phenylcyclopropyl)carbinyl radical (**11**) was prepared by standard methods from acid **10**.[2,3] Reaction of **8** (Scheme I) in the presence of thiophenol gave only 4-phenyl-1-butene (**14**). However, reactions of **8** in toluene in the presence of PhSeH gave acid **10** and small amounts of *trans*-2-methyl-1-phenylcyclopropane (**13**) in addition to **14**.[20] 3-Phenyl-1-butene, the ultimate product from cleavage of the C1–C3 bond in radical **11**, was not detected to the limit of our precision (<0.1%). Accurately calibrated GC measurements of the **13**:**14** ratio permitted determinations of the ratio of rate constants for ring opening and trapping of **11**.[20] With the assumption that the rate constants for trapping **11** are the same as those for trapping **4** (eq 2), the rate constants for ring opening of **11** were 3.7×10^{10} s^{-1} (–45 °C), 1.2×10^{11} s^{-1} (0 °C), and 1.8×10^{11} s^{-1} (20 °C).[21] The lifetime of radical **11** at 20 °C is 5–6 ps.[23]

In advance of this study, one might have questioned whether or not radical **11** would exist as a discrete intermediate. Further, it is likely that **11** cannot be detected by conventional direct methods. Production of **11** would typically require photolysis of a peroxy precursor to give an acyloxy radical followed by decarboxylation. Alkylacyloxy radical decarboxylations, while not especially well studied, apparently are at least an order of magnitude *slower* than the ring opening of **11**.[24] This means that attempts to study the kinetics of ring opening of **11** by direct observation of the formation of **12** probably would instead measure a rate-limiting decarboxylation step.[26] The "slow" decarboxylation step does not hinder the indirect method, however, as long as the acyloxy radical does not react completely with the trapping agent.

Benzeneselenol has been shown to be an especially fast trapping agent in this work with an ultimate kinetic resolution of about 1 ps at room temperature. We can envision its application, along with PTOC radical precursors, for the study of several fast first-order radical reactions including rearrangements and inversion processes.

Acknowledgment. We thank the National Science Foundation (CHE-8816365) for financial support.

Supplementary Material Available: Tables of product yields and k_r/k_T values for reactions of PhSeH in THF and in toluene (2 pages). Ordering information is given on any current masthead page.

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[20] Results with 0.05 M **8** in toluene: temperature, $[\mathrm{PhSeH}]_0$, yield (**13** + **14**), **14**/**13**, k_r/k_T: 20 °C, 1.6 M, 63%, 64.1, 102.6 M; 20 °C, 2.4 M, 58%, 47.5, 114.2 M; 0 °C, 1.4 M, 38%, 67.0, 93.8 M; 0 °C, 2.1 M, 41%, 44.5, 93.4 M; –45 °C, 0.9 M, 38%, 76.0, 68.4 M; –45 °C, 0.9 M, 35%, 72.0, 64.8 M; –45 °C, 1.6 M, 28%, 39.5, 63.2 M. This uncorrected, preliminary data[21] gave an Arrhenius function of $\log (k_r \cdot s) = 13.6\ (1) - 3.2\ (2)/2.3RT$. It will be of interest to determine if the apparent slightly positive ΔS^* value (2 eu) is real; radical **4** displays the expected $\Delta S^* = 0$.[2,8,9a]

[21] The k_r values for **11** actually are upper limits because the viscosities of the toluene solutions should be somewhat greater than those of the solutions used in the calibration studies due to the increased PhSeH concentrations. At 20 °C, a reduction in k_{diff} by a factor of 1.4 can be estimated.[22] This would reduce k_T, and thus k_r, by about 6%.[16]

[22] This estimate is based on results obtained in pulse gradient spin echo NMR measurements of diffusional coefficients for solutions containing PhSH.[7b]

[23] The rate constant for ring opening of **11** is more than 3 orders of magnitude faster than that of the cyclopropylcarbinyl radical.[8] The phenyl-substituted cyclopropylcarbinyl radical clocks[19] thus represent a new generation of "timing" reactions with exciting potential applications. Radical **11** will be an excellent probe because ring opening will predominate even when trapping reactions are diffusion limited. In principle, the ring opening can also compete in measurable amounts against the fastest unimolecular radical process because the decay of a transition state at 20 °C is only about 30 times faster.

[24] Acyloxy decarboxylations at ambient temperatures to give the stabilized radicals 9-methylfluorene-9-yl[25a] and benzyl[25b] have been reported to be 2×10^{10} s^{-1} and 5×10^{9} s^{-1}, respectively.

[25] (a) Falvey, D. E.; Schuster, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 7419. (b) DeCosta, D. P.; Pincock, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 8948.

[26] The direct approach is further complicated by the fact that photochemical production of the acyloxy radical might give a vibrationally excited intermediate that reacts before thermal equilibration is complete.[25a] In the indirect method used here, acyloxy radicals are almost entirely produced as ground-state species in radical chain reactions.

On the Mechanism of a New Metallacycle Annelation Reaction: Evidence for an Intramolecular Methoxy Group Transfer

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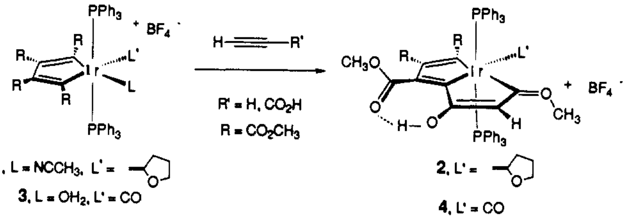
The preparation and elaboration of metallacycle complexes is of central importance for the application of this compound class to organic synthesis[1] and materials science.[2] In an effort to develop fundamental new modes of metallacycle reactivity, we have been exploring the chemistry of metallacyclopentadiene complexes.[3] One of the most surprising and mechanistically ambiguous metallacycle transformations to date is the high-yield conversion of an iridiacyclopentadiene complex, **1**, to a metallabicyclooctatrienone complex, **2**, upon reaction with propiolic acid.[4] The propiolic acid substrate has undergone a decarboxylation, and the two sp alkyne carbons have been incorporated into the new ring of **2**. In addition, a methyl or methoxy group has been transferred from the metallacycle α-substituent in **1** to an α-carbon of the newly formed ring in **2**. Detailed spectroscopic and labeling studies have led us to propose a remarkable new annelation mechanism which includes an intramolecular methoxy group transfer between two ligands.[5]



Complex **3** (50.5 mg, 0.044 mmol) and ethyne (0.17 mmol) react in CDCl$_3$ at 23 °C over the course of days to give a 98% isolated yield of **4**.[6] In order to elucidate the mechanism of the **3** to **4** conversion, we required access to **3-O**, selectively enriched with oxygen-18 at the carbonyl oxygen of the α-methoxycarbonyl substituent adjacent to the aquo ligand (Scheme I). We took advantage of our earlier observation that bis(acetonitrile) complex **5** reacts with methyl propiolate in the presence of ^{18}OH$_2$ to give regioselectively labeled **6-O** in 70% yield.[6-8] Removal of the CO

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[6] Complete spectroscopic and analytical data as well as X-ray crystallographic analysis data for **4** and spectroscopic data for **7** are provided as supplementary material.

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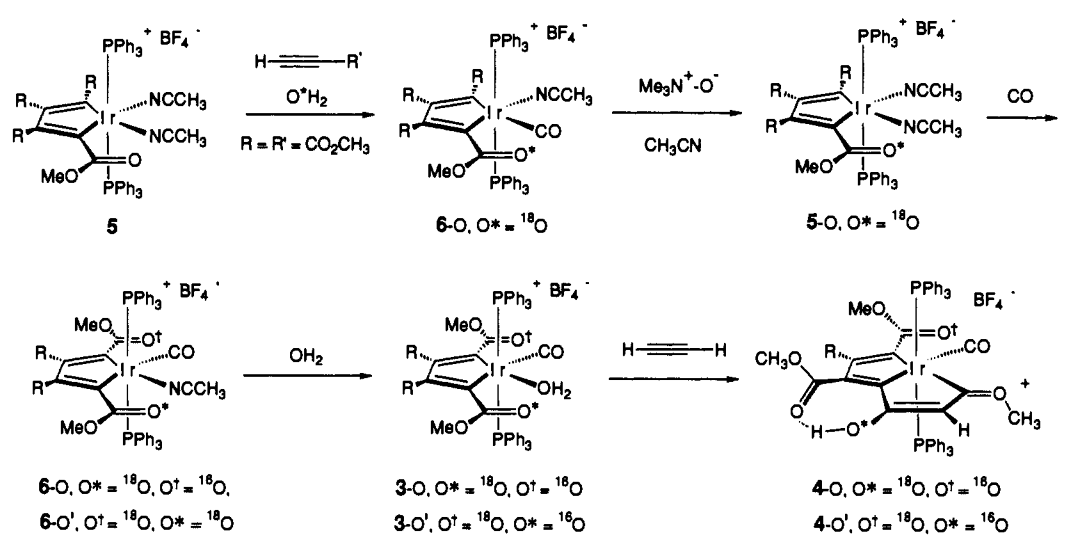
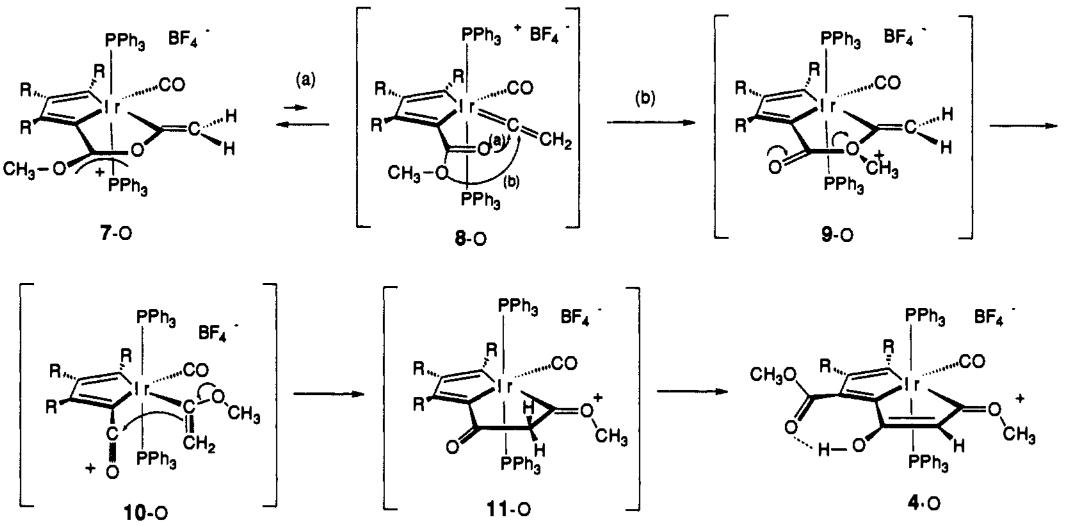
Scheme I



Scheme II



ligand with Me_3N^+–O^- in acetonitrile led quantitatively to **5**-O.[8] Readdition of CO gave a 1:1 ratio of **6**-O and **6**-O' (76% yield).[8] Exchange of OH_2 for CH_3CN gave the requisite starting materials, **3**-O and **3**-O', in a 1:1 ratio (92% yield).[8] In the ^{13}C NMR spectrum of the **3**-O/**3**-O' mixture, two resonances were observed for each of the carbonyl carbons of the α-methoxycarbonyl substituents: 172.564 ($COOCH_3$), 172.527 ($C^{18}OOCH_3$); and 168.940 ($COOCH_3$), 168.904 ($C^{18}OOCH_3$). Each set of resonances was in a ~1.4:1 intensity ratio indicative of ~42% enrichment at each site.[8]

The reaction of ethyne with **3**-O/**3**-O' in $CDCl_3$ was examined by ^1H and ^{13}C NMR spectroscopy (−29 °C) after ~18 min at 23 °C. The ^1H NMR spectrum indicated a mixture consisting of 10% **3**-O/**3**-O', 10% **4**-O/**4**-O', and 80% of a new compound, identified as **7**-O/**7**-O' (Scheme II).[6] In the ^1H NMR spectrum two broad doublets at δ 5.87 (1 H, $=CHH$) and 5.40 (1 H, $=CHH$) are attributed to **7**-O/**7**-O'. In the $^{13}C\{^1H\}$ NMR spectrum, complex **7**-O/**7**-O' gives rise to three resonances which exhibit an isotopic shift: singlets at 179.270 and 179.244 ppm (~1.4:1 ratio, $COOCH_3$ and $C^{18}OOCH_3$); singlets at 169.192 and 169.155 [~1.4:1 ratio, $((CH_3O)CO)$ and $((CH_3O)C^{18}O)$]; and triplets at 156.955 and 156.903 [~1.4:1 ratio, $(IrCO(=CH_2)$ and $IrC^{18}O(=CH_2))$]. The ^1H NMR spectrum after an additional 3.5 h at 23 °C indicated at 1:10 ratio of **7**-O/**7**-O' to **4**-O/**4**-O'. In the $^{13}C\{^1H\}$NMR spectrum (126 MHz, 14 °C), only two of the carbon resonances assigned to **4**-O/**4**-O' exhibited isotopic shifts: 192.123 and 192.110 (COH and $C^{18}OH$); 171.092 and 171.056 ($COOCH_3$ and $C^{18}OOCH_3$). When the reaction of **3** and ethyne was carried out in the presence of excess CD_3OD, there was no incorporation of deuterium into the methyl groups of **4**. Finally, a 1:1 mixture of **3** and $Ir[CR{=}CRCR{=}CR](PPh_3)_2(CO)(OH_2)^+BF_4^-$ (**3**-d_{12}, R = CO_2CD_3) undergoes reaction with ethyne to give **4** and **4**-d_{12}, with no crossover products. Taken together, these NMR spectroscopy/labeling results indicate that the methoxy group of the α-methoxycarbonyl ring substituent in **3** is transferred by an intramolecular process to the α-carbon of the newly formed ring in **4**. We propose the mechanism outlined in Scheme II for the **3** to **4** conversion. Initial formation of vinylidene intermediate **8**-O from **3**-O and acetylene has precedent in related systems.[6b,9] The carbonyl oxygen of the α-methoxycarbonyl ring substituent in **8**-O reversibly attacks the electrophilic vinylidene carbon to give **7**-O. In a slower step, the methoxy oxygen of the α-methoxycarbonyl group in **8**-O attacks the vinylidene carbon to form intermediate **9**-O. Fragmentation of **9**-O leads to a vinyl ether ligand and resonance-stabilized acylium ion as shown in **10**-O.[10] Condensation of the vinyl ether ligand and

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[8] Mass spectral analysis indicates the degree of oxygen-18 enrichment as follows. **6**-O: 1031 [$(M + 2 - BF_4 - CH_3CN)$, $^{18}O = 93\%$, $^{16}O = 7\%$]; 1003 [$(M + 2 - BF_4 - CH_3CN - CO)$, $^{18}O = 73\%$, $^{16}O = 27\%$]. **5**-O: 1003 [$(M + 2 - 2(CH_3CN))$, $^{18}O = 85\%$, $^{16}O = 15\%$]. **4**-O/**4**-O': 1057 [$(M + 2 - BF_4)$, $^{18}O = 85\%$, $^{16}O = 15\%$]. **3**-O/**3**-O': 1031 [$(M + 2 - BF_4)$, $^{18}O = 85\%$, ^{16}O 15%], 1003 [$(M + 2 - BF_4 - CH_3CN - CO)$, $^{18}O = 77\%$, $^{16}O = 23\%$]. All numbers ±10% due to inherent errors in the FAB MS method of analysis.

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acylium ion generates **11**-O, from which tautomerization gives **4**-O.

The chemistry of metallacycle complexes has been largely dominated by reactivity at the metal-carbon bonds. The mechanistic work described herein indicates that metallacycle substituents provide a rich source of new chemical reactivity and points the way to the further development of this unprecedented alkyne cyclization chemistry.

Acknowledgment. Support from the National Science Foundation (CHE-9005973) is gratefully acknowledged. The National Science Foundation (CHE8814866) and National Institutes of Health (RR04733) provided funds for the 500 MHz NMR utilized in this work. We also thank Dr. Ron New of the University of California, Riverside Mass Spectrometry Center, for obtaining the mass spectral analyses and Mr. J. Stankowski for the preparation of **3**-d_{12}. We are grateful to Johnson Matthey for a generous loan of precious metals.

Supplementary Material Available: Full spectroscopic and analytical data for compound **4** and spectroscopic data for **7**, listings of fractional coordinates, bond distances, bond angles, hydrogen atom coordinates, and thermal parameters for **4**, ^{13}C NMR spectra of isotopic shift resonances for **3**-O, **4**-O, and **7**-O, and mass spectral data for **3**-O, **4**-O, **4**/**4**-d_{12}, **5**-O, and **6**-O (53 pages); table of observed and calculated structure factors for **4** (28 pages). Ordering information is given on any current masthead page.

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Stereochemical Aspects of the Hydration of Carbohydrates. Kinetic Medium Effects of Monosaccharides on a Water-Catalyzed Hydrolysis Reaction

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The hydration characteristics of carbohydrates in aqueous solution represent an intriguing and challenging problem[2] and are of direct relevance for understanding the role of glycolipids and glycoproteins in molecular recognition.[3,4] Previous attempts to rationalize carbohydrate hydration have been couched in terms of hydration numbers,[5,6] the ratio of equatorial vs axial OH groups,[7,8] the anomeric effect,[9] the hydrophobic/hydrophilic index,[10] and the hydrophilic volume of the carbohydrate.[11] No comprehensive theory has yet emerged.

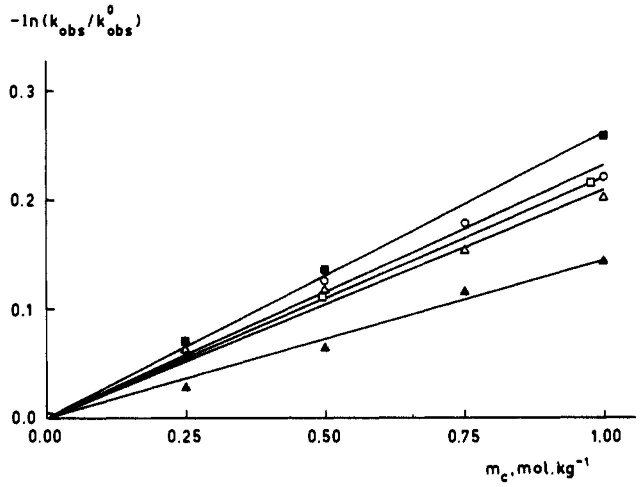
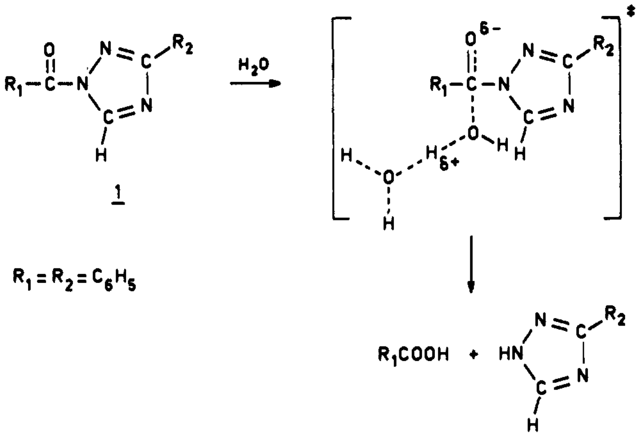


Figure 1. Plots of ln ($k_{\mathrm{obsd}}/k^{\circ}_{\mathrm{obsd}}$) vs molality of hexose for the neutral hydrolysis of **1** at 25 °C: D-glucose (△), D-mannose (○), D-allose (□), D-galactose (▲), and D-talose (■).

Scheme I



Herein we report a new endeavor to frame a picture of the hydration of monosaccharides as a function of their stereochemistry. To this end we have measured pseudo-first-order rate constants for the water-catalyzed hydrolysis of 1-benzoyl-3-phenyl-1,2,4-triazole (**1**) in aqueous solutions in the presence of 0-1.00 mol·kg^{-1} of a series of aldohexoses (**2a-e**), ketohexoses (**3a,b**), and aldopentoses (**4a-d**) (Table I). The neutral hydrolysis of **1** proceeds via an activated complex containing two water molecules in which three OH bonds are stretched (Scheme I).[12] As shown previously, medium effects of mono- and polyhydric alcohols on this reaction can be understood by considering hydration shell overlap effects between the alcohol and the initial and transition states of the hydrolytic process.[13] In a similar approach, we quantify the kinetic medium effect of a carbohydrate via eq 1,[14] in which k_{obsd} is the pseudo-first-order rate constant for hydrolysis of **1** in an aqueous carbohydrate solution (molality m_c) and $k^{\circ}_{\mathrm{obsd}}$ refers to $m_c = 0$. The number of water molecules

$$\ln (k_{\mathrm{obsd}}/k^{\circ}_{\mathrm{obsd}}) = (2/RT)G(\mathrm{C})m_c - n\Phi M_1 m_c \qquad (1)$$

in the transition state is n ($n = 2$), Φ is the practical osmotic

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