The most viable alternative to invoking $RX^{-}\cdot$ to account for our data is to suppose that the presence of NaX in the "cage" [Na^{+} :$TPE^{-}\cdot$ $R\cdot$ $Na^{+}X^{-}$] somehow affects the subsequent chemistry. Perhaps the most likely possibility is that ionic aggregation of NaX with sodium tetraphenylethylene species affects their reactivities. We have sought such effects by saturating :TPE:$^{2-}$ solutions with NaI prior to reactions with 5-hexenyl chloride and 5-hexenyl iodide.[11] In each case the reduction product yield (RCl, 29%; RI, 63%) was within experimental error of the value obtained without added NaI. Thus, this alternative to $RX^{-}\cdot$ is weakened.

When $RX^{-}\cdot$ escapes its geminate radical partner or is generated without a geminate radical partner (as in :$Naph^{-}\cdot$ reactions), its inevitable fate will be decomposition to $R\cdot$.[12] Thus, halogen effects will vanish in such cases.

We have been able to find in the literature very little evidence for or against alkyl halide anion-radicals as species of finite lifetimes in solution.[13,14] Our results are strongly suggestive, but not definitive, since a less attractive alternative hypothesis has not been definitely ruled out. However, our data suggest that future probes for $RX^{-}\cdot$ with alkali metal counterions in ethers should be designed to detect species with lifetimes near 10^{-10} s.

Acknowledgment. This work was supported by grants from the National Science Foundation.

References and Notes

(1) R. D. Roberts, Ph.D. dissertation, The University of Georgia, 1975.
(2) The experimental techniques were the same as in earlier works.[3] Analyses were by VPC using internal standards. 2-Methyltetrahydrofuran was chosen as the solvent because if affords adequate solubility and a large disproportionation equilibrium constant for NaTPE: $2NaTPE \rightleftarrows Na_2TPE + TPE$. ESR measurements indicate that [NATPE = :$TPE^{-}\cdot$] was about 10^{-6} M during our experiments, minimizing its chemical significance except in radical cage reactions (see Scheme I).
(3) (a) J. F. Garst and J. T. Barbas, *J. Am. Chem. Soc.*, **96**, 3239 (1974); (b) J. F. Garst and C. D. Smith, *ibid.*, **98**, 1520 (1976).
(4) J. F. Garst, *Acc. Chem. Res.*, **4**, 400 (1971).
(5) J. F. Garst, J. T. Barbas, and F. E. Barton, II, *J. Am. Chem. Soc.*, **90**, 7159 (1968).
(6) Alkyl halides used (reduction products) (number of experiments): 5-hexenyl chloride (1-hexene, methylcyclopentane) (9); pentyl chloride (pentane) (3); 1,4-dichlorobutane (cyclobutane) (7); pentyl bromide (pentane, decane, 1-pentene) (2); 1,4-dibromobutane (cyclobutane) (3); pentyl iodide (decane, pentane, 1-pentene) (3); 1,4-diiodobutane (cyclobutane, butane) (4). Indicated errors are standard deviations from the mean. Initial :TPE:$^{2-}$ concentrations were ca. 2×10^{-2} M, a stoichiometric excess over RX, upon which yields were based.
(7) R. M. Noyes, *Prog. React. Kinet.*, **1**, 129 (1961).
(8) T. Koenig and H. Fischer in "Free Radicals", J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, pp 157–189, Chapter 4.
(9) J. F. Garst, *J. Am. Chem. Soc.*, **97**, 5062 (1975).
(10) That :$TPE^{-}\cdot$ reacts with alkyl radicals to give almost exclusively alkylation products, as in Scheme I, was verified in studies of NaTPE reactions with alkyl halides in solvents where its disproportionation is not greatly favored.[1]
(11) NaI was generated in situ by the reaction of I_2 with :TPE:$^{2-}$ in 2-methyltetrahydrofuran.
(12) If the rate constant for decomposition of $RX^{-}\cdot$ is 10^{10} s^{-1}, as our data indicate, and if the rate constant for encounters is 10^{10} M s^{-1}, then for solutions 0.1 M or less in a potential reactant with $RX^{-}\cdot$, the decomposition of the latter will be at least ten times faster than *encounters*, much less reactions, with the potential reactant.
(13) Data cited by E. J. Hart and M. Anbar, "The Hydrated Electron", Wiley, New York, N.Y., 1970, pp 130–140, and references therein, in support of $RX^{-}\cdot$ as an intermediate of finite lifetime are equally well accounted for by an early transition state for the one-step process, $e_{aq}^{-} + RX \rightarrow R\cdot + X^{-}$.
(14) Data of P. P. Infelta and R. H. Schuler, *J. Phys. Chem.*, **76**, 987 (1972), from radiolyses of cyclohexane solutions of alkyl halides, can be interpreted in terms of a methyl chloride anion-radical with a lifetime near 3×10^{-8} s and a methyl bromide anion-radical with a lifetime not greater than 3×10^{-9} s. We are grateful to an anonymous referee for drawing our attention to this work. Our work implies halogen effects in the opposite order, i.e., longest lifetimes for alkyl iodide anion-radicals. However, the leaving groups in our systems are better viewed as sodium halide ion pairs NaX than as halide ions.

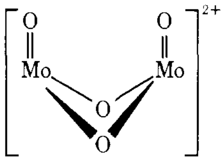
John F. Garst,* Rex D. Roberts, Joseph A. Pacifici
Department of Chemistry, The University of Georgia
Athens, Georgia 30602

Received September 17, 1976

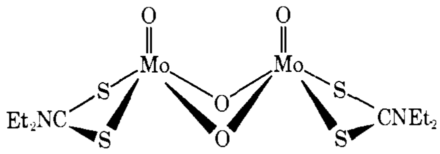
A Triply Bridged Binuclear Molybdenum(V) Compound Containing Two Kinds of Bridging Thiophenolate Groups

Sir:

The suggestion that one or more S atoms may be coordinated to molybdenum in molybdoenzymes has resulted in considerable interest in the coordination chemistry of molybdenum compounds of sulfur-containing ligands.[1] As part of our general studies of the synthesis, structure, and reactivity of molybdenum compounds, we have been investigating the reactions of complexes containing the $[Mo_2O_4]^{2+}$ core (**1**) with thiols.[2-6] Previous chemical and spectroscopic studies of some of the products of these reactions[2,4] led to the prediction that those compounds of stoichiometry $Mo_2O_3(SR')_2(S_2CNR_2)_2$ (**2**) contained a bridging oxo group and two bridging SR′ groups. Support for this concept came from the study of the reaction of an oxinato complex of **1** with 2-mercaptoethanol, which provided the first structurally defined example of a triply bridged binuclear Mo(V) complex.[7] Herein, we confirm stoichiometry **2** for R′ = Ph and R = Et by an x-ray structure determination and show that this red-orange diamagnetic product of the reaction[2,4] of $Mo_2O_4(S_2CNEt_2)_2$ (**3**)[3,8] with excess thiophenol is a triply bridged complex which contains two strikingly different bridging thiophenolate groups.



1



3

A sample of $Mo_2O_3(SPh)_2(S_2CNEt_2)_2$ (**4**) was prepared as previously described,[4] and single crystals were obtained from acetone. Preliminary precession photographs (Mo Kα) established that the crystals were triclinic with $a = 9.352$ (3), $b = 19.245$ (9), $c = 21.426$ (7) Å, $\alpha = 112.78$ (2), $\beta = 119.10$ (2), and $\gamma = 80.00$ (3)°. Space group $P\bar{1}$ was assumed and confirmed by successful refinement of the structure. The calculated and observed densities (1.68 and 1.66 g cm^{-3}, respectively) were consistent with four molecules of **4** and one molecule of acetone per unit cell. This formulation required

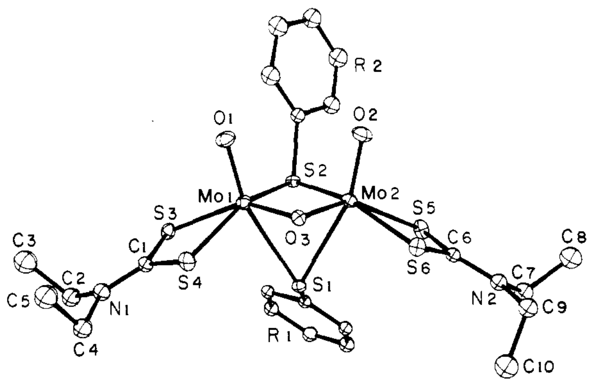


Figure 1. Perspective view of one of the molecules of **4**. The other molecule of **4** in the asymmetric unit has the same coordination environment about the Mo atoms, but slightly different conformations of the ethyl groups of the dithiocarbamate ligands.

Table I. Selected Interatomic Distances (Å) and Angles (deg)[a]

Molecule **1**				Molecule **2**[b]			
Atoms	Distance	Atoms	Angle	Atoms	Distance	Atoms	Angle
Mo(1)-Mo(2)	2.683 (2)	Mo(1)-S(1)-Mo(2)	59.89 (7)	Mo(3)-Mo(4)	2.672 (2)	Mo(3)-S(7)-Mo(4)	59.66 (7)
Mo(1)-O(1)	1.683 (9)	Mo(1)-S(2)-Mo(2)	65.01 (9)	Mo(3)-O(4)	1.684 (8)	Mo(3)-S(8)-Mo(4)	64.86 (8)
Mo(2)-O(2)	1.683 (9)	Mo(1)-O(3)-Mo(2)	83.7 (3)	Mo(4)-O(5)	1.677 (7)	Mo(3)-O(6)-Mo(4)	80.2 (3)
Mo(1)-O(3)	2.006 (8)	S(1)-Mo(1)-S(2)	70.8 (1)	Mo(3)-O(6)	2.065 (7)	S(7)-Mo(3)-S(8)	70.8 (1)
Mo(2)-O(3)	2.015 (8)	S(1)-Mo(2)-S(2)	71.0 (1)	Mo(4)-O(6)	2.085 (8)	S(7)-Mo(4)-S(8)	70.5 (1)
Mo(1)-S(1)	2.702 (3)	S(1)-Mo(1)-O(3)	73.2 (2)	Mo(3)-S(7)	2.681 (3)	S(7)-Mo(3)-O(6)	74.2 (2)
Mo(2)-S(1)	2.673 (3)	S(1)-Mo(2)-O(3)	73.8 (2)	Mo(4)-S(7)	2.691 (3)	S(7)-Mo(4)-O(6)	73.6 (2)
Mo(1)-S(2)	2.487 (3)	S(2)-Mo(1)-O(3)	106.1 (2)	Mo(3)-S(8)	2.490 (3)	S(8)-Mo(3)-O(6)	107.9 (2)
Mo(2)-S(2)	2.505 (3)	S(2)-Mo(2)-O(3)	105.2 (2)	Mo(4)-S(8)	2.493 (3)	S(8)-Mo(4)-O(6)	107.1 (2)
Mo(1)-S(3)	2.501 (4)	O(1)-Mo(1)-S(1)	163.3 (4)	Mo(3)-S(9)	2.472 (3)	O(4)-Mo(3)-S(7)	160.3 (3)
Mo(1)-S(4)	2.452 (4)	O(2)-Mo(2)-S(1)	158.7 (4)	Mo(3)-S(10)	2.452 (3)	O(5)-Mo(4)-S(7)	159.4 (3)
Mo(2)-S(5)	2.465 (4)	S(3)-Mo(1)-S(4)	70.5 (1)	Mo(4)-S(11)	2.474 (3)	S(9)-Mo(3)-S(10)	71.4 (1)
Mo(2)-S(6)	2.441 (4)	S(5)-Mo(2)-S(6)	71.3 (1)	Mo(4)-S(12)	2.440 (3)	S(11)-Mo(4)-S(12)	71.4 (1)

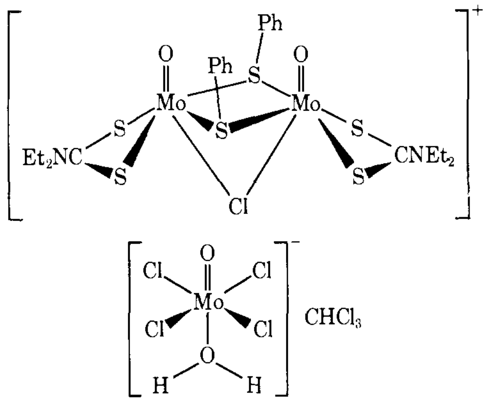
[a] The standard deviation of the least significant figure is given in parentheses. [b] Numbering of atoms in molecule **2** is continued in the same order as in molecule **1**.

that there be two crystallographically independent molecules of **4** and that the acetone molecule be disordered about a symmetry center. A total of 8820 reflections having $2\theta \leq 50°$ and $F_0^2 \leq 3\sigma(F_0^2)$ was collected on a Picker FACS-I diffractometer using graphite monochromated Mo Kα radiation and the θ-2θ scan technique. The data were corrected for absorption and the positions of the Mo atoms were located by direct methods. The remaining nonhydrogen atoms were located by subsequent least-squares refinement and difference electron density maps. In the final refinements the Mo, S, and O atoms of **4** were refined anisotropically and the phenyl rings were treated as rigid groups to give $R_1 = 0.057$ and $R_2 = 0.079$.[9]

A perspective view of one of the molecules of **4** is shown in Figure 1. The two Mo atoms are triply bridged by an oxo group and two SPh ligands as originally suggested.[2,4] However, the two bridging SPh ligands are strikingly different. One of the bridging SPh ligands is cis to the terminal oxo group of each Mo atom, whereas the other bridging SPh ligand is trans to the terminal oxo group of each Mo atom. The bond distances for the inner coordination sphere (Table I) show that the two types of bridging Mo-S distances differ by ~0.2 Å. Another interesting feature of the bridging system is the near planarity of the Mo(1), S(2), O(3), Mo(2) moiety. The dihedral angle between planes S(2)-Mo(1)-O(3) and S(2)-Mo(2)-O(3) is 181°. The Mo···Mo distance is 2.678 (9) Å.

The ^{1}H NMR spectrum of **4** in $CDCl_3$ at room temperature shows two kinds of phenyl groups and two ethyl resonances of equal intensity, indicating that structure **4** persists in solution at room temperature. The spectrum also confirms the presence of one acetone of crystallization per four molecules of **4**. The ^{1}H NMR spectrum of **2** with R′ = Me and R = Et shows two widely separated (δ 1.57 and 2.87) methyl signals, suggesting a structure similar to **4**. The IR spectrum of **4** shows a ν(Mo=O) doublet[10] at 948 and 930 cm^{-1}, shifted from 973 and 956 cm^{-1} in **3**. Other members of **2** show doublets at 936 and 918 cm^{-1} (R′ = Me, R = Et) and 933 and 920 cm^{-1} (R′ = R = Et). The last two complexes also have a band at 695 cm^{-1}, which we tentatively assign to ν(MoOMo) by comparison with the spectra of related variously bridged Mo(V) dimers.[10]

Trace amounts of water readily cause **4** and its alkyl analogues to revert to **3**, a reaction promoted by the presence of pyridine. Prolonged exposure of **4** to $CHCl_3$ results in a complicated reaction. One of the products is a green crystalline material shown to be **5** by an x-ray structure determination.[6] The cation of **5** is triply bridged by a Cl atom and two *equivalent* SPh ligands.[11] The details of this unusual $CHCl_3$ reaction of **4** which results in rearrangement of the bridging thiophenolate groups remain unknown.



5

The facile formation of **4** from the reaction of **3** with thiophenol supports the suggestion[7] that triply bridged dimeric complexes may be a common feature of the chemistry of oxomolybdenum(V). The reactivity of **4** toward water and $CHCl_3$ further suggests that triply bridged binuclear species may also be important intermediates in reactions of Mo(V) complexes.

Acknowledgment. We thank Mr. K. Haller for computational assistance. This work was supported in part by Grant ES-00966 from the National Institutes of Health. We gratefully acknowledge the University of Arizona Computer Center for an allocation of computer time.

References and Notes

(1) For recent reviews of the coordination chemistry of Mo related to molybdoenzymes see: R. A. D. Wentworth, *Coord. Chem. Rev.*, **18**, 1 (1976); E. I. Stiefel, *Prog. Inorg. Chem.*, **22**, 1 (1977).

(2) W. E. Newton, J. L. Corbin, and J. W. McDonald, Abstracts, 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974, INOR 35.

(3) W. E. Newton, J. L. Corbin, D. C. Bravard, J. E. Searles, and J. W. McDonald, *Inorg. Chem.*, **13**, 1100 (1974).

(4) W. E. Newton, G. J.-J. Chen, and J. W. McDonald, *J. Am. Chem. Soc.*, **98**, 5387 (1976).

(5) J. W. McDonald, J. L. Corbin, and W. E. Newton, *Inorg. Chem.*, **15**, 2056 (1976).

(6) G. Bunzey, J. H. Enemark, J. I. Gelder, K. Yamanouchi, and W. E. Newton, in "Proceedings of the Climax Second International Symposium on the Chemistry and Uses of Molybdenum", P. C. H. Mitchell, Ed., Climax Molybdenum Co., London, in press.

(7) J. I. Gelder, J. H. Enemark, G. Wolterman, D. A. Boston, and G. P. Haight, *J. Am. Chem. Soc.*, **97**, 1616 (1975).

(8) L. Ricard, C. Martin, R. Wiest, and R. Weiss, *Inorg. Chem.*, **14**, 2300 (1975).

(9) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = [\Sigma w|F_o| - |F_c|^2/\Sigma wF_o^2]^{1/2}$.

(10) W. E. Newton and J. W. McDonald in ''Proceedings of the Climax Second International Symposium on Chemistry and Uses of Molybdenum, P. C. H. Mitchell, Ed., Climax Molybdenum Co., London, in press.

(11) Compound **5** has Mo•••Mo = 2.822 (2) Å and a dihedral angle between the two SPh–Mo–SPh planes of 182°.

Katsumoto Yamanouchi, John H. Enemark*
*Department of Chemistry, University of Arizona
Tucson, Arizona 85721*

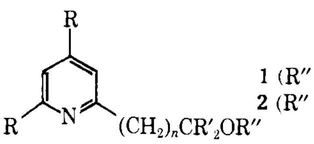
John W. McDonald, W. E. Newton
*Contribution No. 586
Charles F. Kettering Research Laboratory
Yellow Springs, Ohio 45387*

Received October 29, 1976

Platinum(II)-Catalyzed Alcohol Acetylations by N-Acetylimidazole

Sir:

In our search for template reactions where two reactants are coordinated simultaneously to a metal ion, prior to reaction,[1-5] we have investigated the catalysis by platinum(II) complexes of the acetylation of pyridinic alcohols (**1**) by *N*-acetylimidazole (AcIm) expecting an activation of the coordinated AcIm and an induced proximity between the reactants involved in a ligand exchange on the transition metal.



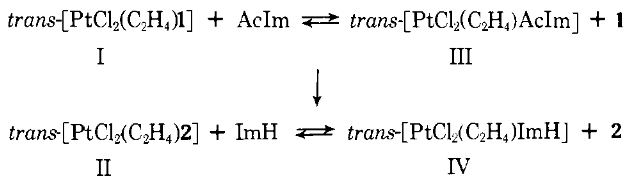
1 (R'' = H)
2 (R'' = COCH₃)

	n	R	R'
a	1	CH₃	H
b	1	H	H
c	2	CH₃	H
d	2	CH₃	CH₃
e	3	CH₃	H
f	6	CH₃	H

trans-$[\mathrm{PtCl_2(C_2H_4)}\,\mathbf{1}]$ I
trans-$[\mathrm{PtCl_2(C_2H_4)}\,\mathbf{2}]$ II
trans-$[\mathrm{PtCl_2(C_2H_4)(AcIm)}]$ III
trans-$[\mathrm{PtCl_2(nBu_3P)(AcIm)}]$ V

We have found that while no acetylation reaction takes place between alcohols **1** and pure AcIm in chloroform at room temperature, this reaction occurs when either one of the two reactants is initially bound in an olefinic complex of platinum(II), according to Scheme I. For instance ^{1}H NMR monitoring of the reaction starting from Ic + AcIm or III + **1c** ($CDCl_3$) shows that a fast ligand exchange first occurs, within mixing time, between AcIm and the pyridinic group of alcohol **1c**, leading to an equilibrium largely in favor of bound AcIm (ca. 80:20 at 32 °C); then the acetylation reaction gives a new equilibrium in which complex IV and the free acetate **2c** largely predominate (>95%).

Scheme I



$$\underset{\mathrm{I}}{trans\text{-}[\mathrm{PtCl_2(C_2H_4)}\mathbf{1}]} + \mathrm{AcIm} \rightleftharpoons \underset{\mathrm{III}}{trans\text{-}[\mathrm{PtCl_2(C_2H_4)AcIm}]} + \mathbf{1}$$

$$\downarrow$$

$$\underset{\mathrm{II}}{trans\text{-}[\mathrm{PtCl_2(C_2H_4)}\mathbf{2}]} + \mathrm{ImH} \rightleftharpoons \underset{\mathrm{IV}}{trans\text{-}[\mathrm{PtCl_2(C_2H_4)ImH}]} + \mathbf{2}$$

The yields, reaction times, and rate constants of the acetylation reactions of several alcohols in the presence of a stoichiometric amount of Pt(II) are compared in Table I.

Pt(II) behaves as a superacid catalyst toward nucleophilic attack of AcIm by the alcohols,[7] but, when AcIm is bound to Pt(II) in complex III, there is no acetylation of a primary alcohol in the absence of base (ligand) (expt 8). In the presence of *s*-collidine the acetylation takes place and is faster the higher the proportion of *s*-collidine (expt 9, 10). (There is no acetylation reaction with **3** + AcIm + P_{246} 1:1:1.) The acetylation reaction is faster with the pyridinic alcohols **1** and depends on the *n* value (expt 1–2, 4, 6, 7). The best result is obtained for $n = 2$ (expt 4): $k_4{:}k_1 = 4.05$; $k_4{:}k_6 = 3.2$; $k_4{:}k_7 = 44$. It is noteworthy that Pt(II) allows a slow but quantitative acetylation of the tertiary alcohol **1d** (expt 5). The influence of the chain length of the pyridinic alcohols **1** could be related to the expected template effect resulting from the observed ligand exchange between alcohols **1** and AcIm or to intramolecular general base catalysis of the reaction by the pyridinic group. The following results support the second proposition. In chloroform a slow reaction can be initiated between alcohols **1** and AcIm by addition of acetic acid;[8] the reactions of various alcohols **1** with AcIm and AcOH, 0.16 M each, give the fol-

Table I. Stoichiometric Acetylation of Alcohols **1a–1f** and Phenyl-3-propanol (**3**) by AcIm in the Presence of Pt(II)[6]

	Reaction	Concn of reactants in $CDCl_3$, M[a]	Acetate yield, %[b]	Reaction time, h (23 °C)[c]	10^3k, $M^{-1}\,s^{-1}$,[f] 23 °C
(1)	Ia + AcIm (*n* = 1)	0.16	62	0.78	3. ± 0.4
(2)	III + **1a** (*n* = 1)	0.16	66	0.80	3.8 ± 0.4
(3)	III + **1b** (*n* = 1)	0.16	52.4	7.5	0.24 ± 0.02
(4)	Ic + AcIm (*n* = 2)	0.16	87.5	0.43	15 ± 1.5
(5)	Id + AcIm (*n* = 2)	0.25	100	312[d]	
(6)	Ie + AcIm (*n* = 3)	0.16	85	1.4	4.7 ± 0.5
(7)	If + AcIm (*n* = 6)	0.16	51	5.5	0.34 ± 0.03
(8)	III + **3** (1:1.2)	0.25	ε[g]	144[d]	
(9)	III + **3** + P_{246}[h] (1:1:0.1)	0.25	32	21[d]	
(10)	III + **3** + P_{246}[h] (1:1:1)	0.26	80	21[d]	
(11)	III + **3** + Et_3N (1:1:1)	0.25	50	0.33[c]	
			70	2.8	
(12)	V + **3** + Et_3N (1:1:1)	0.23	50	0.67[e]	
			70	1.08	
(13)	V + **1c** (*n* = 2)	0.16	74	3.9	0.93 ± 0.1

[a] When the reactions are not stoichiometric for each reactant, Pt complex concentration is given. [b] Results from at least two runs, determined by integration of the ^{1}H NMR signals of the $-CH_2-$ α to OAc and the ImH 2-H proton in the case of primary acetates, and of the OAc methyl signal in the case of **2d**. [c] The fast reactions are monitored by ^{1}H NMR, at 23 °C, on a Bruker WH 90 working in FT mode, using tape FID's recording when necessary; the other reactions are run at either [d]23 °C and the NMR spectra recorded on a Varian A60 (insert temp 32 °C), or [e] 33 °C in the insert of a varian EM 390. [f] Second-order rate constants determined by linear regression ($r > 0.992$ with at least six points and up to 50% conversion). [g] Acetate detected by NMR, but <5% yield. [h] P_{246} = 2,4,6-trimethylpyridine (*s*-collidine).