalyst is ImH^+ (or its kinetic equivalent, H^+ followed by Im, as in Scheme I).

The mechanism that this implies was described[1] (Scheme I), and we showed[2] that it probably can be extended to the mechanism of the enzyme ribonuclease A (with suitable modification, in which some sequential steps in the model become simultaneous in the enzyme). Calculations by the Karplus group are consistent with our proposals.[3] The mechanism also guided us in the redesign of a ribonuclease enzyme mimic.[4,5] However, the issue is sufficiently important that it needed to be checked further. We now report that our findings are not special to uridine nucleotides, but are also seen with adenosine derivatives. Most importantly, we

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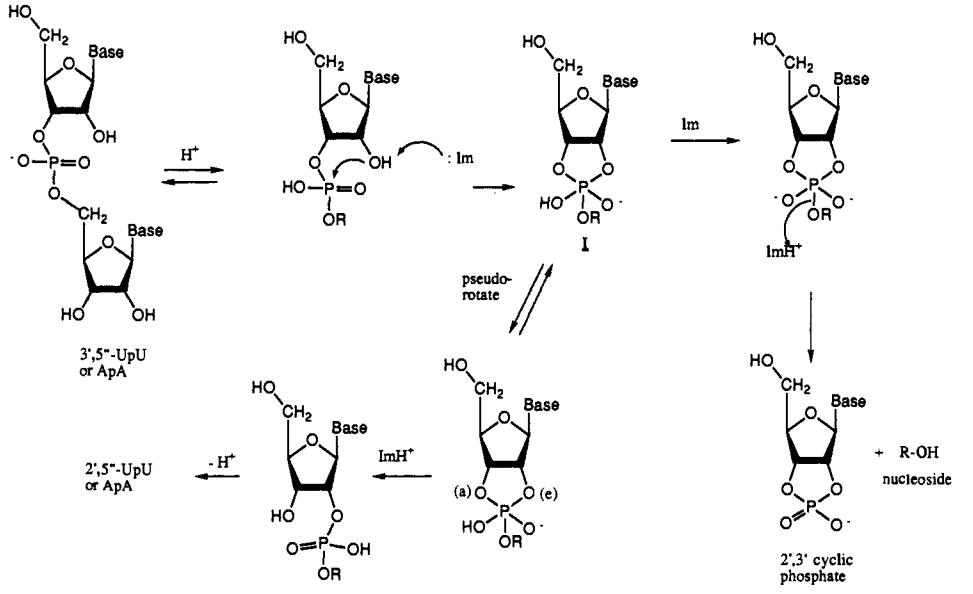
Scheme I



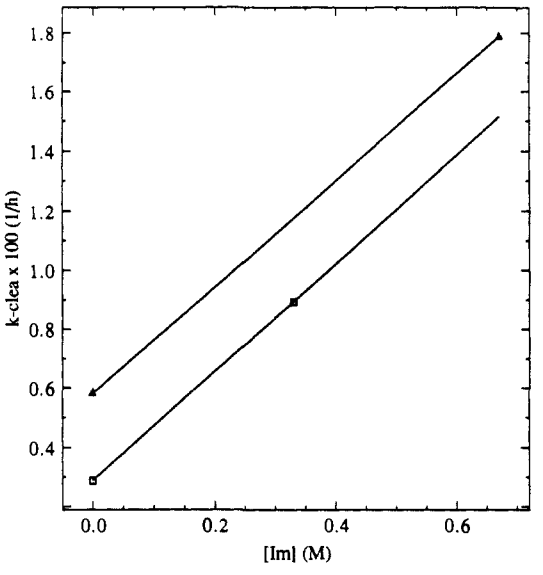


Figure 1. Pseudo-first-order rate constant for cleavage of 3',5"-ApA at 80 °C as a function of imidazole concentration at two different fixed imidazolium ion concentrations. □, $[ImH^+]$ = 0.5 M; △, $[ImH^+]$ = 1.0 M. The values are interpolated from plots of the data in Table I.

use an unusual kinetic tool to demonstrate that the cleavage and the rearrangement reactions indeed proceed through a common intermediate.

The cleavage and isomerization of 3',5"-ApA with imidazole buffers were studied by techniques similar to those we have described for UpU; the data are listed in Table I. When they are plotted they again exhibit a bell-shaped rate vs buffer ratio dependence, with a maximum rate when both Im and ImH^+ are present. This shows bifunctional catalysis involving both buffer species. The rate vs buffer concentration plot is again linear, so the two species operate in separate steps and the bifunctionality is sequential. The similarity to our data for UpU means that there was no special mechanism operating with the uridine system. As before with UpU, the isomerization of ApA to the 2',5"-isomer is catalyzed only by ImH^+.

We also show these data in Figure 1 as the rate of cleavage with two different values of [Im] when $[ImH^+]$ is held constant; as expected from the mechanism of Scheme I, the cleavage rate increases at higher [Im] since Im catalyzes the conversion of the phosphorane intermediate to the cleavage product. However, the same plot for the isomerization reaction, Figure 2, shows that the rate of isomerization *decreases* when the [Im] is increased. We

Table I. Pseudo-First-Order Rate Constants ($\times 10^3$ h^{-1}) for the Cleavage and Isomerization of 3',5"-ApA Catalyzed by Various Concentrations and Ratios of Imidazole Buffer at 80 °C, Corrected for the Buffer Independent Rate

Im/Im·HCl	concn, M	*k*(cleavage)	*k*(isom)
100/0	0.8	8.6 ± 0.2	−0.31 ± 0.26
40/60	0.8	8.6 ± 2.0	−0.51 ± 0.46
0/100	0.8	4.7 ± 0.6	0.19 ± 0.72
100/0	1.3	11.4 ± 1.7	−1.26 ± 0.34
40/60	1.3	13.9 ± 0.3	−0.93 ± 0.23
0/100	1.3	7.6 ± 1.5	1.13 ± 0.75
100/0	2.0	20.1 ± 1.1	−1.20 ± 0.09
40/60	2.0	21.5 ± 1.0	−1.33 ± 0.12
0/100	2.0		0.91 ± 0.04

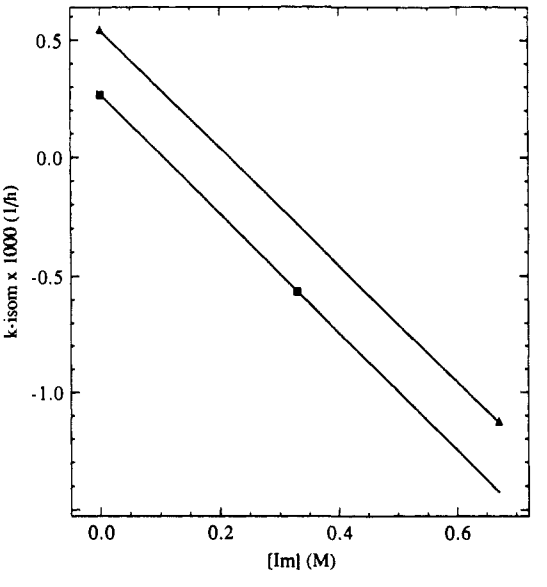


Figure 2. Pseudo-first-order rate constant for isomerization of 3',5"-ApA to 2',5"-ApA at 80 °C as a function of imidazole concentration at two different fixed imidazolium ion concentrations. ■, $[ImH^+]$ = 0.5 M; ▲, $[ImH^+]$ = 1.0 M. The values are interpolated from plots of the data in Table I.

see a similar negative catalysis when we plot our previous data on UpU isomerization in this fashion. The negative rate constants in Table I also reflect a decrease in the rate of uncatalyzed (by buffer) isomerization when imidazole is added.

This negative catalytic term is expected for our mechanism, whose kinetics are expressed in eqs 1 and 2. For cleavage [Im]

rate of cleavage =

$$\frac{k_{1k2}[\mathrm{ApA}][\mathrm{ImH^+}][\mathrm{Im}]}{k_{-1}[\mathrm{ImH^+}] + k_2[\mathrm{Im}] + k_3 + k_w} + k'[\mathrm{Im}] + k''[\mathrm{ImH^+}] \quad (1)$$

$$\text{rate of isomerization} = \frac{k_1k_3[\mathrm{ApA}][\mathrm{ImH^+}] + k_w}{k_{-1}[\mathrm{ImH^+}] + k_2[\mathrm{Im}] + k_3 + k_w} \quad (2)$$

appears in both numerator and denominator of eq 1, but for isomerization [Im] appears only in the denominator of eq 2. An increase in [Im] at constant [ImH^+] diverts the common intermediate 1 toward cleavage; this decreases the steady-state concentration of 1 and thus the rate of isomerization.

Such a negative kinetic effect would not be seen if the cleavage and isomerization paths did not branch from a common intermediate whose concentration is decreased when we catalyze one of the branches; the kinetic data are at early times, so Im does not appreciably decrease the concentration of the starting material itself. The effect is intellectually related to the demonstration that an isotope effect on one path affects the rate of another path,[6,7] first used by Katz[6] to show that two paths diverge from a common intermediate. Our kinetic version of it does not seem to be widely known or used. In any case, this work shows that the mechanistic conclusions from our previous studies of UpU reactions are indeed soundly based.

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A Planar Oxocuprate(II) Array via Heterometallic Alkoxide Chemistry

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Application of the molecular precursor method[1,2] to the synthesis of copper-based high-temperature superconductors[3] rests on our ability to produce copper-containing heterometallic alkoxides.[4] We have reported recently[5,6] on the chemistry of the anion $Zr_2(O^iPr)_9^-$, which is related to recent reports by the group of Mehrotra.[7,8] We report here our investigation of the coupling of this and related anions to $CuCl_2$ of relevance to hydrolytic routes to copper/oxo superconductors.

The reaction of $K_4Zr_2O(O^iPr)_{10}$,[6] $CuCl_2$, and water (2:4:1 mole ratio) in a refluxing THF solution produces a deep olive green solution. Workup (i.e., removal of solvent, extraction with pentane, concentration, and layering with 2-propanol) yields a blue-green solid (25% yield), which was established[9] to have the formula $Cu_4^{II}Zr_4^{IV}O_3(O^iPr)_{18}$ (**1**), eq 1. The centrosymmetric structure

$$2K_4Zr_2O(O^iPr)_{10} + 4CuCl_2 + H_2O \rightarrow Cu_4Zr_4O_3(O^iPr)_{18} + 8KCl + 2HO^iPr \quad (1)$$

is shown in Figure 1. The molecule contains a planar central

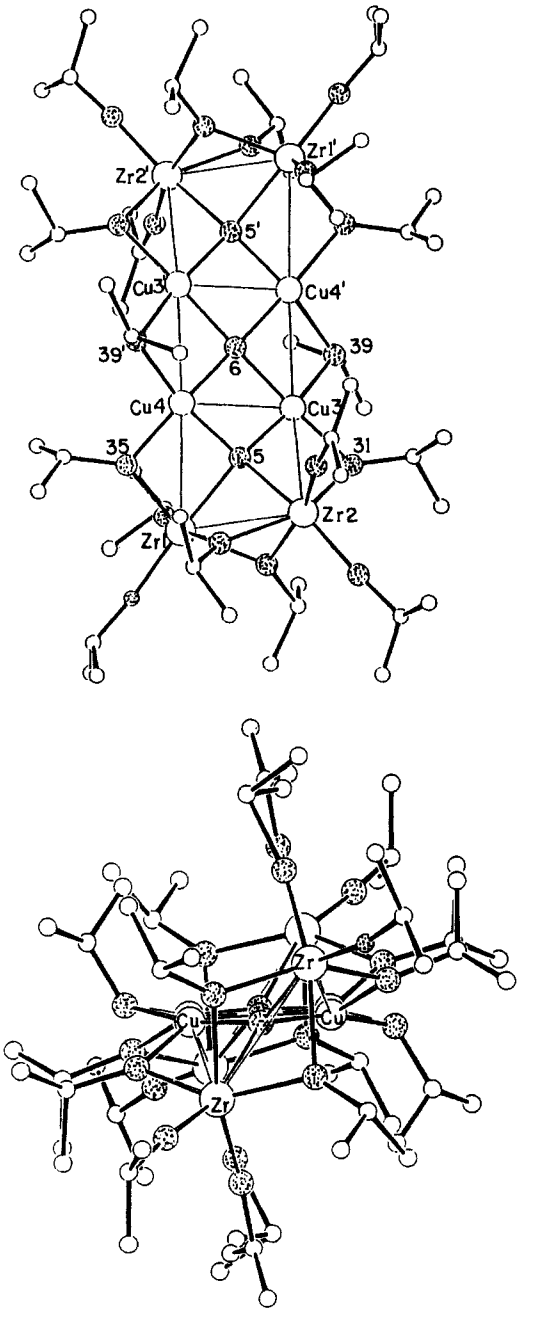

Figure 1. ORTEP drawing of the non-hydrogen atoms of $Cu_4Zr_4O_3(O^iPr)_{18}$ (top) viewed perpendicular to the Cu_4O_3 plane and (bottom) viewed along the edge of the Cu_4O_3 plane. Oxygen atoms are stippled. Lines between metals are for clarity and are not bonds. Primes indicate atoms related by a center of symmetry. Selected structural parameters (distances, Å; angles, deg): Cu3–O6, 1.968 (3); Cu4–O6, 1.966 (2); Cu3–O5, 1.880 (18); Cu4–O5, 1.896 (11); Cu3–O39, 1.892 (12); Cu4–O39′, 1.901 (12); Cu3–O31, 1.965 (11); Cu4–O35, 1.966 (11); Cu3′–Cu4 = Cu3–Cu4, 2.781 (8); cis angles O–Cu–O range from 84.5 (5)° to 104.0 (5)°.

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0002-7863/90/1512-9623$02.50/0