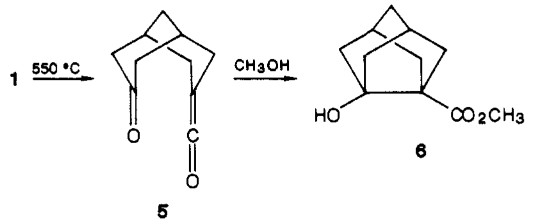
50% decomposition. However, even at this temperature CO_2 extrusion did not occur, for the product was keto ketene **5**, formed by cleavage of the β-lactone ring in **1** in the undesired sense. The keto ketene was identified by its IR spectrum (2125 and 1720 cm^{-1})[4] and by its conversion to hydroxy ester **6**[5,6] on addition of methanol.

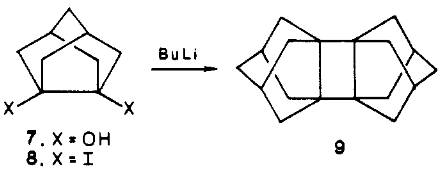


This mode of β-lactone cleavage is, to the best of our knowledge, unprecedented. From the heats of formation of the products,[7] fragmentation of the parent 2-oxetanone to ethylene plus CO_2 is computed to be enthalpically more favorable than cleavage to formaldehyde plus ketene by 39.3 kcal/mol. In addition, loss of CO_2 from **1** is entropically more favorable than its cleavage to **5**. The fact that formation of keto ketene **5** is, nevertheless, the preferred reaction pathway of β-lactone **1** at 550 °C is thus indicative of the very high energy of the pyramidalized alkene **3** that would be formed by extrusion of CO_2 from **1**.

At temperatures above 550 °C, CO_2 loss from **1** was observed. However, only a very small amount of the dimer of **3** was isolated. The major product (>95%) was an isomer of **3**.[8] From its ^1H NMR spectrum [$(CDCl_3)$ δ 1.48 (t, 2 H, J = 1.5 Hz), 2.00 (d of d, 2 H, J = 16.2, 1.5 Hz), 2.26 (d of d, 2 H, J = 16.2, 4.4 Hz), 2.48 (d of d, 1 H, J = 4.4, 1.5 Hz), 3.15 (br s, 1 H), 4.62 (s, 2 H), 4.92 (s, 2 H)] and ^{13}C NMR spectrum [$(CDCl_3)$ δ 36.48, 36.87, 39.97, 55.31, 102.91, 152.41] this hydrocarbon was identified as 2,6-dimethylenebicyclo[2.2.1]heptane. Based on studies of the thermal chemistry of alkene **4**,[9] the mechanism for formation of this isomer of **3** appears to involve a reverse vinylcyclopropane rearrangement, followed by subsequent bond reorganization in the strained intermediate that is thus generated.

Although β-lactone **2** is an excellent precursor of **4**, the greater strain in alkene **3** apparently renders **1** a poor source of **3**. This finding prompted us to look for a different precursor of **3**. Toward this end, we succeeded, after trying many different routes, in converting diol **7**[10] to diodide **8**.[8] Heating 200 mg of **7** at 110 °C in 10 mL of 95% phosphoric acid containing 3.0 g of sodium iodide[11] afforded **8**, mp 130–131 °C, in 40% yield after purification by chromatography and sublimation. The ^1H and ^{13}C NMR spectra of **8** $(CDCl_3)$ showed resonances at respectively δ 1.63 (s, 2 H), 1.90 (s, 2 H), 2.43 (d, 4 H, J = 10.3 Hz), 2.76 (d, 4 H, J = 10.3 Hz) and δ 30.78, 39.45, 53.14, 57.79.

When diiodide **8** was treated with one equivalent of butyllithium in THF at −78 °C, the "2 + 2" dimer of **3** (**9**),[8] mp 211–212 °C, was isolated in almost quantitative yield after chromatography and sublimation. The simplicity of the dimer's 500-MHz ^1H NMR spectrum [$(CDCl_3)$ δ 1.40 (d, 8 H, J = 10.1 Hz), 1.50 (s, 4 H), 1.92 (d, 8 H, J = 10.1 Hz), 2.42 (br s, 4 H)] and ^{13}C NMR spectrum [$(CDCl_3)$ δ 37.23, 42.34, 44.01, 50.18] was indicative of the high (D_{2h}) symmetry of this hydrocarbon.



In order to provide evidence for the intermediacy of **3** in the dimerization reaction, the reaction was repeated in the presence of diphenylisobenzofuran (DPIBF) as a trap for the pyramidalized olefin. From this reaction was isolated in 90% yield, after chromatography and sublimation, a white solid, 131–132 °C. The product was identified spectroscopically as the expected Diels–Alder adduct of **3** with DPIBF.[8]

The results reported here show that **3** is a highly strained alkene but that it can be generated at low temperatures and chemically trapped before undergoing rearrangement. Attempts to matrix isolate **3** and to obtain its IR and UV spectra for comparison with those of **4**[3] are in progress.

Acknowledgment. We thank the National Science Foundation for support of this research.

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[4] Although the IR spectrum of keto ketene **5** can be obtained in solution at room temperature, the spectrum was first observed in matrix isolation, initially by Dr. Richard A. Hayes and Professor Orville L. Chapman and subsequently by Dr. Juliusz G. Radziszewski and Professor Josef Michl. We thank both groups for performing the matrix-isolation experiments for us.

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Intramolecular C–H Bond Activation in Aqueous Solution: Preparation of a Unique Cobalt(III)–Alkyl Complex by Deprotonation of an Agostic Intermediate. Crystal Structure of $[Co^{III}(dacoda\text{-}C(2))(H_2O)]\cdot 2H_2O$

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The covalent interaction between an unactivated C–H bond and the central metal in transition-metal complexes, termed an agostic interaction,[2a] has recently received a great deal of attention in relation to the general problem of C–H activation.[2–5] The minimum requirement for the three-center, two-electron M–H–C bond is that the metal center have a suitably oriented low-energy empty orbital to receive the two electrons of the C–H bond.[2a] The quadridentate ligand dacoda (1,5-diazacyclooctane-*N*,*N*′-diacetic acid) forms square-pyramidal five-coordinate $[M^{II}(dacoda)(H_2O)]$ complexes with Ni(II), Co(II), and Zn(II).[6] A crystal structure

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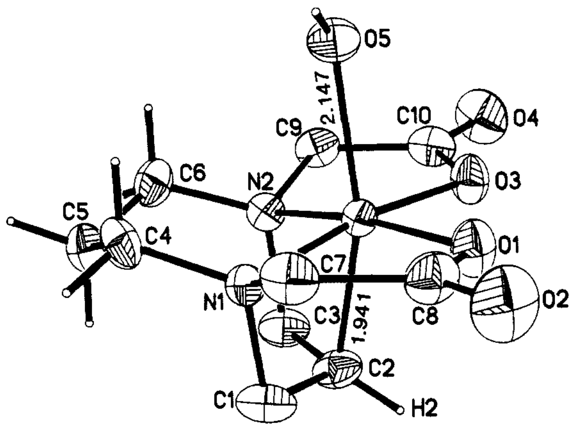


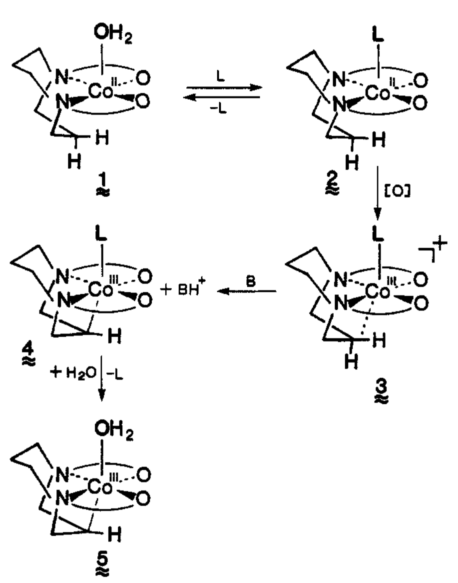
Figure 1. ORTEP drawing and labeling scheme for [Co^{III}(dacoda-*C*-(2))(H_2O)] (**5**).

of the Ni(II) complex,[6b] which is isomorphous with the Co(II) complex,[6c] demonstrated that the stereochemical requirement of the ligand forces five-coordination about the nickel atom by placing a C–H bond over the sixth coordination position. With this in mind, we reasoned that oxidation of [Co^{II}(dacoda)(H_2O)] (**1**) to Co(III) would result in a system meeting the requirements for an agostic interaction: coordinatively unsaturated (16e⁻) Co(III) with an empty d_{z^2} orbital directed at a properly oriented C–H bond. We anticipated that this would lead to stabilization of classically five-coordinate[7] Co(III) through an agostic interaction in the sixth position or to some type of C–H activation. We report here the structural characterization of an unusual oxidation product of **1**, [Co^{III}(dacoda-*C*(2))(H_2O)]·$2H_2O$ (**5**), where dacoda-*C*(2) refers to dacoda coordinated in a quinquedentate fashion with the C(2) carbon of the 1,5-diazacyclooctane portion of the ligand directly bonded to the cobalt center; see Figure 1.

The reaction of **1**[6c] in an aqueous solution containing 0.8 equiv of KCN with 1 equiv of H_2O_2 gave a dark red solution. Passage of this solution through QAE-Sephadex (Cl^- form) and Dowex 50W-X8 (H^+ form) followed by rotary evaporation to a small volume, and addition of acetone, resulted in the precipitation of the red complex **5**, which was recrystallized from warm H_2O. The complex is very stable in water, showing negligible decomposition after boiling for 3 h. The oxidation state of the cobalt center in **5** was confirmed to be 3+ (low-spin d^6 in solution) by observation of a high-resolution ^1H NMR spectrum.[8]

The structure of **5** was determined by single-crystal X-ray crystallography and is shown in Figure 1.[9] A unique feature of the molecular structure is the direct cobalt–carbon bond to the C(2) carbon in the boat ring of the daco backbone. The Co–C(2) bond (1.941 (4) Å) is very short when compared to typical Co–alkyl bonds with trans N donors or water (1.98–2.01 Å)[10] and, in fact, is one of the shortest Co(III)–alkyl bonds reported to date. A Co–C distance of 1.95 Å was reported for [$Co^{III}(acacen)_2(CH_3)$].[11] The shortness of the bond in the present dacoda complex is surprising since the cobalt is bonded to a 2° carbon, and the bond is part of the strained Co–N(1)–C(1)–C(2) and Co–N(2)–C(3)–C(2) chelate rings. The strain in the four-membered rings, which is induced by the Co–C(2) bond, is manifested in rather severely distorted bond angles. The Co–N(1)–C(1) and the Co–N(2)–C(3) angles are 91.4 (2)° and 91.1 (2)°, respectively. In addition, the N(1)–C(1)–C(2) and the N(2)–C(3)–C(2) angles are 101.3 (3)° and 101.2 (3)°, respectively, while the C(1)–C(2)–C(3) angle is 119.3 (3)°.

Scheme I



Although many Co(III)–alkyl bonds are known from B_{12} and related organocobalt chemistry,[10] most are found in complexes containing highly unsaturated ligands. The only exceptions may be the Co(III)–alkyl complexes of [14]aneN_4 (cyclam) and Me_6[14]aneN_4, which were prepared by Endicott et al.[12] To our knowledge this paper is the first report of a stable Co(III)–alkyl complex with a polyamine carboxylate-type ligand. This structure is also somewhat unique in that the alkyl group is rigidly chelated to the Co(III) center,[13] which certainly lends to the stability of the complex.

A number of observations have been made concerning the preparation of **5**: (1) An oxidant (e.g., H_2O_2 or PbO_2) is required. (2) A relatively strong field ligand, L (CN^-, NO_2^-, SO_3^{2-}, or NH_3), is essential for production of the organocobalt(III) species. (3) The reaction is catalytic in L. (4) Changes in the electronic absorption spectra are consistent with coordination of L to Co(II)–dacoda prior to addition of an oxidant.[14] (5) When L = SO_3^{2-}, an isolable Co(III) agostic intermediate, **3**, is obtained, which can be converted to **5** by MeO^-/MeOH. The structure of the agostic intermediate **3** (L = SO_3^{2-}) has been confirmed by X-ray crytallography.[15]

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(7) Octahedral coordination is the predominant geometry for Co(III) complexes, although there are several examples of five- and four-coordinate complexes: (a) Fikar, R. J.; Koch, S. A.; Millar, M. M. *Inorg. Chem.* **1985**, *24*, 3311. (b) Dorfman, J. R.; Rao, C. P.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 453. (c) Bailey, N. A.; McKenzie, E. D.; Worthington, J. M. *J. Chem. Soc., Dalton Trans.* **1977**, 763 and references therein. (d) Collins, T. J.; Richmond, T. G.; Santersiero, B. D.; Treco, B. G. R. T. *J. Am. Chem. Soc.* **1986**, *108*, 2088.

(8) **5**: ^1H NMR (D_2O) δ 4.0 (m, 1 H, H(2)), 3.74–3.49 (m, 4 H), 2.94 (AB quartet, 4 H, glycinate H, J = 16.3 Hz), 2.50–1.85 (m, 6 H); UV–vis 510 nm (155), 370 (sh), 339 (168). Anal. Calcd for $CoC_{10}H_{21}N_2O_7$: C, 35.30; H, 6.22; N, 8.23. Found: C, 35.33; H, 6.28; N, 8.24.

(9) Crystallographic data: orthorhombic space group $P2_12_12_1$ with a = 6.943 (1) Å, b = 12.940 (3) Å, c = 15.393 (4) Å, $\alpha = \beta = \gamma = 90.00°$, V = 1379.2 (5) $Å^3$, and ρ(calcd) = 1.64 g cm^{-3} for $Z = 4$. Solution of the structure by direct methods and Fourier techniques using the SHELXTL-84 (Sheldrick, G. SHELXTL Nicolet Analytical Instruments, 1984) solution package was followed by least-squares refinements which converged to a final unweighted R value of 0.028. All hydrogens were found on a ΔF map and were fixed except the hydrogens on C(2), O(5), and the waters of crystallization (W(1) and W(2)), which were refined. The resulting positions for these hydrogens are reasonable and only one hydrogen (H(2)) was found on the C(2) carbon atom (C(2)–H(2), 0.92 (4) Å). The remaining crystal data are presented as supplementary material.

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(14) Na[Co^{II}(dacoda)(NO_2)]·$0.5H_2O$ has been isolated. Anal. Calcd for $CoC_{10}H_{17}N_3O_{6.5}$: C, 32.89; H, 4.69; N, 11.51. Found: C, 32.79; H, 4.70; N, 11.24. $\mu_{eff} = 4.5\ \mu_B$ (25 °C).

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The above observations are consistent with the mechanism shown in Scheme I.[16] A key feature of this mechanism is the intermediacy of oxidized species **3** in which the C–H bond is activated for deprotonation by an agostic interaction. The dependence on L can be rationalized by considering the conditions necessary for an agostic interaction; specifically, an unfilled metal orbital directed at the C–H bond is needed, which in this case is the d_{z^2} orbital. Although almost all octahedral Co(III) (d^6) complexes are diamagnetic (low spin), and thus the d_{z^2} orbital is normally assumed to be empty, there are paramagnetic square-pyramidal pentacoordinate Co(III) complexes,[7c,18] with weak axial ligands such as Cl^-, Br^-, or I^- where presumably the d_{xy} and d_{z^2} orbitals contain a single electron each. If this were the case in $[Co^{III}(dacoda)L]^+$, where L is a weak field ligand, the d_{z^2} orbital would be occupied and there would be no agostic interaction to promote deprotonation of the C–H bond. The nature of L would also affect the redox potential of the oxidation depicted in Scheme I, with stronger field ligands increasing the oxidation potential. The loss of L in the last step of Scheme I is consistent with the strong trans influence of alkyl ligands (which is evidenced here by the long Co–OH_2 bond, 2.15 Å in **5**).

The overall reaction shown in Scheme I represents an electrophilic attack of low-spin Co(III) on the C–H bond of the coordinated dacoda ligand. There is precedence for electrophilic attack on aliphatic C–H centers by Co(III) species, as exemplified by the $Co(OAc)_3$ and $Co(OAc)_2/O_2$ systems[3b,19] which oxidize alkanes (although organometallic intermediates have not been isolated in this case). In addition, a number of metal complexes that are capable of C–H activation by electrophilic pathways have recently been described.[3b,20–24]

The results presented here further illustrate the importance of agostic interactions in promoting C–H reactivity.[2a,3b] This system demonstrates that the essential requirements of the agostic interaction, heretofore satisfied only by organometallic-type systems, can be met in an (aqueous) Werner-type complex with similar results in reactivity. Thus, activation of C–H bonds in a biological system in a similar fashion would appear to be plausible.

Acknowledgment. We gratefully acknowledge Professor J. P. Hunt for helpful discussions. The Nicolet X-ray diffraction system was acquired with the aid of NSF Grant CHE-8408407 and The Boeing Corp. The Nicolet 200-MHz NMR spectrometer was also acquired with the aid of The Boeing Corp. This investigation was supported in part by funds provided by Washington State University.

Supplementary Material Available: Details of the X-ray structure solutions for **5**, with listings of coordinates, thermal parameters, bond distances, and bond angles (5 pages); table structure factors for **5** (8 pages). Ordering information is given on any current masthead page.

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(15) The structure of $K[Co^{III}dacoda(SO_3)]\cdot 5H_2O$ has been refined to an unweighted *R* value of 0.051. Some disorder exists in the waters of crystallization. The Co–"agostic" H and C distances are 2.26 (5) and 2.524 (4) Å, respectively, while the Co–H–C angle is 93 (3)°. The "agostic" C–H distance is 0.98 (5) Å. Full details will be described elsewhere.

(16) Although the possibility of a free-radical mechanism is not ruled out,[17] this reaction takes place under aerobic conditions, and since dioxygen is a free-radical scavenger, this pathway seems unlikely.

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Jack Bean Urease (EC 3.5.1.5). 8. On the Inhibition of Urease by Amides and Esters of Phosphoric Acid

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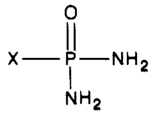
Our idea that phosphoramidate (**1**, $H_3N^+{-}PO_3^{2-}$) might be a substrate for urease led to the discovery in 1975 that it inhibits urease by virtue of stoichiometric coordination to active-site nickel ion.[1,2] Further, a large fraction of **1** is released intact upon reactivation of the inhibited enzyme under appropriate conditions.[3] Since that time, the inhibition of urease by amides and esters of phosphoric acid has been extensively pursued because of its potential application in agriculture,[4a] medicine,[4b] and veterinary science.[4c]

General structure **2** is illustrative of the range of compounds which has been investigated.[4,5] Although Kobashi and co-workers have reported that *N*-acylphosphoric triamides are degraded by urease to the corresponding carboxamide, ammonia, and inorganic phosphate,[6] no details of this work have been published and the chemistry of the urease inhibition has remained obscure.



$$X{-}P(=O)(NH_2){-}NH_2$$

2a, X = ArO
b, X = HO
c, X = H_2N
d, X = AlkC(O)NH
e, X = ArC(O)NH

We now adduce evidence that diamidophosphate [**2b**, $(H_2N)_2PO_2^-$] is the inhibitory species and that its interaction with the active site of urease must involve two isomeric complexes with active-site nickel ion. Moreover, we establish that phosphoramidate is a very poor substrate for the enzyme.

Phenyl phosphoramidate (**2a**, Ar = Ph, PPD), *N*-(3-methyl-2-butenyl)phosphoric triamide [**2d**, Alk = $(H_3C)_2C{=}CH$, MBPT], and phosphoric triamide (**2c**) each stoichiometrically inactivates urease, since the residual specific activity after reaction with excess urease in 0.05 M *N*-ethylmorpholinium chloride (NEM) buffer at pH 7.0 is within 5% or better of the predicted value $[(1 - [I]_0/[E]_0) \times$ initial specific activity$]$. The inactivation is rapid,[7] and the inactive enzyme slowly regains full activity.

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