Table I. Spectral Data for Alkynyl Tosylates **6**

$$H_3C-\!\!\underset{5}{\overset{}{\langle}}\!\!\underset{4}{\overset{3}{\bigcirc}}\!\!\underset{1}{\overset{2}{\rangle}}\!\!-SO_2O\overset{6}{C}\!\equiv\!\overset{7}{C}R$$

compd	R	IR,[a] cm^{-1}	mass spectrum,[b] m/e (%)	^{1}H NMR,[c] δ	^{13}C NMR,[d] δ
6a	CH$_3$	2280 (C≡C), 1595 (Ar), 1395 (SO$_2$), 1215 (d), 1185 (d, SO$_2$), 810 (para disub Ar), 685 (≡COS)	251 (2.2, M + 41), 239 (3.0, M + 29), 225 (1.8, M + 15), 211 (100, M + 1), 185 (27), 157 (72), 155 (31), 139 (35)	7.71 (d, J = 8 Hz, 2 H, H$_2$), 7.24 (d, J = 8 Hz, 2 H, H$_3$), 2.35 (s, 3 H, H$_5$), 1.59 (s, 3 H, H$_8$)	148.2 (C$_1$), 130.9, 130.6 (C$_4$), 129.7, 77.9 (C$_6$), 44.1 (C$_7$), 22.0 (C$_5$), 1.6 (C$_8$)
6b	n-C$_4$H$_9$	2275 (C≡C), 1594 (Ar), 1395 (SO$_2$), 1185 (d, SO$_2$), 814 (para disub Ar), 690 (≡COS)	294 (3.3, M + 42), 281 (2.1, M + 29), 267 (8.3, M + 15), 253 (11.2, M + 1), 251 (11.5, M − 1), 155 (100), 139 (61), 97 (21.3, C$_6$H$_9$O), 91 (49), 85 (72)	7.87 (d, J = 8.2 Hz, 2 H, H$_2$), 7.44 (d, J = 8.7 Hz, 2 H, H$_3$), 2.48 (s, 3 H, H$_5$), 2.10 (t, J = 5.9 Hz, 2 H, H$_8$), 1.42–1.21 (m, 4 H, H$_{9,10}$), 0.85 (t, J = 7.3 Hz, 3 H, H$_{11}$)	148.2 (C$_1$), 130.8, 130.6 (C$_4$), 129.8, 79.2 (C$_6$), 48.4 (C$_7$), 31.1, 22.1, 22.0, 16.9, 13.7
6c	C$_6$H$_5$	2260 (C≡C), 1596 (Ar), 1390 (d, SO$_2$), 1185 (d, SO$_2$), 810 (para disub Ar), 685 (≡COS)		7.96 (d, J = 8.5 Hz, 2 H, H$_2$), 7.46 (d, J = 8.1 Hz, 2 H, H$_3$), 7.31 (s, 5 H, H$_{9-13}$), 2.48 (s, 3 H, H$_5$)	148.3 (C$_1$), 131.9, 130.4 (2 C), 129.4, 128.6 (2 C), 120.8 (C$_8$), 87.2 (C$_6$), 48.2 (C$_7$), 21.7 (C$_5$)

[a] Neat with **6a–c** as Nujol mull. [b] Chemical ionization, CH$_4$ ionizing gas. [c] All spectra run in CD$_2$Cl$_2$, **6a** at 90 MHz, **6b** at 300 MHz, **6c** at 80 MHz and at −50 °C. [d] All spectra run in CD$_2$Cl$_2$ at 75 MHz, **6c** at −57 °C.

Scheme III
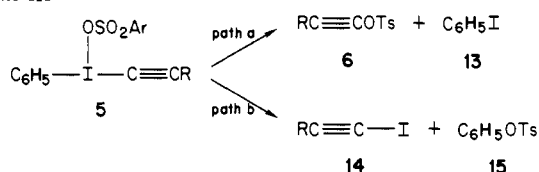
electronic effects of sulfonates and in particular a σ_p = +0.29 and σ_I = +0.54 but a σ_R = −0.21 for the tosylate group.

Further proof for the structures of **6** comes from methanolyses and hydrogenation as shown in Scheme II. Reaction with basic methanol gives saturated esters **9**, presumably via ketenes RCH=C=O or ketene equivalents RC≡C—O$^-$, along with methyl tosylate **10**, identical in all respects with authentic materials prepared by standard procedures. Likewise hydrogenation affords saturated tosylates **11** identical with authentic samples prepared, from the appropriate alcohols **12** and tosyl chloride, by standard procedures. Hence there is no doubt about the structure of these alkynyl sulfonate esters.

Decomposition of **5** to **6** deserves further comment. As Scheme III indicates there are two modes of decomposition for the hypervalent[11] 10-I-3 species **5**. Path a gives the desired esters **6** along with iodobenzene **13**, whereas path b results in iodoalkynes **14** along with phenyl tosylate **15**. In a formalistic sense both pathways represent ligand—ligand couplings in a hypervalent nonmetallic species,[11] analogous to the well-known reductive eliminations in organometallic chemistry. It is difficult to predict a priori which pathway should predominate. Preliminary studies indicate that thermolyses[12] or photolyses[12] of **5c** favors path b whereas simple stirring with CuOTf favors the desired path a. We do not understand this dichotomy of behavior and the mechanism of decomposition of **5** is under active investigation.

In summary, we have developed a mild, simple, general means of synthesizing novel alkynyl tosylates from readily available precursors via hypervalent iodine intermediates. Alkyl-substituted acetylenic sulfonates **6a** and **6b** are stable, nearly colorless oils, with characteristic, consistent spectral properties. The full scope of this methodology along with the mechanism involved are under active investigation as are the reactions and chemistry of these

unique alkynyl sulfonates and will be the subject of future reports.

Thermodynamic and Kinetic Properties of the Metaphosphate Anion, PO$_3^-$, in the Gas Phase

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Whereas PO$_3^-$ is proposed to be a reactive intermediate in solution, we report here that PO$_3^-$ is thermodynamically stable and undergoes no chemical reactions in the gas phase.

The metaphosphate anion, PO$_3^-$, was first suggested as an intermediate in the aqueous hydrolysis of phosphate esters some 30 years ago,[3] and this possibility has been investigated vigorously ever since.[4] The metaphosphate anion has proved to be elusive, with, even today, only indirect evidence for its presence in solution, and a plausible explanation is that it reacts too fast to be observed.[5] Recent studies provide evidence for "free" PO$_3^-$ in some systems[6] but not in others.[7]

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(2) Air Force Geophysics Scholar.
(3) Butcher, W. W.; Westheimer, F. H. *J. Am. Chem. Soc.* **1955**, *77*, 2420. Barnard D. W. C.; Bunton, C. A.; Llewellyn, D. R.; Oldham, K. G.; Silver, B. L.; Vernon, C. A. *Chem. Ind. (London)* **1955**, 760.
(4) Westheimer, F. H. *Chem. Rev.* **1981**, *81*, 313.
(5) See, for example, discussion following: Jencks, W. P. *Brookhaven Symp. Biol.* **1962**, *15*, 134.
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(7) Skoog, M. T.; Jencks, W. P. *J. Am. Chem. Soc.* **1983**, *105*, 3356; **1984**, *106*, 7597. Bourne, N.; Williams, A. *Ibid.* **1983**, *105*, 3357; **1984**, *106*, 7591. Buchwald, S. L.; Friedman, J. M.; Knowles, J. R. *Ibid.* **1984**, *106*, 4911.

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(11) For an excellent review on hypervalent nonmetallic species, see: Martin, J. C. *Science (Washington, D.C.)* **1983**, *221*, 509.
(12) Thermolyses were carried out in refluxing benzene and photolyses in chlorofom with a Hanovia lamp equipped with a Pyrex filter. The resulting products C$_6$H$_5$C≡CI and **15** were identified by comparison with authentic materials. C$_6$H$_5$C≡CI was made by reaction of C$_6$H$_5$C≡CLi with I$_2$.

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Communications to the Editor

Table I. Comparison of the Thermodynamic Properties of NO_3^- and PO_3^- and of Associated Nitrogen and Phosphorus Species

property	nitrogen species (X = N)	phosphorus species (X = P)
$\Delta H_f^\circ(XO_3)$	-17 ± 5^a	-78 ± 25^b
$\Delta H_f^\circ(XO_3^-)$	-73 ± 2	-190 ± 8^c
$\Delta H_f^\circ(HXO_3)$	-32	-135 ± 15^d
EA(X)	<0	17
EA(XO)	0.5 ± 0.2	25
EA(XO$_2$)	53 ± 7	76 ± 5^e
EA(XO$_3$)	92^f	113 ± 30^c
$\Delta H^\circ(HXO_3 \rightarrow H^+ + XO_3^-)^g$	324 ± 2	$314 (+1, -15)^h$

^{a} All values in kcal/mol; enthalpies refer to 300 K. Unless indicated otherwise, data from ref 13. ^{b} Reference 9b. ^{c} Reference 9c. ^{d} Derived from data in this table, supreceding the value given in ref 9b. ^{e} Reference 14. ^{f} Reference 15. ^{g} Written also as $\Delta H^\circ_{acid}(HXO_3)^{13}$ and $HD(HXO_3)$.^{16} ^{h} Derived from kinetic data on reaction 5, Table II.

In contrast, the metaphosphate anion *has* been observed in the gas phase as a stable species. The PO_3^- ion has been identified in the mass spectra of various pesticides,[8] in phosphate-doped plasmas,[9] in fission-fragment ionization of phosphates,[10] and in the mass spectra of phosphoric acid, adenosine 5'-monophosphate,[11] and various phosphotriesters.[12]

We report here experimental measurements of some thermodynamic and kinetic properties of PO_3^- and the comparison of these with the properties of its nitrogen congener, NO_3^-.

Studies of phosphate-doped plasmas have yielded estimates of the thermochemistry of PO_3^- and related species.[9] When phosphate is added as a trace component (mole fraction of P $\sim 10^{-4}$) to the exhaust stream of a methane/oxygen/air combustor, mass spectrometric detection identifies the major negative ion as PO_3^- at temperatures below 2000 K.[9b] Modeling of separate conductivity measurements then sets the heat of formation of PO_3^- to be -190 ± 8 kcal/mol.[9c] Estimates of the heat of formation of PO_3 are less certain (Table I)[9b] but, nevertheless, require PO_3 to have a large electron affinity (~ 5 eV) exceeding that of NO_3 by ~ 1 eV. Comparison of the thermochemical properties in Table I of various phosphorus compounds and their nitrogen congeners reveals parallel and monotonic trends. Of particular interest is the similarity of PO_3^- to NO_3^-, with PO_3^- showing even greater stability than NO_3^-, which is itself so stable that it is the terminal ion in the earth's mesosphere.[17] The low heat of formation of PO_3^- and the large electron affinity of PO_3 emphasize that PO_3^- *is a species of low chemical potential.* As such, it will feature strongly not just in the plasmas that yielded the thermochemistry reported in Table I but generally in the mass spectra of phosphites, phosphates, etc.

The data in Table II allow the calculation of a property of direct interest to chemists—the heat of deprotonation[16] of HPO_3—and this is a direct measure of the gas-phase or intrinsic acidity of HPO_3 and, hence, of the basicity of PO_3^-. Kinetic measurements (discussed below) set an upper bound on the heat of deprotonation of HPO_3 of 314 kcal/mol, since PO_3^- fails to abstract a proton from HI. This sets HPO_3 in the following order of decreasing acid strength:[18] H_2SO_4, $HPO_3 >$ HI $>$ $CF_3COOH >$ HBr $>$

(8) Harvan, D. J.; Hass, J. R.; Busch, K. L.; Bursey, M. M.; Ramirez, F. Meyerson, S. *J. Am. Chem. Soc.* **1979**, *101*, 7409.

(9) (a) Wormhoudt, J. C.; Kolb, C. E. *NBS Spec. Publ.* (*U.S.*) **1979**, *No. 561*, 457. (b) Freedman, A.; Wormhoudt, J. C.; Kolb, C. E. *ACS Symp. Ser.* **1982**, *No. 179*, 601. (c) Unkel, W.; Freedman, A. *AIAA* **1983**, *21*, 1648.

(10) Field, F. H.; Chait, B. T., personal communication.

(11) Bruins, A. P., personal communication to S. Meyerson.

(12) Meyerson, S.; Harvan, D. J.; Hass, J. R.; Ramirez, F.; Marecek, J. F. *J. Am. Chem. Soc.* **1984**, *106*, 6877. This paper contains a listing of recent identifications of PO_3^- using a variety of negative ion techniques.

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(14) Wu, R. L. C.; Tiernan, T. O. *Bull. Am. Phys. Soc.* **1982**, *27*, 109. This supercedes earlier work. Miller, W. T. *J. Chem. Phys.* **1978**, *69*, 3709.

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(16) Moylan, C. R.; Brauman, J. I. *Annu. Rev. Phys. Chem.* **1983**, *34*, 187.

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(18) The acids are ranked in order of increasing heat of deprotonation.[13,16]

Table II. Comparison of Ionic Reaction Products and Rate Constants for NO_3^- and PO_3^- Reacting with a Series of Substrates

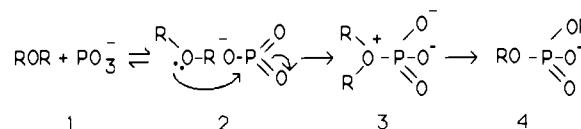| reactn	neutral substr	ionic reactant			
		NO_3^- prod	k^a	PO_3^- prod	k^a
1	H_2	NR		NR	<0.001
2	HCl	$NO_3^- \cdot HCl$	2.3^b	$PO_3^- \cdot HCl$	4.6
3	HBr	Br^-	c		
4	HI			$PO_3^- \cdot HI$	5.2
5	H_2O	$NO_3^- \cdot H_2O$	0.8	NR	<8
6	D_2S			NR	<1
7	NH_3			NR	<0.1
8	HNO_3	$NO_3^- \cdot HNO_3$	230^d	NR	<50
9	CH_3Cl			NR	<1
10	CH_3CN	$NO_3^- \cdot CH_3CN$	5.4^e	$PO_3^- \cdot CH_3CN$	2
11	CH_3OCH_3			NR	<2

^{a} Rate constants, measured at 300 K in helium buffer gas at 0.4 torr pressure, are expressed as third-order rate constants $k^{(3)}$ in units of 10^{-28} cm^6 molecule^{-2} s^{-1}. Note only reactions 2, 5, and 10 for NO_3^- as reactant are in the low-pressure region of three-body reactions. To express $k^{(3)}$ as a second-order rate constant $k^{(2)}$ in units of cm^3 molecule^{-1} s^{-1}, use $k^{(2)}/k^{(3)} = 1.3 \times 10^{16}$. NR means no reaction observed with upper bound given on $k^{(3)}$. Blanks indicate that the reaction was not studied. ^{b} Reference 20. ^{c} $k^{(2)} = 3 \times 10^{-10}$ (ref 21). ^{d} Reference 22. ^{e} Reference 23.

HNO_3. At the present time no substance is established to be a stronger acid than HPO_3; correspondingly, no base has been shown to be a weaker base than PO_3^-.

We have made a preliminary study of the chemical reactivity of PO_3^- using the Air Force Geophysics Laboratory selected-ion flow tube.[19] Metaphosphate ions have been prepared from two different sources (trimethyl phosphate, dimethyl phosphite); they are selected by mass, injected into a flow reactor, and reacted with gaseous reagents under controlled conditions. Results are given in Table II.

The noteworthy result is that PO_3^- *undergoes no chemical reactions* with a variety of reactants.[24] Its quality as an exceedingly weak base is shown by its inability to abstract a proton from HI or acids with larger heats of deprotonation (reaction 1–11). Predictably it fails to react as a nucleophile with methyl chloride (reaction 9). It shows no ability to react as an electrophile with the nucleophiles HCl, H_2O, NH_3, CH_3CN, and $(CH_3)_2O$ (reactions 2, 5, 7, 10, and 11). The reactions with dimethyl ether and water (reactions 11 and 5) are of particular interest—the latter because of its obvious relevance to the reaction of PO_3^- in aqueous solution. We write a mechanism

where R = Me and H for the two reactions, respectively.[25] With water, the formation of $H_2PO_4^-$ (**4**) is expected to be exothermic;[4] if formed, the formation would be rapid; thus the lack of reactivity

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(22) Viggiano, A. A.; Paulson, J. F.; Dale, F. *J. Geophys. Res.*, in press.

(23) Viggiano, A. A.; Paulson, J. F. In "Swarms of Ions and Electrons in Gases"; Lindinger, W., Mark, T. D., Howorka, F., Eds.; Springer Verlag: Vienna, 1984; p 226.

(24) This conclusion is not vitiated by the formation of ionic metaphosphates, such as $NaPO_3$, monomeric or polymeric. See, for example: Gingerich, K. A.; Miller, F. *J. Chem. Phys.* **1975**, *63*, 1211. Steblevskii, A. B.; Alikhanyan, A. S.; Sokolova, I. D.; Gorgoraki, V. I. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1977**, *22*, 11. Jenny, S. N.; Ogden, J. S. *J. Chem. Soc., Dalton Trans* **1978**, 1465.

(25) Kirby, A. J. In "Phosphate Chemistry Directed Towards Biology"; Stec, W. J., Ed.; Pergamon Press: Oxford, England, 1980; p 79.

observed suggests that the system does not proceed beyond the ion-cluster intermediate **2**: either the formation of the zwitterion intermediate **3** or the subsequent prototropic shift from **3** to **4** could present barriers that are inaccessible at thermal energies. The similarly negative result for dimethyl ether is also of interest because the reverse reaction, (12), is a major pathway for forming

$$(CH_3O)_2PO_2^- \rightarrow (CH_3)_2O + PO_3^- \qquad (12)$$
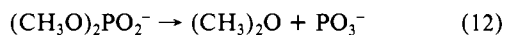
PO_3^- in the mass spectra of various phosphotriesters.[12] The sole reactions shown in Table II for PO_3^- are not chemical reactions at all but the physical clustering of polar molecules to a negatively charged ion. Such clustering reactions are third-order reactions involving collisional stabilization of the cluster by the buffer gas. The rate constants for forming $X^- \cdot HY$ clusters in Table II follow expected trends, correlating with the binding energy of the cluster, which, for a given X^-, depends on the heat of deprotonation of HY.[26]

We have verified the identity of the reactant ion (m/z 79) to be PO_3^- in several ways. A major ion in the ion source (m/z 125) suggests the formation of PO_3^- by reaction 12, which is a pathway already established for PO_3^- formation.[12] We have evidence for the collisional dissociation of PO_3^- to PO_2^- when PO_3^- is injected into the flow tube at high energy and this is confirmed by drift-tube experiments;[27] again, this pathway has been established previously.[12] Using trimethyl phosphate or dimethyl phosphite to produce PO_3^- gives identical results for reaction 2. Finally, at the highest pressure of HCl used, we see evidence that PO_3^- will bind a maximum of three HCl molecules.

On the basis of the thermodynamic and kinetic evidence presented here, we conclude that PO_3^-, *qua* PO_3^-, *is a highly stable and unreactive anion*. Consistently PO_3^- behaves as NO_3^- behaves, but with greater stability. Our very limited study has produced no evidence in the gas phase for the intriguing suggestion that PO_3^- is both an electrophile and an anion.[28] Such studies in the gas phase do test directly theoretical predictions of the properties of PO_3^-,[29] but the relationship of the gas-phase chemistry to the more interesting biochemical environment is less clear. The gas-phase results suggest that reactivity shown in solution cannot be due to PO_3^- per se but must reflect the environment as well. In this respect, it may be relevant to note that properties of phosphate ions in aqueous solution are influenced by hydrogen bonding.[30]

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(28) Westheimer, F. H. *Adv. Chem. Ser.* **1980**, *No. 191*, 17.

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(30) Kirby, A. J., private communication.

# Transient Ferracyclobutanes during Protonation of η³-Homoallyliron(0) Complexes

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Nucleophile addition to $(\eta^4\text{-}1,3\text{-diene})Fe(CO)_3$ (**1**) produces the reactive intermediate $(\eta^3\text{-}3\text{-butenyl})$tricarbonyliron anionic complexes (**2**)[1–3] which rearrange to η^3-allyl complexes via carbon

Scheme I

Series a: X = OMe
b: X = Me
c: X = Et

R = CHPh₂
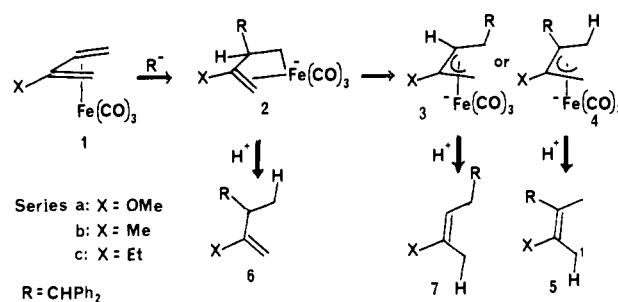
shift (to give **3**) or hydrogen shift (to give **4**).[3,4] The structures of the intermediate **2–4** are generally inferred from the simple products of protiolytic cleavage.[4] Connected with the study of the hydrogen shift (**2a → 4a**)[4] (Scheme I), we report in this paper a rearrangement process that was uncovered through the use of deuterium labels. The rearrangement appears to be quite general and can lead to skeletal changes; it is best understood in terms of a transient ferracyclobutane intermediate.[5]

Reaction of tricarbonyl(η^4-2-methoxy-1,3-butadiene)iron (**1a**) with diphenylmethyllithium (LiR) initially at −78 °C and then warmed at 25 °C for 2 h produced an intermediate (suggested to be **4a**). Cleavage with excess trifluoroacetic acid-d (−78 °C) gave primarily **5a** with deuterium exclusively at C-1 (66% yield), as expected.[6,7] The same reaction mixture held at −78 °C for 1 h and quenched in exactly the same way produced primarily the skeleton represented by **6a** (71% yield), as expected,[4] but ^{2}H NMR spectroscopy established that deuterium was located as indicated in A (Figure 1), with 20 ± 5% of the deuterium at the CH_3 group (C-4) and 80% at the C-1 vinyl positions (H_a, H_b; unresolved in the ^{2}H NMR spectrum).[6–8] In the ^{1}H NMR spectrum, the signals assigned to H_a (δ 3.7) and H_b (δ 3.6) are clearly resolved; they show equal areas (0.60 H relative to H_c as 1.0 H, δ 3.9) and patterns consistent with a mixture of unlabeled (H_a, H_b = H) and monolabeled compounds (H_a = H, H_b = D; H_a = D, H_b = H). The mass spectrum[9] allowed estimation of the number of deuterium atoms per molecule: 16% d_0, 71% d_1, 13% d_2. The main monodeuterated components in the mixture

(1) Semmelhack, M. F.; Herndon, J. W. *J. Organomet. Chem.* **1984**, *265*, C15–C18.

(2) (a) Semmelhack, M. F.; Herndon, J. W.; Springer, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 2497. (b) Semmelhack, M. F.; Herndon, J. W.; Liu, J. K. *Organometallics* **1983**, *2*, 1885.

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(4) Semmelhack, M. F.; Le, H. T. M. *J. Am. Chem. Soc.* **1984**, *106*, 2715.

(5) We are aware of no simple ferracyclobutanes that have been characterized. However, such intermediates have been suggested as the key intermediates in the reaction of (alkylidene)tetracarbonyliron complexes with alkenes: (a) Semmelhack, M. F.; Tamura, R. *J. Am. Chem. Soc.* **1983**, *105*, 6750. With other metals, metallacyclobutane complexes have been implicated in important catalytic reactions and a few have been isolated. For leading references, see: Rappe, A. K.; Goddard, W. A. *J. Am. Chem. Soc.* **1982**, *104*, 297.

(6) The structures of **5a** and **6a** were firmly established during general studies of nucleophile addition to **1a**, with proton quenching.[4]

(7) The presence of deuterium at the site(s) and in the relative amounts indicated is based on chemical shift assignments and integration of the ^{2}H NMR spectrum, assuming chemical shifts exactly parallel with the ^{1}H NMR chemical shift values for the unlabeled compound. For a discussion of the correlation of ^{2}H and ^{1}H chemical shifts, see: Harris, R. K.; Mann, B. E. "NMR and the Periodic Table", Academic Press: New York, 1978. For details of the experimental data see the supplementary material. Integration of the ^{1}H NMR spectrum and analysis of the ^{2}H shifts on the ^{1}H NMR chemical shift positions were entirely consistent with the assignment but less easily used for quantitation.

(8) Simple chromatography of **6a** on silica gel leads efficiently to the

ketone i. The unlabeled version has been fully characterized.[4] Deuterium appears primarily in the α-keto methyl group. Similarly, the mixture **18/19** has been cleaved with ozone to give the same ketone, i, in both the labeled and unlabeled series.