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Reactions of Alkynes and Carbene Equivalents with Oxo(salen)chromium(V) Complexes

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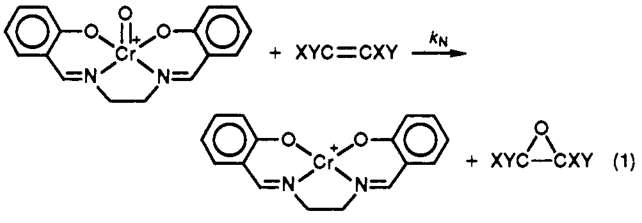
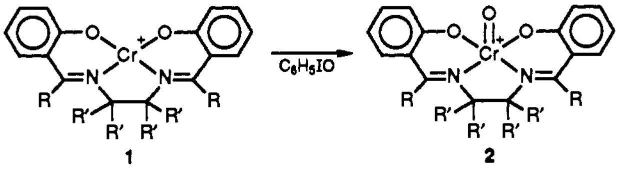
Abstract: Alkynes are oxidized by oxo(salen)chromium(V) triflate and related complexes **2** to form 1,2-diones. The oxidation of diphenylacetylene proceeds by formation of an intermediate which reacts more rapidly with a second equivalent of oxometal complex to form benzil. The intermediate is most likely a metallaoxetene or a related species, such as a metallocarbene. Reactions of phosphorus or nitrile ylides with **2** proceed to form carbonyl compounds (and phosphine oxide or nitrile) in a manner consistent with participation of similar intermediates. The reactions appear to be related mechanistically to alkene epoxidation by the same oxometal complexes.

Introduction

The proposal, originally by Sharpless et al., that metallaoxetane intermediates may form in olefin epoxidations involving metal-catalyzed oxygen transfer[1] remains controversial. In a few cases, metallaoxetane structures have been fully characterized and shown to be intermediates in oxygen transfer reactions.[2] However, generalization of the involvement of such species on the reaction coordinate to other systems[3] may be unfounded. The obligatory formation of metallaoxetanes has been ruled out in several reactions for which such structures apparently are inaccessible.[4] Even the participation of oxometal complexes as in eq 1 remains uncertain with some oxidants.[5]



In order to investigate the behavior of oxometals as catalysts for oxygen transfer to unsaturated hydrocarbons, we have selected for an initial study the reactions of alkynes with oxo(salen)chromium(V) cations **2**, prepared from the (salen)chromium(III) complexes as shown in eq 2. These oxometal derivatives form isolable salts, and have been characterized definitively by spectroscopic techniques and by single-crystal X-ray structure determinations.[6] Consequently, there is no ambiguity concerning the identity of the active oxidizing agent. Isolation of the oxo(salen)chromium(V) complexes also allows reactions to be carried out stoichiometrically, in the absence of co-oxidants, facilitating kinetics studies and mechanistic evaluation.[7]



a: R = H; R' = H (2)
b: R = CH_3; R' = H
c: R = H; R' = CH_3

Alkynes are a different class of unsaturated organic substrates which, unlike alkenes, cannot form stable products by a single, direct oxygen transfer. The reactions of **2** with alkynes should help reveal the nature of oxygen transfer from oxometal species to carbon–carbon multiple bonds.

Experimental Section

Chemicals. Acetonitrile (Waters) was distilled from CaH_2 (Aldrich) and then P_4O_{10} (Aldrich) immediately before use. Benzonitrile (Matheson) was distilled from P_4O_{10} under reduced pressure. Anhydrous diethyl ether (Mallinckrodt) in sealed metal containers was used as received. Tetrahydrofuran (Waters) was distilled from sodium benzophenone ketyl anion. Diphenylacetylene (Aldrich) was recrystallized from ethanol and thoroughly dried before use. Norbornene (Fluka) was sublimed. Benzil (MCB) was recrystallized from ether. Benzaldehyde (Aldrich), butyraldehyde (MCB), diethyl fumarate (Aldrich), diethyl maleate (MCB), 4-octyne (Pfaltz & Bauer), 4-octene (prepared by reaction of $(C_6H_5)_3P{=}CHC_3H_7$ and butyraldehyde), and phenylacetylene (Aldrich) were distilled before use. Benzaldehyde dimethyl acetal (Aldrich) was distilled at reduced pressure. Benzoic acid (Mallinckrodt), *trans*-dibenzoylethylene (Aldrich), ethyl pyruvate (Aldrich), *exo*-norbornene oxide (Aldrich), phenylglyoxal monohydrate (Aldrich), *trans*-stilbene (MCB), and triphenylphosphine oxide (Aldrich) were used as received.

Wittig reagents were prepared from reagent grade triphenylphosphine (Aldrich) and ethyl bromoacetate (Baker), ethyl 2-bromopropionate (Baker), phenacyl bromide (Aldrich), 1-bromobutane (MCB), or benzyl bromide (Aldrich) according to literature procedures.[8] Iodosobenzene was prepared by oxidation of iodobenzene (Aldrich).[9] Oxidation of diaquo(salen)chromium(III) triflate complexes with iodosobenzene according to literature syntheses[6,10] afforded the corresponding oxo(salen)-

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chromium(V) triflate complexes as dark crystalline solids (salen = *N*,*N'*-ethylenebis(salicylideneiminato)). Diazofluorene was prepared from fluorenone (Aldrich) following a procedure of Moss and Joyce.[11]

Instrumentation. Product analyses were performed by EI at 70 eV on a Finnigan TSQ 45 GC/MS/MS/DS equipped with Hewlett Packard cross-linked 5% phenyl methyl silicone capillary columns, using He (2 mL/min) carrier gas. Yields of volatile products were obtained by GC on a Hewlett Packard 5890A GC. These products were isolated by preparatory GC on a Hewlett Packard 5710A GC using a 3% OV-25 on 80/100 Supelco B2558 column. Isolated products (including stereoisomeric alkenes) were examined by ^{1}H NMR spectra, obtained on Varian FT-80A (80 MHz) and Bruker AC300F (300 MHz) spectrometers. Kinetic studies were performed by optical measurement using a Hewlett Packard 8452A diode array UV/vis spectrophotometer.

Transient Absorption Measurements. Flash photolysis experiments were performed using the frequency-doubled (532 nm) emission from a Quantel YG481 Nd:YAG laser (11 ns, Q-switched)[12] as described previously.[13] Wire-mesh filters (4–100% transmission) were used to attenuate the light intensity, in order to vary the concentration of transients to test the kinetic order. A 5-mm fluorescence cuvette containing solution was purged gently with nitrogen preceding and throughout the measurements. Excitation (355 nm) of dilute solutions of diazofluorene in acetonitrile or benzonitrile solvent produced the corresponding fluorenylidene nitrile ylides.[14] The absorptions near 400 nm were monitored,[14] and decays (s.d. ±10–15%) were obtained at this wavelength at 22 ± 1 °C. The metal(salen) complexes were used in excess to achieve pseudo-first-order decays of the ylides. The decays were determined to be independent of the concentration of diazofluorene under these conditions.

Reactions. In a typical experiment, 1 equiv of phosphorus ylide or a 20-fold excess of norbornene or alkyne was added to a 0.1 mM solution of **2** in 5 mL of solvent. (To avoid reaction with the solvent, $(C_6H_5)_3P{=}CHC_3H_7$ and $(C_6H_5)_3P{=}CHC_6H_5$ were prepared in diethyl ether.) The solution was stirred at room temperature for about 24 h, at which time dilute aqueous HCl was added and the organic products were extracted with ether or benzene. The organic layer was washed with water and dried and then submitted to GC or GC/MS analysis. Product yields were determined by comparison with authentic samples. 1,2-Diones were formed by reaction of arylacetylenes and dialkylacetylenes with **2a**, and ylides afforded carbonyl compounds, together with alkenes in some cases (Table II). Reactions of dialkylacetylenes were very slow, and further study was not pursued.

The following Wittig reactions were examined to decide whether the alkenes were formed in a secondary process by reaction of ylide with carbonyl product. Reaction of $(C_6H_5)_3P{=}CHC_3H_7$ with butyraldehyde in ether resulted in complete conversion to (*E*)-4-octene. Under the same conditions, reaction of $(C_6H_5)_3P{=}CHC_6H_5$ with benzaldehyde in ether formed (*E*)- and (*Z*)-stilbene in a slower reaction and conversion of benzaldehyde was incomplete. The ylide $(C_6H_5)_3P{=}C(CH_3)CO_2C_2H_5$ did not react with ethyl pyruvate in THF under these conditions. Thus, the conversions and stereochemical outcomes of these Wittig reactions were the same as those found in reaction of the ylides with **2** in Table II (see entries 4, 6, and 7).

Treatment of the (salen)Cr^{III} complexes **1** with any of the reactants or products examined (including diazofluorene) resulted in complete recovery of the original materials. Phenylglyoxal afforded benzoic acid and CO_2 with **2** under the reaction conditions. Carbon dioxide was detected by GC and GC/MS.

Kinetics. The kinetics of reactions were studied in acetonitrile rather than THF because **2** slowly oxidized THF to butyrolactone. A solution containing 0.1 mM **2** and 0.1–1.3 M norbornene or diphenylacetylene was prepared and the decay of the absorbance of **2** was monitored at wavelengths >400 nm. Exponential decay of **2** was observed over at least 5 half-lives with norbornene and 3 half-lives with diphenylacetylene. The kinetics were unaffected by a 20-fold change in the initial concentration of **2** (0.05–1.1 mM), and the same decay was obtained when **2** was monitored at 500, 570, or 600 nm. An excess of triphenylphosphine was added and the absorption spectrum was measured. This spectrum was used as an "infinity" value (A_∞) for the absorption of (salen)Cr^{III} products. The pseudo-first-order rate constants were determined from the linear relationship of $\ln(A_t - A_\infty)$ with time. In each case, the (salen)Cr^{III} products could be isolated as brown solids which could be reoxidized to the oxochromium complexes **2** in 80–90% yield. Repetition of this cycle (without isolation of the Cr^{III} product) leads to catalytic oxidation by **2** with turnover numbers of 5–10, after which the recovered metal complex can no longer be converted into **2**.

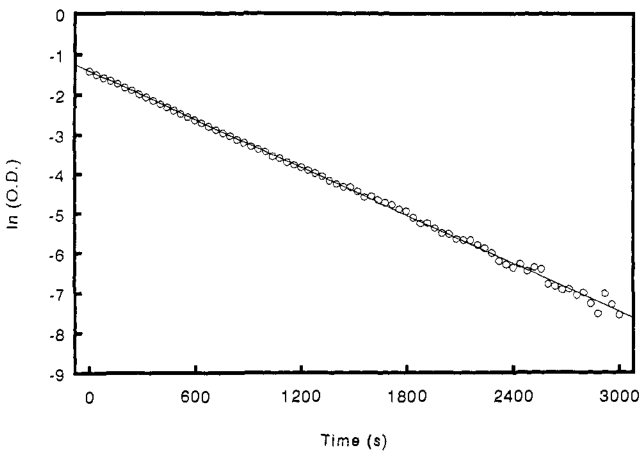


Figure 1. Decay of 0.1 mM **2a** in the presence of 0.1 M norbornene in acetonitrile at 21 °C monitored at 570 nm.

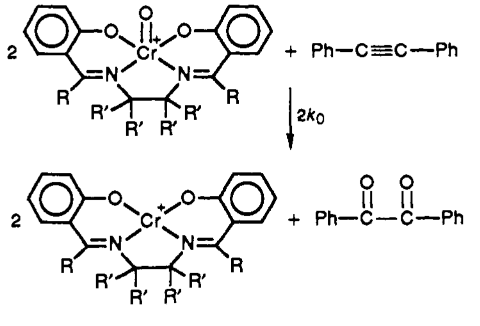
The oxo(salen)chromium complexes and reductants which could be studied were limited by the stabilities of the complexes relative to the rate with which reductant oxidizes. In the presence of ≥100 mM norbornene, autodecomposition was negligible compared to the rate of formation of epoxide. However, alkynes were oxidized much more slowly, so that the autodecomposition of metal complex was competitive with substrate oxidation even with molar concentrations of alkyne. Thus, for example, the kinetics of reactions of alkynes with oxo complexes containing a salen ligand with electron-withdrawing substituents (such as dichlorosalen) could not be obtained because of the relatively short lifetimes of these complexes in solution.

Results

Alkenes react with oxometal complexes **2** to afford epoxides and other products. The catalytic reaction of **1** or **2** and iodosobenzene with norbornene to form *exo*-norbornene oxide (eq 1) has been reported to be an efficient process in the presence of co-catalysts such as amine or phosphine oxides.[6b] We studied the stoichiometric reaction of **2a–c** with norbornene in the absence of co-catalysts to simplify the kinetics. The reactions were second order (eq 3). The exponential decay of oxometal complex **2** is shown in Figure 1, and the slope is invariant of the concentration of **2**. The first-order dependence of the decay of **2** on the concentration of norbornene is indicated in Figure 2. The yield of norbornene oxide is nearly quantitative in the presence of excess norbornene, the conditions under which the kinetics were examined (see the yields associated with k_N in Table I).

$$-d[\mathbf{2}]/dt = k_N[\mathbf{2}][\text{norbornene}] \tag{3}$$

Reaction of an alkyne, diphenylacetylene, occurred slowly with **2a** and afforded the 1,2-dione, benzil, in 87% yield over a period of hours, according to the stoichiometry in eq 4. This reaction



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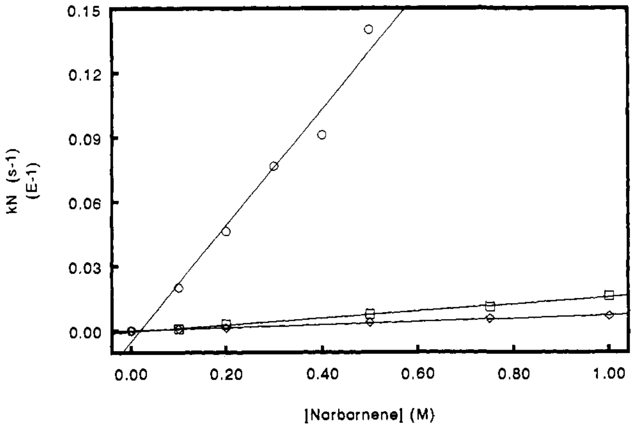


Figure 2. Dependence of pseudo-first-order rate constants for decay of **2a** (circles), **2b** (squares), and **2c** (diamonds) on the concentration of norbornene.

also was found to be first-order in oxometal complex (Figure 3) and pseudo-first-order in alkyne as described in eq 5 (see Figure 4). The kinetics results are given in Table I.

$$-\mathrm{d}[\mathbf{2}]/\mathrm{d}t = 2k_{\mathrm{D}}[\mathbf{2}][\text{diphenylacetylene}] \qquad (5)$$

Phenylacetylene also reacted slowly with **2a**. Dione (phenylglyoxal) was isolated in very low yield, and the major product was benzoic acid. Control experiments demonstrated that phenylglyoxal is converted into benzoic acid under the reaction conditions (eq 6 and 7). The yields of these products were 8% and 56%, respectively, using the stoichiometry described by eqs 6 and 7. Dialkylacetylenes similarly were found to afford 1,2-diones, indicating that the reaction is general.

$$2\,\mathbf{2a} + \mathrm{C_6H_5C{\equiv}CH} \rightarrow 2\,\mathbf{1a} + \mathrm{C_6H_5COCHO} \qquad (6)$$

$$2\,\mathbf{2a} + \mathrm{C_6H_5COCHO} \rightarrow 2\,\mathbf{1a} + \mathrm{C_6H_5CO_2H} + \mathrm{CO_2} \qquad (7)$$

Phosphorus ylides were observed to react rapidly with oxometals **2** to afford an alkene, a carbonyl compound, and/or a carboxylic acid as organic product(s), as shown in eq 8 (see Table II). Control experiments indicated that the carbonyl compounds formed first

$$\mathrm{(C_6H_5)_3P{=}CXY} \xrightarrow{\mathbf{2}} \mathrm{(C_6H_5)_3PO} + \mathrm{XYC{=}CXY} + \mathrm{O{=}CXY} + \mathrm{X'CO_2H} \quad (\mathrm{Y} = \mathrm{H}) \qquad (8)$$

(eq 9). Alkenes were formed subsequently by Wittig reaction of carbonyl compound with ylide (eq 10). Benzoic acid was formed by oxidation of phenylglyoxal as shown in eq 7. Oxidation of benzaldehyde did not occur. It is noteworthy that secondary

$$2\,\mathbf{2} + \mathrm{(C_6H_5)_3P{=}CXY} \rightarrow 2\,\mathbf{1} + \mathrm{(C_6H_5)_3P{=}O} + \mathrm{O{=}CXY} \qquad (9)$$

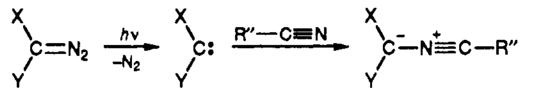
$$\mathrm{(C_6H_5)_3P{=}CXY} + \mathrm{O{=}CXY} \rightarrow \mathrm{(C_6H_5)_3P{=}O} + \mathrm{XYC{=}CXY} \qquad (10)$$

ylides, which did form ketones, did not afford any alkene (see entry 5 in Table II). This is consistent with the lower reactivity of ketones than aldehydes toward ylides (see Experimental Section). Furthermore, a higher yield of alkene or carboxylic acid was obtained when addition of ylide was performed gradually, so that the oxochromium complex initially was present in excess (see entries 4 and 6 in Table II).

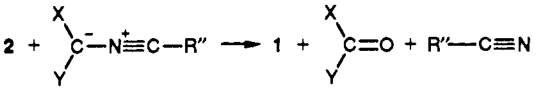
The reaction of phosphorus ylide with **2** occurred essentially upon mixing and was too fast to monitor conventionally. However, kinetic information about the reaction of another carbon nucleophile with **2** was obtained by flash photolysis. These experiments utilized nitrile ylides, formed by addition of carbenes to nitrile solvents (eq 11).[14] Fluorenylidene nitrile ylides (X = Y = $\mathrm{C_6H_4}$) have suitable absorptions for use in the flash experiments,[13] and the decays of these ylides were examined in the presence of **2**. The nitrile ylides decayed by clean second-order kinetics (eq 12) with very large rate constants (k_{Y} in Table

$$-\mathrm{d}[\text{ylide}]/\mathrm{d}t = k_{\mathrm{Y}}[\mathbf{2}][\text{ylide}] \qquad (12)$$

I). A carbonyl product (fluorenone) was obtained in high yield (eq 13).


(11)

$$\mathrm{XYC{=}N_2} \xrightarrow[-\mathrm{N_2}]{h\nu} \mathrm{XYC{:}} \xrightarrow{\mathrm{R''{-}C{\equiv}N}} \mathrm{XY\overset{-}{C}{-}\overset{+}{N}{\equiv}C{-}R''} \qquad (11)$$


(13)

$$\mathbf{2} + \mathrm{XY\overset{-}{C}{-}\overset{+}{N}{\equiv}C{-}R''} \rightarrow \mathbf{1} + \mathrm{XYC{=}O} + \mathrm{R''{-}C{\equiv}N} \qquad (13)$$

Second-order reaction of the nitrile ylides also was observed to occur with **1**. These reactions reportedly lead to metallocarbene and related products.[13]

Discussion

Reactions of Alkynes and Alkenes. Metal-catalyzed oxygen atom transfer reactions play an important role in enzymatic systems,[15] and model systems such as metal(salen) complexes have proved useful in clarifying the process by which the transfer of oxygen occurs.[16] Hypervalent oxometal species have been identified as the active oxidants with a number of systems,[2,6,17,18] although the possibility of alternative species participating in the oxidations has been proposed.[5] Use of oxo(salen)chromium(V) complexes in the absence of other oxygen source removes any ambiguity about the identity of the active oxidant. The oxo substituent is the origin of the oxygen incorporated into reductants such as alkenes.[6,19]

Several mechanisms have been proposed for oxygen transfer by hypervalent oxometal species. Oxygen transfer may be proceeded by electron transfer,[4b,20] radical addition,[21] carbocation formation,[15a,17b,18e,20,22] metallaoxetane formation,[1,17c,d,23a,b] or a combination of these mechanisms.[17a,24] The intermediacy of

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Table I. Rate Constants[a] (k) and Product Yields for Reactions of (Salen)chromium Triflate Derivatives[b]

metal complex	k_N (k_{rel})	yield[c] (%)	$2k_D$ (k_{rel})	yield[c] (%)
OCr^V(salen)__	$(2.85 \pm 0.17) \times 10^{-2}$ (1.000)	103	$(4.7 \pm 0.9) \times 10^{-5}$ (1.00)	87
OCr^V(DMesalen)	$(1.61 \pm 0.11) \times 10^{-3}$ (0.056)	102	$(3.0 \pm 1.3) \times 10^{-6}$ (0.06)	63
OCr^V(TMesalen)	$(6.86 \times 0.50) \times 10^{-4}$ (0.024)[d]	96	$(1.1 \pm 0.8) \times 10^{-6}$ (0.02)	45

	k_Y	yield[c] (%)	k_Y'	yield[c] (%)	λ (ε)
OCr^V(salen)	$(5.5 \pm 0.8) \times 10^9$	80	$(6.3 \pm 0.7) \times 10^8$	81	580 (1800)
OCr^V(DMesalen)	$(2.1 \pm 0.4) \times 10^9$	83	$(2.1 \pm 0.3) \times 10^8$	77	580 (790)
OCr^V(TMesalen)	$(2.8 \pm 0.4) \times 10^9$	88[e]	$(2.5 \pm 0.4) \times 10^8$	91[e]	580 (750)
Cr^{III}(salen)[f]	$(7.3 \pm 0.7) \times 10^7$		$(7.7 \pm 1.2) \times 10^7$		500 (430)
Cr^{III}(DMesalen)[f]	$(6.1 \pm 0.9) \times 10^7$		$(4.3 \pm 3.6) \times 10^7$		500 (220)
Cr^{III}(TMesalen)[f]	$(6.6 \pm 1.0) \times 10^7$		$(6.0 \pm 0.9) \times 10^7$		500 (430)

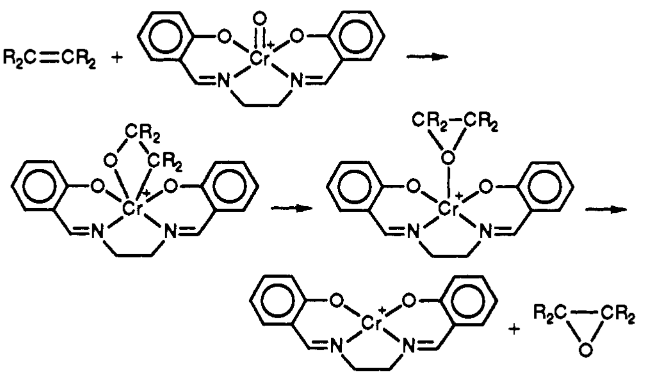
[a] Second order rate constants in $M^{-1}\ s^{-1}$ (±3 S.D.). [b] Determined at room temperature (21 ± 2 °C) in CH_3CN ($k_{N'}$ $k_{D'}$ and k_Y) or C_6H_5CN (k_Y') using 100 μM **1** or **2** and 0.1–1.3 M reductants. [c] Yields (±10%) of ketone based on **2** consumed at 1 M alkene and alkyne or 1 equiv of diazofluorene. [d] Literature value $8 \times 10^{-4}\ M^{-1}\ s^{-1}$ (ref 6b). [e] Single measurement. [f] Diaquo complexes.

Table II. Products and Yields for Reactions of Oxo(salen)chromium Triflate[a]

entry	reductant	product	yield[b] (μM)
1	$C_6H_5C{\equiv}CC_6H_5$[c]	$C_6H_5COCOC_6H_5$	43
2	$C_6H_5C{\equiv}CH$[c]	C_6H_5COCHO $C_6H_5CO_2H$	4 10
3	$C_3H_7C{\equiv}CC_3H_7$[c]	$C_3H_7COCOC_3H_7$	nd[d]
4	$(C_6H_5)_3P{=}CH{-}CO_2C_2H_5$[e]	(E)-/(Z)-$C_2H_5O_2CCH{=}CHCO_2C_2H_5$ (E/Z ratio 85/15)	24 (47)[f]
5	$(C_6H_5)_3P{=}C(CH_3){-}CO_2C_2H_5$[e]	$CH_3COCO_2C_2H_5$	39
6	$(C_6H_5)_3P{=}CHC{-}OC_6H_5$[e]	(E)-$C_6H_5COCH{=}CHCOC_6H_5$ C_6H_5COCHO $C_6H_5CO_2H$	5 (4)[f] 8 (1)[f] 2 (24)[f]
7	$(C_6H_5)_3P{=}CHC_3H_7$[g]	(E)-$C_3H_7CH{=}CH_3H_7$	22
8	$(C_6H_5)_3P{=}CHC_6H_5$[g]	(E)-(Z)-$C_6H_5CH{=}CHC_6H_5$ (E/Z ratio 45/55) C_6H_5CHO	21 12
9	$C_6H_5COCHO{\cdot}H_2O$[e]	$C_6H_5CO_2H$	40

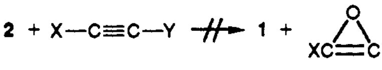
[a] Stoichiometric reductant added in one portion to **2a** at room temperature using 100 μM **2a** unless otherwise noted. [b] Yields ±10%. [c] Alkynes in CH_3CN; molar ratio 20:1 (24 h). [d] Not determined. [e] Ylides, about 30 min; aldehyde, 4 h in THF. [f] Ylides added to **2a** in ten 10 μM increments (about 60 min). [g] Ylide in ether (about 30 min).

Scheme I



metallaoxetanes in oxygen atom transfer to alkenes (Scheme I) remains arguable in many cases.[4]

We have investigated the reaction of oxochromium complexes **2** with alkynes in order to explore the nature of oxygen transfer to this class of unsaturated reductants. The "epoxidation" of an alkyne is not expected to occur, since the product, an oxirene (eq 14), would be a relatively high-energy material.[25] Theoretical studies indicate, for example, that oxirenes are similar in energy to ketocarbenes (eq 15).[26]



(14)

(15)

Reaction of **2** with phenylacetylene and diphenylacetylene resulted in slow oxidation of the alkynes to form 1,2-diones (eq 4).[27,28] Two equivalents of **2** are consumed for each equivalent of alkyne. The kinetics of this reaction are first-order in alkyne and first-order in **2** (eq 5). This reveals that one molecule of alkyne and only one molecule of oxometal complex are involved prior to the rate-determining step. The second oxygen must be delivered in a subsequent step which is fast relative to the transfer of the first oxygen. This result demands that an intermediate [I] is formed following reaction of alkyne with the first oxochromium complex, as shown in eq 16.

$$O{=}Cr(salen)^+ + C_6H_5C{\equiv}CC_6H_5 \xrightarrow{\text{slow}} [I] + Cr(salen)^+$$

$$O{=}Cr(salen)^+ + [I] \xrightarrow{\text{fast}} C_6H_5COCOC_6H_5 + Cr(salen)^+ \qquad (16)$$

A mechanism consistent with the kinetics results is shown in Scheme II, in which a metallaoxetene structure for the intermediate is indicated. Unfortunately, since the intermediate reacts faster than it is formed, its concentration always remains relatively low. A careful spectroscopic search failed to reveal direct evidence for the existence of the intermediate. However, the possible formation of oxirenes and carbenes can be ruled out. Oxirenes have been proposed as intermediates in the oxidation of alkynes by peracids[27a,b] and microsomes.[27a] The primary products formed from arylacetylenes by this process have been determined to be ketenes[27a] (eq 17) rather than diones. Thus the formation of an oxirene from **2** is excluded by the product studies, which show

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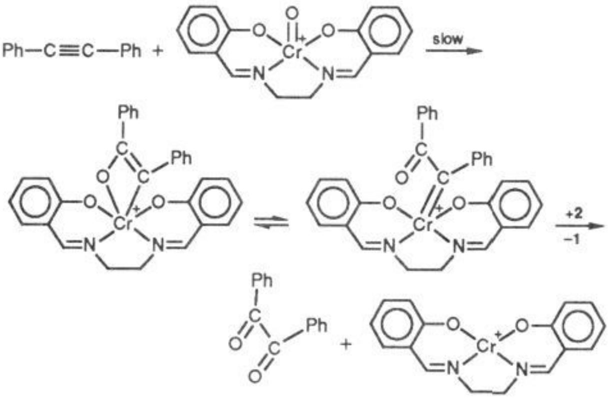
(25) Tatsuno, Y.; Tatsuda, M.; Otsuka, S.; Tani, K. *Chem. Lett.* **1984**, 1209.

(26) (a) Bachmann, C.; N'Guessan, T. Y.; Debû, F.; Monnier, M.; Pourcin, J.; Aycard, J.-P.; Bodot, H. *J. Am. Chem. Soc.* **1990**, *112*, 7488. (b) Tanigaki, K.; Ebbesen, T. W. *J. Am. Chem. Soc.* **1987**, *109*, 5883.

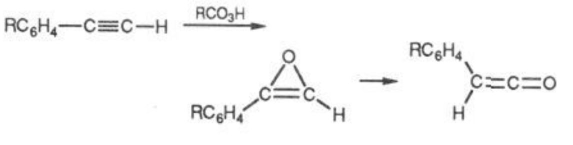
(27) (a) Ortiz de Montellano, P. R.; Kunze, K. L. *J. Am. Chem. Soc.* **1980**, *102*, 7373. (b) Lewars, E. G. *Chem. Rev.* **1983**, *83*, 519. (c) Matlin, S. A.; Sammes, P. G. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2851.

(28) Thus, the oxidations resemble the action of dioxygenases: Sheu, C.; Sobkowiak, A.; Jeon, S.; Sawyer, D. T. *J. Am. Chem. Soc.* **1990**, *112*, 879.

Scheme II



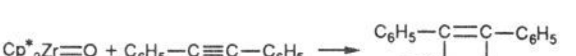
phenylglyoxal as the primary product from phenylacetylene.[27c] The formation of a free carbene also apparently can be ruled out by flash photolysis experiments with a carbene equivalent (vide



(17)

infra) which indicate that addition of the carbene to **1** occurs irreversibly.[13]

On the other hand, the metallaoxetene structure seems reasonable for several reasons. There is precedent for formation of metallaoxetenes involving the early transition metals.[29,30] For example, a reaction which is related to the processes proposed in Scheme II was reported by Bergman et al. (eq 18),[29b] and the metallaoxetene product was characterized structurally by X-ray diffraction.[29]



$$\mathrm{Cp^*_2Zr{=}O + C_6H_5{-}C{\equiv}C{-}C_6H_5 \longrightarrow \begin{array}{c} C_6H_5{-}C{=}C{-}C_6H_5 \\ \;\;|\quad\;\;| \\ Cp^*_2Zr{-}O \end{array}} \quad (18)$$

A metallaoxetene itself may be oxidized by a second equivalent of **2**, or it may rearrange to a metallo(ketocarbene) isomer,[31] as shown in Scheme II, before oxidation by **2**.[32]

Metallaoxetanes are inaccessible for systems constrained by sterically bulky ligands.[4] Examination of molecular models reveals that formation of a metallocyclic intermediate at least should be possible in the reactions of (salen)chromium cations. Schematic representations of two oxo(salen)chromium(V) complexes (which contain the dimethylsalen or tetramethylsalen ligand), based on X-ray crystallographic structure determinations,[6] are shown in Figure 5.[33] The metal atom is accessible from the perspective indicated in the figure. These structure determinations also show that the salen ligand may be somewhat flexible and can change its bite to accommodate different coordination of chromium.[6a]

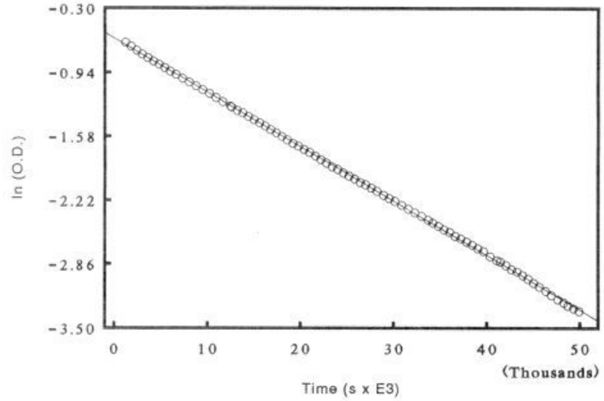


Figure 3. Decay of 0.1 mM **2a** in the presence of 1.0 M diphenylacetylene in acetonitrile at 21 °C monitored at 570 nm.

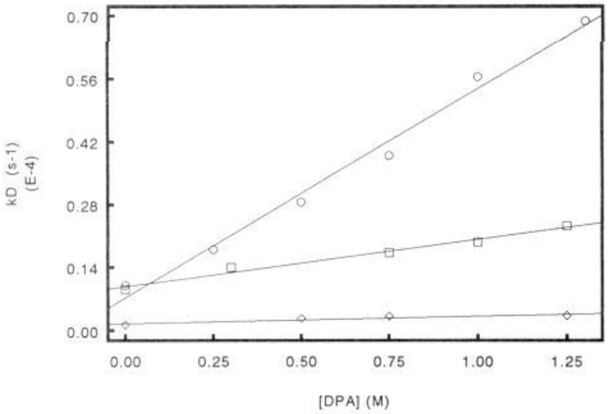


Figure 4. Dependence of pseudo-first-order rate constants for decay of **2a** (circles), **2b** (squares), and **2c** (diamonds) on the concentration of diphenylacetylene.

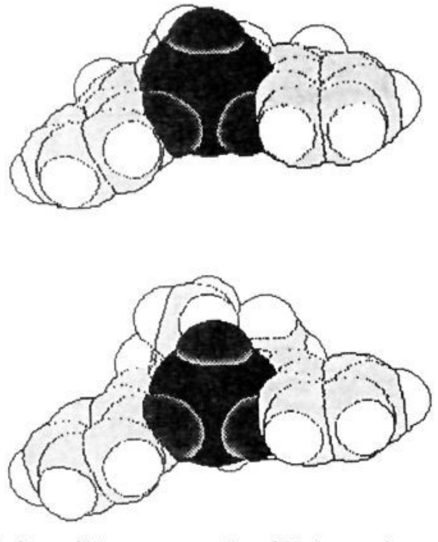


Figure 5. Space-filling representation of **2b** (counterion omitted) and oxo[*N,N'*-tetramethylethylenebis(5,5'-dichlorosalicylidineaminato)-chromium(V) cation adduct with pyridine *N*-oxide (triflate counterion, axial ligand, and chlorine atoms omitted); coordinates from ref 6a.

The presence of methyl substituents results in substantial reductions in the rates of reaction for **2b** and **2c**, compared to the unsubstituted case **2a**. Consideration of Figure 5 indicates that

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[29] (a) Vaughan, G. A.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 7994. (b) Carney, M. J.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 6426. Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 8751.

[30] Oxametallacycles of (a) Pt and (b) Ir and (c) methyleneoxametallacycles of Ti have been characterized: (a) Lenarda, M.; Ros, R.; Traverso, O.; Pitts, W. D.; Baddley, W. H.; Graziani, M. *Inorg. Chem.* **1977**, *16*, 3178. Schlodder, R.; Ibers, J. A.; Lenarda, M.; Graiani, M. *J. Am. Chem. Soc.* **1974**, *96*, 6893. (b) Klein, D. P.; Hayes, J. C.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 3704. Day, V. W.; Klemperer, W. G.; Lockledge, S. P.; Main, D. J. *J. Am. Chem. Soc.* **1990**, *112*, 2031 (we thank a reviewer for this reference). (c) Ho, S. C.; Hentges, S.; Grubbs, R. H. *Organometallics* **1988**, *7*, 780.

[31] Carbonyl complexes of metallacyclobutenes have been proposed to ring open to the isomeric group VIB metal carbene complexes: McCallum, J. S.; Kunng, F. A.; Gilbertson, S. R.; Wulff, W. D. *Organometallics* **1988**, *7*, 2346. Wulff, W. D.; Kaesler, R. W.; Peterson, G. A.; Tang, P.-C. *J. Am. Chem. Soc.* **1985**, *107*, 1060.

[32] (a) (Porphyrin)metal carbene complexes in the presence of mild oxidants, such as air, afford carbonyl compounds: Mansuy, D. *Pure Appl. Chem.* **1980**, *52*, 681. (b) See also: Pruchnik, F. P. *Organometallic Chemistry of the Transition Elements*; Plenum Press: New York, 1990.

[33] In solution, solvent may coordinate as an axial ligand.

these complexes still have at least one open face for approach of the reductant to the metal. A decrease in the electrophilicity of the complexes with electron donating ligands, together with increasing steric demand of the substituents, probably serves to reduce the oxidizing abilities of **2b** and **2c**. For comparison, the rates of epoxidation of an alkene, norbornene, were determined with the same three oxochromium derivatives. Interestingly, the same trend in reactivity is observed with norbornene as was found with diphenylacetylene (Table I); even the turnover numbers (ca. 5) are similar. This result indicates that the oxidations of alkenes and alkynes share some common mechanistic features, at least with respect to these three closely related oxometal complexes.

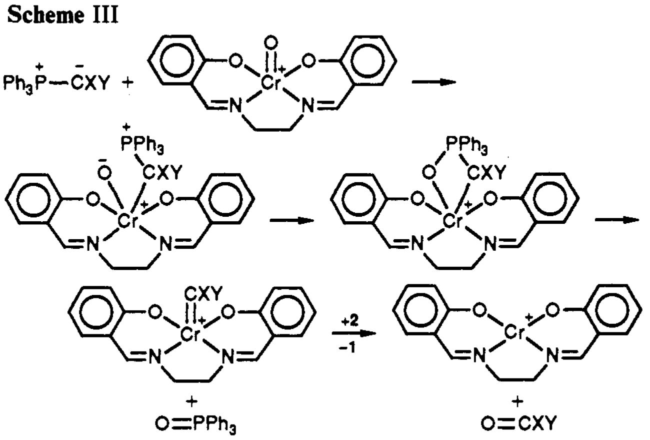
Reactions of Ylides. Additional experiments were undertaken in order to obtain some information about the nature of the intermediate formed in alkyne oxidation by **2**. Because the intermediate may resemble a carbene complex (Scheme II), alternative reactions which potentially would lead to related complexes of this type were considered.

The reaction of phosphorus ylides with **2** was found to produce carbonyl compounds (O=CXY) and phosphine oxide according to the stoichiometry in eq 9. The ylides are good carbon nucleophiles due to the charge distribution indicated in eq 19.

$$(C_6H_5)_3P{=}CXY \leftrightarrow (C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}XY \qquad (19)$$

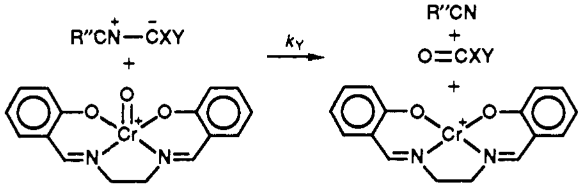
Since the oxochromium complexes behave as electrophiles,[7,13] reaction of the ylides may be proposed to occur as indicated in Scheme III. Oxygen atom transfer in Scheme III initially occurs to produce phosphine oxide and a carbene complex. Therefore, the yield of carbonyl product, together with secondary products derived from the carbonyl compounds, cannot exceed 50%, consistent with observation (Table II).[34,35] The remaining ylide (50%) may react in a subsequent step with aldehyde to form the alkene products listed in Table II.

Scheme III



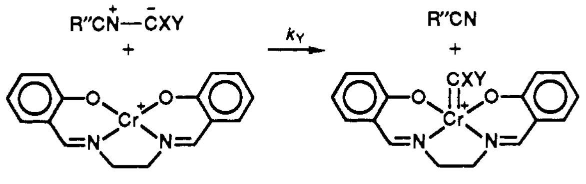
The change in product distribution upon slow addition of ylide to **2** also may be explained by the mechanism of Scheme III. Competition between ylide and an intermediate, such as a metallocarbene, for **2** would reduce the amount of **2** available to react with ylide. Therefore, slow addition results in consumption of **2** after 50% of the ylide has been added, producing phosphine oxide and carbonyl (eq 9). Additional ylide could only react with the carbonyl compound to produce alkene (the yield of which increases from 48% to 93% for entry 4 in Table II). A similar increase in the yield of aldehyde occurs for entry 6 in Table II, although in this case the phenylglyoxal formed is oxidized to benzoic acid by **2** (10% of the theoretical yield of benzoic acid is produced even upon rapid addition of ylide). The overall yield of aldehyde-derived products was observed to increase from 36% to 100% of the theoretical amount upon slow addition of ylide.

Oxidation of ylide (as well as any intermediate species formed) by **2** occurs within minutes after mixing. In order to study directly reaction of carbon nucleophiles with **2**, flash photolysis experiments were performed with nitrile ylides (eq 11). Nitrile ylides are less stable and more nucleophilic than phosphorus ylides.[39] Indeed, the reaction of nitrile ylides of diazofluorene with **2** occurred with exceptional facility, being nearly diffusion-limited in acetonitrile (k_Y) or benzonitrile (k_Y'), as indicated for entries 4–6 of Table I.[40] The product fluorenone was formed in 80–90% yields (see eq 22, where X = Y = C_6H_4). The rate constants once again appear lower for the methylsalen complexes **2b** and **2c** than the unsubstituted complex **2a**. Because the absolute rate constants are so large, however, the values cannot be compared to obtain the relative reactivities of **2a–c** without explicit consideration of the rates of diffusion (unknown for the compounds considered here).



(22)

Metallocarbenes can form directly from reaction of a metal complex with a carbene or carbene equivalent. Metallocarbenes or related species are formed in the reaction of fluorenylidene ylides with (salen)Cr^{III} complexes **1** (eq 23).[13] Noteworthy is the similarly high reactivity of **1a–c** toward the ylides derived from acetonitrile (k_Y) and benzonitrile (k_Y') in this process (see the final three entries in Table I).[41] Rapid and irreversible capture



(23)

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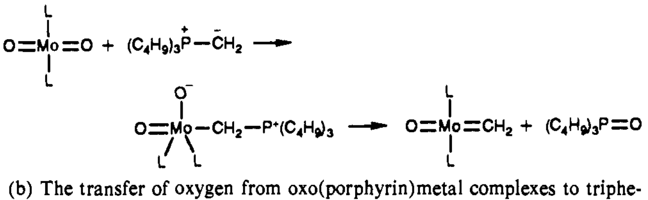
[34] Reaction of **2** with ylides according to Scheme III resembles the Wittig reaction of carbonyl compounds with ylides to form alkenes.

[35] Although initial oxygen atom transfer to carbon (eq 20) cannot be ruled

$$\mathbf{2} + (C_6H_5)_3P{=}CXY \rightarrow \mathbf{1} + (C_6H_5)_3P + O{=}CXY \qquad (20)$$

out, this possibility is less likely for several reasons. (a) There is precedent for the transfer of the ylide carbon to oxometal centers as described in Scheme III, viz.[36]



(b) The transfer of oxygen from oxo(porphyrin)metal complexes to triphenylphosphine is relatively slow (eq 21),[37] whereas the

$$\mathbf{2} + (C_6H_5)_3P \rightarrow \mathbf{1} + (C_6H_5)_3P{=}O \qquad (21)$$

reactivity of **2** with ylides is relatively fast (vide infra). (c) The increase in the overall yields of carbonyl-derived products with slow addition of ylide (vida infra) is not explained by eq 20. (d) A mechanism very similar to Scheme III, involving a metallaoxetene, has been found in the permanganate oxidation of alkynes to diones.[38] In the permanganate reactions, both oxygens originate from the same metal center.

[36] (a) Laï, R.; Bot, S. L.; Baldy, A.; Pierrot, M.; Arzoumanian, H. *J. Chem. Soc., Chem. Commun.* **1986**, 1208. (b) See also: Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907. Schmidbaur, H.; Pichl, R.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 574 and references therein.

[37] Groves, J. T.; Kruper, W. J., Jr. *Isr. J. Chem.* **1985**, *25*, 148.

[38] Lee, D. G.; Lee, E. J.; Chandler, W. D. *J. Org. Chem.* **1985**, *50*, 4306.

[39] Hansen, H. J.; Heimgartner, H. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley-Interscience: New York, 1984; Vol. 1, Chapter 2.

[40] The difference between $k_Y \approx 10k_Y'$ for reaction of **2** is due to the different solvent viscosities, so that diffusion in benzonitrile is slower than diffusion in acetonitrile.

[41] The rate constants k_Y–k_Y' for reaction of **1** are well below the diffusion limit and exhibit no dependence upon the solvent (R″ = CH_3 or C_6H_5).[40]

of the ylides by **1** is consistent with the expectation of thermodynamic instability of the carbene equivalents compared to their respective metal carbene complexes.

The origin of the contrasting pattern in the behavior of **1** and **2** has not been determined. Differences in coordination of solvent or ligands in the complexes may be responsible. The steric demands of the oxo ligand, not present in **1**, when the metal is approached by a nucleophile, also may contribute. Additional studies will address these possibilities.

Conclusion

Alkynes are oxidized slowly by oxo(salen)chromium(V) triflate and related oxo(methylsalen)chromium(V) complexes **2** to form 1,2-diones. This reaction is first-order in both alkyne and **2**, which requires one molecule of alkyne and one molecule of **2** to be involved in the rate-determining step. Therefore, an intermediate forms and is oxidized in a faster follow-up step by a second molecule of **2**. This intermediate is most likely a metallaoxetene and/or a related species, such as a metallocarbene. Reactions of phosphorus ylides with **2** proceed in two steps to form phosphine oxide and a carbonyl compound in a manner consistent with participation of similar metallocarbene intermediates.

Oxochromium complexes **2b** and **2c**, which contain methyl-substituted salen ligands, are less reactive than the parent **2a**. Formation of a metallaoxetene may be responsible for these reactivity differences; experiments involving nitrile ylides and **1** indicate that the methyl substituents do not affect formation of a metallocarbene. Similar relative rates are observed for reaction of an alkene, norbornene, as for reaction of diphenylacetylene, despite the oxidation of the alkene occurring nearly 3 orders of magnitude faster than oxidation of diphenylacetylene. This suggests a mechanistic similarity exists in the oxidation of these two substrates using this particular catalyst.[42] We hope further studies, involving reaction of ketocarbenes and sulfur ylides with **1** and **2**, will reveal more about the nature and reactivity of the intermediates formed in these and related systems.[43]

Acknowledgment. Support from the Ohio Board of Regents under the Research Challenge Program and from the CSU College of Graduate Studies is gratefully acknowledged. Flash photolysis was performed at the Center for Fast Kinetics Research, supported by the NIH (Grant RR 00886) and by the University of Texas at Austin. The authors would like to acknowledge P. R. S. Sharma and B. Morrison for technical assistance. S.S. thanks the Government of India for a scholarship.

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(42) This interpretation does not exclude formation of intermediates, such as involved in side-on attack of substrate at the oxo ligand, which may precede the rate-determining step. Other species, including radical cations, cations, radicals, etc., are expected to be relatively unstable and short-lived and are unlikely to survive long enough to be intercepted in a bimolecular reaction with **2**.[17,18,20–22,27] However, formation of a short-lived species in proximity to the metal complex, followed by collapse to a metallaoxetene, is not ruled out. The viability of such alternative processes will depend upon structural and electronic considerations of the substrate and the oxidant. Especially, the disposition of the earlier transition metals toward formation of metallocyclic species may not carry through to those later in the series (such as Fe), which form more reactive oxo complexes.[43]

(43) For a brief comparison of related enzymatic oxidations, see: Sharma, P. R. S.; Rihter, B.; SriHari, S.; Masnovi, J. *Trends in Inorganic Chemistry*; Menon, J., Ed.; Research Trends, in press.