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Alkyne Oxidations by *cis*-Dioxoruthenium(VI) Complexes. A Formal [3 + 2] Cycloaddition Reaction of Alkynes with *cis*-$[(\mathrm{Cn^*})(\mathrm{CF_3CO_2})\mathrm{Ru^{VI}O_2}]\mathrm{ClO_4}$ (Cn* = 1,4,7-Trimethyl-1,4,7-triazacyclononane)

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Abstract: *cis*-Dioxoruthenium(VI) complexes, $[\mathrm{Cn^*}(\mathrm{CF_3CO_2})\mathrm{Ru^{VI}O_2}]\mathrm{ClO_4}$ (**1**) (Cn* = 1,4,7-trimethyl-1,4,7-triazacyclononane) and *cis*-$[(\text{Tet-Me}_6)\mathrm{Ru^{VI}O_2}](\mathrm{ClO_4})_2$ (**2**) (Tet-Me$_6$ = *N,N,N′,N′*-tetramethyl-3,6-dimethyl-3,6-diazaoctane-1,8-diamine), oxidize disubstituted alkynes to 1,2-diketones selectively in good to excellent yields under ambient conditions. The reactions proceed via the formation of dark blue $[(\mathrm{Cn^*})(\mathrm{CF_3CO_2})\overline{\mathrm{Ru^{IV}\text{-}OC_2R^1R^2O}}]^+$ intermediates, which display a characteristic UV−visible absorption band at 550−680 nm. With bis(trimethylsilyl)acetylene as substrate and **1** as the oxidant, the intermediate was isolated and structurally characterized by X-ray crystallography as a [3 + 2] cycloadduct. The kinetics of the cycloaddition of **1** with various substituted trimethylsilylacetylenes has been studied by stopped-flow spectrophotometry. With the exception of bis(trimethylsilyl)acetylene, the second-order rate constants were found to vary over a range of less than an order of magnitude irrespective of a 2.3 eV change of the calculated I_p of the alkynes; therefore, a rate-limiting single electron-transfer mechanism is unlikely. The participation of oxirene (oxene insertion) and metallaoxetene ([2 + 2] cycloaddition) intermediates appears to be implausible based on product analysis. A linear Hammett correlation was established using σ^+ and $\sigma_{JJ}{}^\bullet$ parameters for the cycloaddition of **1** with para-substituted aryl trimethylsilylacetylenes, and the rate-limiting vinyl radical intermediate formation is proposed.

Introduction

Highly oxidizing metal−oxo (M=O) complexes are widely invoked to play a key role in many catalytic and enzymatic oxidations[1] such as the Mn(III)-catalyzed asymmetric organic oxidations[2] and the cytochrome P-450 mediated biological oxidations.[3] Because of their importance, much effort has been directed to study their reactivities toward organic substrates.[1,3,4] Previously we and others also reported several studies on the mechanism of organic oxidations using well-characterized M=O complexes under stoichiometric conditions.[3c,5−9] Compared to *trans*-dioxometal complexes, the oxidation chemistry of *cis*-dioxometal complexes is less developed. Indeed, apart from $\mathrm{RuO_4}$,[10−11] $\mathrm{OsO_4}$,[12] $\mathrm{KMnO_4}$,[8,13] and $\mathrm{CrO_2Cl_2}$[14] there are few structurally characterized oxidizing *cis*-dioxo metal

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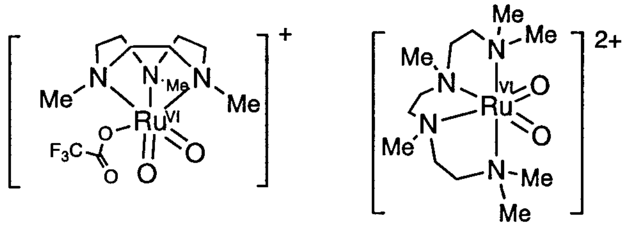
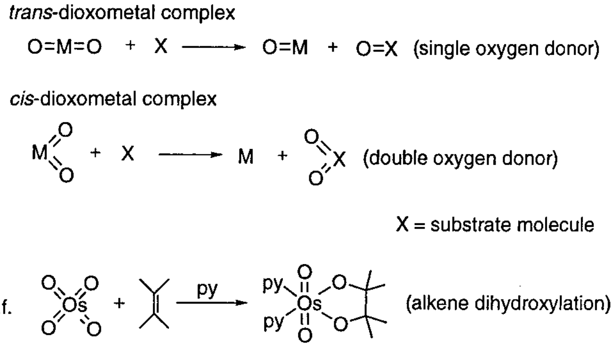
complexes.[15-19] Holm and co-workers[1c,20] had reported the oxygen atom transfer reactions of *cis*-dioxomolydenum(VI) complexes to phosphines and related substrates; however, this class of complexes cannot oxidize hydrocarbons such as alkenes and alkynes. In this connection, it is conceivable that *cis*-dioxometal complexes having a high *E*° value would be effective for organic oxidations. Of particular interest is that *cis*-dioxo complexes may react with substrates by transferring two oxygen atoms analogous to the alkene cis-dihydroxylations mediated by OsO_4 and $KMnO_4$ (Scheme 1). In 1988 Davison and co-workers reported a [3 + 2] cycloaddition reaction between a $[(L)(Cl)Tc^{VII}O_3]$ complex (L = 1,10-phenanthroline or 2,2′-biyridine) with alkenes under ambient conditions. A technetium(V)–oxo complex, formulated as a $[(L)(Cl)Tc^{V}(O)(O_2C_2H_2R^1R^2)]$ ($R^1 \neq R^2$ = alkyl, aryl or H), was isolated and spectroscopically characterized.[16a] Later Gable and co-workers also reported that Cp^*ReO_3 can transfer two oxygen atoms to a C=C bond of alkenes in a cis manner.[16b]



(1) (2)

Figure 1.

Scheme 1



The oxidation chemistry of several classes of Ru=O compounds has been extensively investigated in the past decades.[5,6,21] Important features of these compounds are that they possess very high *E*° values yet can be readily isolated and structurally characterized. Several years ago, we successfully isolated and obtained the X-ray crystal structures of two *cis*-dioxoruthenium(VI) complexes, $[Cn^*(CF_3CO_2)Ru^{VI}O_2]ClO_4$ (**1**) (Cn* = 1,4,7-trimethyl-1,4,7-triazacyclononane)[19b] and *cis*-$[(Tet\text{-}Me_6)Ru^{VI}O_2](ClO_4)_2$ (**2**) ($Tet\text{-}Me_6$ = *N*,*N*,*N*′,*N*′-tetramethyl-3,6-dimethyl-3,6-diazaoctane-1,8-diamine)[19a] (Figure 1). These complexes are competent oxidants for organic oxidations, and their reactions with the alkenes under stoichiometric conditions have been reported.[5d,22] Here, we demonstrate that the *cis*-dioxoruthenium(VI) complexes **1** and **2** react with alkynes by transferring two oxygen atoms to a C≡C bond, which we formally describe as a [3 + 2] cycloaddition.[23] Although it is generally accepted that the oxidation of alkynes to 1,2-diketones by M=O reagents involves the [3 + 2] cycloaddition reaction as the principal step, *cycloadduct intermediates have never been hitherto isolated or characterized*.[10] To our knowledge, the present report features the first evidence for [3 + 2] cycloaddition in the alkyne oxidation by M=O reagents. In this work, we have also examined the mechanism of the cycloaddition by kinetic studies and product analysis.

Results

Synthesis of *cis*-$[(Cn^*)(CF_3CO_2)Ru^{VI}O_2]ClO_4$. Monooxo- and *trans*-dioxoruthenium complexes are usually prepared by sequential oxidation/deprotonation reactions of the aqua-

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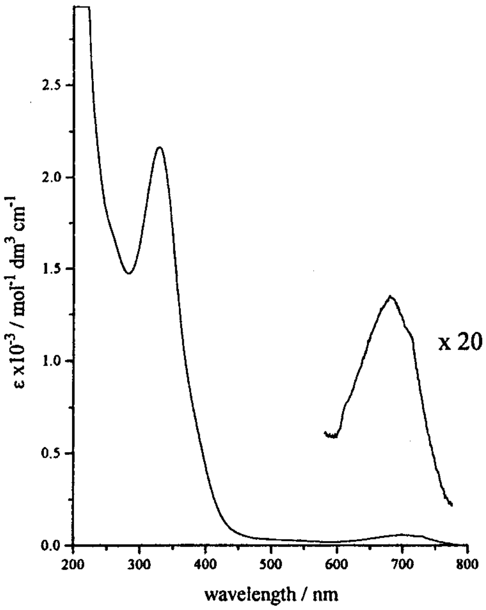

Figure 2. UV−vis spectrum of **1** in 0.1 M CF_3CO_2H.

ruthenium (Ru−H_2O) precursors in aqueous solution.[21b,c] In an attempt to synthesize *cis*-dioxoruthenium(VI) complexes, Meyer and co-workers noted that oxidative deprotonation reactions of *cis*-$[(bpy)_2Ru^{VI}(H_2O)_2]^{2+}$ (bpy = 2,2′-bipyridine)[18a] and [(tpm)-$Ru^{II}(H_2O)_3]^{2+}$ [tpm = tris(1-pyrazolyl)methane][18b] complexes had resulted in partial ligand loss and extensive formation of *trans*-dioxoruthenium(VI). The *trans*-dioxo formation can be avoided by employing bipyridine ligands with sterically bulky substituents at the 6,6′-positions as in *cis*-$[(L)_2Ru^{VI}O_2](ClO_4)_2$ (where L = 6,6′-dichloro-2,2′-bipyridine[24] and 2,9-dimethyl-1,10-phenathroline[17]). Previously we also demonstrated the use of macrocyclic tertiary amine ligands with small bite angle in the preparation of *cis*-dioxo complexes such as *cis*-$[(Cn^*)(CF_3CO_2)Ru^{VI}O_2]ClO_4$ (**1**)[19b] and *cis*-$[(Tet\text{-}Me_6)Ru^{VI}O_2](ClO_4)_2$ (**2**).[19a]

Treatment of $[(Cn^*)Ru^{III}(CF_3CO_2)_3]\cdot H_2O$[22b] by $(NH_3)_2Ce^{IV}(NO_3)_6$ in 0.2 M CF_3CO_2H afforded *cis*-$[(Cn^*)(CF_3CO_2)Ru^{VI}O_2]ClO_4$ (**1**) in 55% yield. Complex **1** is a diamagnetic light-green microcrystalline solid and is stable as a solid for several hours at room temperature. Its infrared spectrum shows two absorptions at 842 and 856 cm^{-1} that we assign to the asymmetric and symmetric RuO_2 stretches, respectively. Comparable spectral feature was obtained for the structurally related *cis*-$[(Tet\text{-}Me_6)Ru^{VI}O_2](ClO_4)_2$ (**2**), in which case the asymmetric and symmetric RuO_2 stretches are located at 855 and 874 cm^{-1}.[19a] The UV−visible spectrum of a freshly prepared sample of **1** in 0.2 M CF_3CO_2H (Figure 2) exhibits an intense charge-transfer absorption band at 329 nm ($\epsilon_{max} = 2400$ dm^3 mol^{-1} cm^{-1}) and a weak d−d absorption at 695 nm ($\epsilon_{max} = 50$ dm^3 mol^{-1} cm^{-1}). The solution is stable for more than 1 h at room temperature. The UV−vis spectra of the *trans*-dioxoruthenium(VI) analogues usually display a vibronic-structured absorption band at 380−400 nm arising from the spin-allowed $p_\pi(O^{2-})\rightarrow Ru(VI)$ charge-transfer transition.[25] However, a similar vibronic-structured UV−vis band is not observed for the cis complexes **1** and **2** at room temperature.[19]

Stoichiometric Oxidation of Alkynes by *cis*-$[(Cn^*)(CF_3CO_2)Ru^{VI}O_2]ClO_4$. Treating excess diphenylacetylene (0.2 g, 1.1 mmol) with complex **1** (0.11 μmol) in a degassed 0.2 M CF_3CO_2H/CH_3CN solution (10 mL) at room temperature afforded instantaneously a dark blue solution. The reaction mixture gradually decolorized within 15 min to give a pale yellow solution. After workup, the organic product benzil was obtained in 98% yield (Table 1, entry 1). No other organic side-products such as benzoic acid (C≡C cleavage) or diphenylacetic acid (rearrangement) were detected. The percentage yield of benzil was calculated based on the stoichiometry of Ru:PhC≡CPh = 1:1. The ruthenium(VI) oxidant was quantitatively reduced to *cis*-$[(Cn^*)(CF_3CO_2)Ru^{II}(CH_3CN)_2]ClO_4$ (93% isolated yield, see Experimental Section).

The presence of trifluoroacetic acid is essential for obtaining benzil in good yield. In neutral acetonitrile the diphenylacetylene oxidation also proceeds through a dark blue intermediate, and benzil and *cis*-$[(Cn^*)(CF_3CO_2)Ru^{II}(CH_3CN)_2]ClO_4$ are isolated in 45% and 97% yields, respectively. Just as for acidified conditions, no side-products from C≡C bond cleavage and rearrangement reactions could be detected. The low yield of benzil under these conditions remains ill-understood at present because we could not establish other organic products.

Oxidation of other disubstituted alkynes including 1-phenyl-1-propyne, 4-octyne, 2-butyne, and 1-trimethylsilyl-1-propyne by **1** was equally effective under the typical reaction conditions: i.e., 1.1 mmol of alkyne, 0.11 μmol of **1**, and 0.2 M CF_3CO_2H in CH_3CN, and 1,2-diketones were produced in 94−98% yields (Table 1, entries 2−5). In all cases, the 1,2-diketone formations were preceded by transient appearance of a dark blue solution. It has been reported that $Ru^{VIII}O_4$, generated in situ by the action of NaOCl on ruthenium dioxide,[26] readily oxidized internal alkynes to give a substantial amount of carboxylic acids arising from oxidative C−C bond cleavage of the 1,2-diketones.[26a,b] For example, 4-octyne reacted with RuO_4 to give 4,5-octanedione and butyric acid in 60 and 40% yields,[26b] respectively. In this work, when subjecting 4-octyne (1.1 mmol) to the oxidizing conditions, i.e., **1** (0.11 μmol) in a degassed 0.2 M CF_3CO_2H/CH_3CN solution, 4,5-octanedione was obtained in 94% yield (Table 1, entry 3) without any detectable formation of butyric acid.

Common organic oxidants such peracids[27] and dioxiranes[28] are known to oxidize alkynes to produce 1,2-diketones but in poor yields. For example, 2-butyne and 1-trimethylsilyl-1-propyne reacted with dioxiranes to afford 2-hydroxy-2-methylpropanoic acid and 2-hydroxy-2-(trimethylsilyl)propanoic acid as the major products, respectively.[28b] In this work, we found that complex **1** oxidized 2-butyne and 1-trimethylsilyl-1-propyne to their 1,2-diketone derivatives in 97−98% yields (see Table 1, entries 4 and 5). As has been noted in the literature, 1-oxo-1-(trimethylsilyl)-2-propanone readily undergoes photolysis under ambient lighting to afford 2-hydroxy-2-(trimethylsilyl)-propanoic acid;[29] therefore, the 1-trimethylsilyl-1-propyne oxidation by **1** and its subsequent workup were carried out with protection from light.

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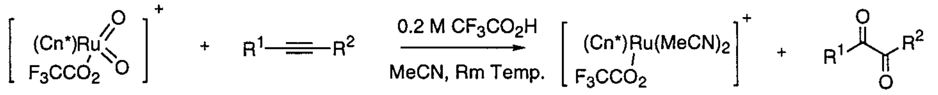
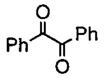
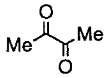
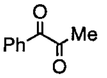
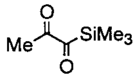
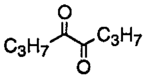
Table 1. Stoichiometric Oxidation of Alkynes by *cis*-$[(Cn^*)(CF_3CO_2)Ru^{VI}O_2]ClO_4$ (**1**)



entry	alkyne	product	% yield[a,b]	entry	alkyne	product	% yield[a,b]
1	Ph—≡—Ph		98	4	Me—≡—Me		97 87[c]
2	Ph—≡—Me		97	5	Me—≡—SiMe₃		98[d] 85[c, d]
3	C_3H_7—≡—C_3H_7		94	6	Ph—≡—H	$PhCO_2H$	~30

[a]: The diketones were characterized by comparing with authentic samples, which were prepared by the literature procedure (ref: Muller, P.; Godoy, J. *Helv. Chim. Acta* **1981**, *64*, 2531). [b]: The yields were based on the amount of ruthenium oxidant in a 1 : 1 stoichiometery of [alkyne] : [Ru] . [c]: *cis*-$[(TetMe_6)Ru^{VI}O_2](ClO_4)_2$ (**2**) was the oxidant. [d]: The reaction and subsequent work-up were conducted in dark conditions.

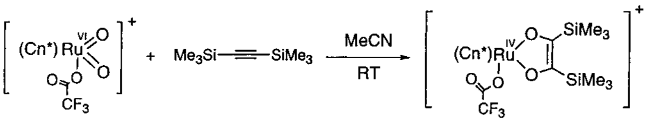
We found that the oxidation of phenylacetylene by **1** gave benzoic acid as the only isolable product, in ~30% yield. Presumably, the phenylglyoxylic acid ($PhCOCO_2H$) product decomposed to benzoic acid during the reaction.

Unlike **1**, *cis*-$[(Tet\text{-}Me_6)Ru^{VI}O_2](ClO_4)_2$ (**2**) failed to oxidize diphenylacetylene to benzil in CF_3CO_2H/CH_3CN, and the starting alkyne was recovered. But it is noteworthy that **2** can oxidize the less bulky 2-butyne and 1-trimethylsilyl-1-propyne to give the corresponding 1,2-diketones in 87 and 85% yields, respectively (Table 1, entries 4 and 5). Similar to the alkyne oxidation by **1**, these oxidations were accompanied by transient formation of a dark blue solution. The lack of reactivity of **2** toward diphenylacetylene is probably due to steric effects imposed by the *N*-methyl groups of the Tet-Me$_6$ ligand.

It has been reported that two-electron oxidants such as oxochromium(V) salen complexes can effect diphenylacetylene oxidation to benzil at ambient conditions, albeit with very small reaction rate constants (ca. 10^{-5} dm^3 mol^{-1} s^{-1}).[30] However, in this work, we found that strong two-electron oxidants such as *trans*-$[(N_2O_2)Ru^{VI}O_2](ClO_4)_2$ [31] and *trans*-$[(pytn)Ru^{VI}O_2](ClO_4)_2$ [31] complexes [N_2O_2 = 1,12-dimethyl-3,4:9,10-dibenzo-1,12-diaza-5,8-dioxocyclopentadecane; pytn = *N,N*′-dimethylbis-(2-pyridylmethyl)propylenediamine] (respective $E°$ [Ru(VI)/(IV)] = 0.92 and 0.89 V vs SCE at pH 1.0) do not exhibit any appreciable reactivity toward diphenylacetylene, 2-butyne, and 1-trimethylsilyl-1-propyne under similar reaction conditions. In all cases, no 1,2-diketones were detected, and all the starting alkynes were recovered. We suggest that the reactions of these complexes with alkynes are slow so that reduction to *trans*-$[Ru(L)(CH_3CN)_2]^{2+}$ complexes (L = N_2O_2 and pytn) by acetonitrile solvent prevails.

The [3 + 2] Cycloaddition of *cis*-Dioxoruthenium(VI) and Disubstituted Acetylenes. Pertinent to the mechanism of alkyne oxidation, we have sought to characterize the transient dark blue intermediate. Upon mixing excess diphenylacetylene with **1** in neutral CH_3CN, a dark blue solution with a strong absorption band at λ_{max} = 658 nm develops,[19b] and the color gradually fades out within 30 min. This absorption band does not originate from diphenylacetylene or *cis*-$[(Cn^*)(CF_3CO_2)Ru^{VI}O_2]ClO_4$, since neither of these species have comparable absorptions in the 500−700 nm spectral region.

Scheme 2. Reaction of Bis(trimethylsilyl)acetylene with **1** in Neutral MeCN



3a

Likewise, the reactions of 4-octyne, 1-phenyl-1-propyne, and 2-butyne gave rise to dark colored intermediates (λ_{max} = 639, 647, and 649 nm, respectively), which converted spontaneously to $[(Cn^*)(CF_3CO_2)Ru^{II}(CH_3CN)_2]ClO_4$ in CH_3CN at room temperature. Unfortunately, attempts to isolate these species were futile.

When **1** was treated with excess bis(trimethylsilyl)acetylene in neutral CH_3CN, complex **3a** showing an intense absorption band at λ_{max} = 566 nm was immediately formed (Scheme 2). Unlike the other acetylenes we examined, this complex was found to be stable at ambient conditions over 24 h in solution and could be isolated by slow solvent evaporation from aqueous acetone.

In CH_3CN, a purified sample of **3a** exhibits an identical UV−vis spectral feature to the initial reaction mixture [λ_{max} = 566 nm (ϵ_{max} = 5100)] (see Experimental Section). Its infrared spectrum shows strong absorption peaks at 1698 and 1091 cm^{-1}, which we assign to the $\nu_{C=O}$ stretch of the trifluoroacetate ligand and the $\nu_{Cl=O}$ stretch of the ClO_4^- anion, respectively. Notably the RuO_2 stretches at 842 and 856 cm^{-1} of the starting complex **1** are absent. Complex **3a** gave well-resolved ^{1}H and ^{13}C NMR spectra, indicative of its diamagnetic nature. All the ^{1}H and ^{13}C resonances of the Cn* ligand are at their normal positions, but the ^{13}C signal(s) of the acetylenic carbon atoms (ca. δ 115 ppm) corresponding to free bis(trimethylsilyl)acetylene are not observed. A striking characteristic of **3a** is that the compound shows a very downfield ^{13}C signal at δ 239.1 ppm, indicative of a very deshielded carbon atom (see Supporting Information). On the basis of FAB-MS (m/z = 588 M$^+$) and elemental

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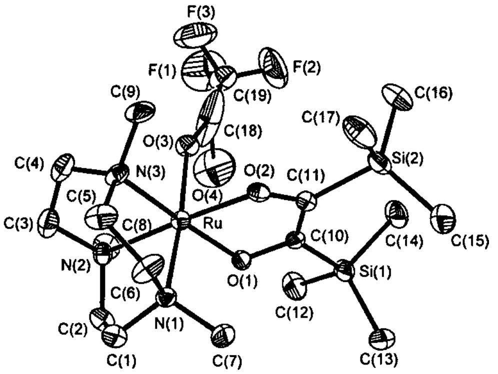

Figure 3. Molecular structure of the $[(\mathrm{Cn^*})(\mathrm{CF_3CO_2})\mathrm{Ru^{IV}}\overline{\mathrm{OC_2(SiMe_3)_2\text{-}}}\mathrm{O}]^+$cation complex and atom labeling scheme. Selected bond distances (Å): Ru−O(1) 1.977(5), Ru−O(2) 1.979(6), Ru−O(3) 2.075(6), Ru−N(1) 2.089(6), Ru−N(2) 2.109(7), Ru−N(3) 2.095(6). Selected bond angles (°): O(1)−Ru−O(2) 78.1(2), O(1)−Ru−O(3) 89.4(2), O(2)−Ru−O(3) 87.0(2), O(1)−Ru−N(1) 95.9(2), O(2)−Ru−N(1) 95.5(3), O(3)−Ru−N(1) 174.5(2), O(1)−Ru−N(3) 176.7(3), O(2)−Ru−N(3) 98.7(3), O(3)−Ru−N(3) 91.0(3), N(1)−Ru−N(3) 83.9(3), O(1)−Ru−N(2) 99.4(2), O(2)−Ru−N(2) 117.1(2), O(3)−Ru−N(2) 94.5(3), N(1)−Ru−N(2) 83.2(3), C(11)−O(2) 1.305(10), C(10)−O(1) 1.301(9), C(11)−C(10) 1.439(12).

analyses, we formulate complex **3a** to be an adduct of **1** and bis(trimethylsilyl)acetylene.

The molecular structure of **3a** has been established by X-ray crystallography (Figure 3). Figure 3 shows that the *cis*-configured O(1)−Ru−O(2) moiety is directly bound to the acetylenic carbon atoms C(10) and C(11) to form a five-membered planar metallacycle, and the compound can be regarded as a [3 + 2] cycloadduct of complex **1** and bis(trimethylsilyl)acetylene. Although similar cyclic intermediates have been proposed in the oxidation of acetylenes by OsO_4, such complexes have never been isolated or well characterized (see later sections).[12a,32] In complex **3a**, the ruthenium atom adopts a distorted octahedral geometry coordinating to the Cn* ligand and a η^1-bound trifluoroacetate. The bond angles around C(10) and C(11) atoms are O(1)−C(10) −Si(1) = 112.9(6)°, O(1)−C(10)−C(11) = 113.6(7)°, and C(11)−C(10)−Si(1) = 133.4(7)°; O(2)−C(11) −Si(2) = 112.8(6)°, O(2)−C(11)−C(10) = 114.0(7)°, and C(10)−C(11)−Si(2) = 133.0(7)°. The sizable deviation from an ideal bond angle of 120° for a sp^2 hybridized carbon atom is ascribed to steric repulsion between the two *cis*-$SiMe_3$ groups. The Ru(1)−O(1) and Ru(1)−O(2) distances are 1.977(5) and 1.979(6) Å, respectively, comparable to the related Ru−O distances found in $[{}^n\mathrm{Bu_4N}][\mathrm{Ru^{VI}(N)(L)}]$ [1.956(3) and 1.957(3) Å; L = 1,2-bis(2-hydroxyphenyl-1-carboxamido)benzene tetraanion][33] and $[\mathrm{Ru_2(Cl_4Cat)_4}]^{3-}$ complexes [1.998(2), 1.965(2), 1.990(2), and 1.973(2) Å] (Cl_4Cat = tetrachlorocatecholate) (see Table 2).[34]

The respective C(11)−O(2) and C(10)−O(1) bond distances are 1.305(10) and 1.301(9) Å, which are slightly shorter than the related $C(sp^2)$−O single bond distances (1.32−1.35 Å) found in $[\mathrm{Ru_2(Cl_4Cat)_4}]^{3-}$ [34] and $[{}^n\mathrm{Bu_4N}][\mathrm{Ru^{VI}(N)(L)}]$.[33] On the other hand, the measured C(11)−C(10) bond distance [1.439(12) Å] is significantly elongated from a typical C═C double (1.33 Å); this value is comparable to that of a CH$\overset{...}{-}$C(O) linkage [1.382(11) Å] found in $[\mathrm{Cn^*Ru^{III}(acac)(OH)}]\mathrm{PF_6{\cdot}H_2O}$ (acac = acetylacetonate).[35] These findings suggest that the ligand π-electrons are in fact delocalized among the O(1), C(10), C(11), and O(2) atoms, and we propose that the metallacycle is a resonance hybrid between a dioxolene and a diketone.

Table 2. Crystal Data and Structure Refinement for Complex **3a**

compound	**3a**
empirical formula	$C_{19.67}H_{40}ClF_3N_{3.33}O_8RuSi_2$
formula wt	700.92
temp	295(2) K
wavelength	0.710 73 Å
crystal system	monoclinic
space group	$P2_1/n$ (No. 14)
unit cell dimens	a = 23.4294(2) Å; α = 90° b = 8.5762(2) Å; β = 90.960(1)° c = 48.8457(9); γ = 90°
vol, Z	9813.2(3) Å^3, 12
density (calcd)	1.423 mg/m^3
$F(000)$	4336
reflectns collected	40 484
independent reflectns	17 207 (R_{int} = 0.0488)
no. of data used	16 231
no. of parameters	1047
goodness-of-fit on F^2	1.105
final R indices $[I > 2\sigma(I)]^a$	R_1 = 0.085, wR_2 = 0.20
R indices (all data)^a	R_1 = 0.12, wR_2 = 0.22

[a] $R = \sum||F_0| - |F_c||/\sum|F_0|$; $R_w = [\sum w(|F_0| - |F_c|)^2/\sum wF_0^2]^{1/2}$ where $w = 4F_0^2/\sigma^2(F_0^2)$.

As expected, the Cn* ligand is facially coordinated to the Ru atom. The respective Ru(1)−N(1), Ru(1)−N(2), and Ru(1)−N(3) distances of 2.089(6), 2.109(7), and 2.095(6) Å are comparable to the corresponding Ru−N distances in *cis*-$[(\mathrm{Cn^*})(\mathrm{CF_3CO_2})\ \mathrm{Ru^{VI}O_2}]\mathrm{ClO_4}$ (**1**) [2.097(9), 2.23(2), and 2.197(9) Å].[19b]

Aryl- and alkyl-substituted trimethylsilylacetylenes and dimethyl acetylenedicarboxylate reacted with complex **1** in a similar manner to afford dark blue to purple solutions with $\lambda_{\max}$ ranging from 553 to 626 nm. The spectral data are summarized in Table 3. Unlike the bis(trimethylsilyl)acetylene derivative, these intermediates are unstable in solution and readily converted to $[(\mathrm{Cn^*})(\mathrm{CF_3CO_2})\mathrm{Ru^{II}(MeCN)_2}]\mathrm{ClO_4}$ at room temperature. Their instabilities were manifested by the decay of the 523−626 nm band (ca. 55% from its initial absorbance) after standing the solutions for 24 h at room temperature. Although dark blue solids could be isolated by precipitation with diethyl ether, they deteriorated rapidly and could not be purified in our hands.

Characterization of the Cycloadducts by Electrospray Ionization Mass Spectroscopy. Electrospray ionization mass spectroscopy (ESI-MS) has been useful for characterization of large biomolecules and multiply charged metal complexes in solution.[36] Because of the mildness of this ionization method, it has recently been applied to detect the formation of reactive transient intermediates such as $[\mathrm{O{=}Mn^V(salen)}]^+$ (salen = Schiff bases)[37] and (hydroxperoxy)iron(III) ($\mathrm{HOOFe^{III}}$) species.[38]

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Table 3. UV−Visible and Electrospray Spectral Data for the Ruthenium(IV) Cycloadduct Complexes

entry	alkynes	λ_{max}/nm (ϵ_{max}/dm^3 mol^{-1} cm^{-1})	ions (m/z and relative abundance)
1	$Me_3SiC\equiv CSiMe_3$	566 (5100)	$[Cn^*(CF_3CO_2)Ru^{IV}OC_2(SiMe_3)_2O]^+$ (**3a**) (588, 100%)
2	$Me_3SiC\equiv CCO_2Et$	553 (5400)	$[Cn^*(CF_3CO_2)Ru^{IV}OC_2(SiMe_3)(CO_2Et)O]^+$ (**3b**) (588.1, 100%)
3	$Me_3SiC\equiv CC(CH_3)_3$	581 (5600)	$[Cn^*(CF_3CO_2)Ru^{IV}OC_3(SiMe_3)(CH_3)_3O]^+$ (**3c**) (571.9, 100%)
4	$Me_3SiC\equiv CCH_3$	588 (5200)	$[Cn^*(CF_3CO_2)Ru^{IV}OC_2(SiMe_3)(CH_3)O]^+$ (**3d**) (529.9, 100%)
5	$Me_3SiC\equiv CC_4H_9$	604 (5300)	$[Cn^*(CF_3CO_2)Ru^{IV}OC_2(SiMe_3)(C_4H_9)O]^+$ (**3e**) (571.9, 100%)
6	*p*-$ClC_6H_4C\equiv CSiMe_3$	605 (5200)	$[Cn^*(CF_3CO_2)Ru^{IV}OC_2(SiMe_3)(ClC_6H_4)O]^+$ (**3f**) (625.9, 100%)
7	$C_6H_5C\equiv CSiMe_3$	606 (5200)	$[Cn^*(CF_3CO_2)Ru^{IV}OC_2(SiMe_3)(C_6H_5)O]^+$ (**3g**) (591.9, 100%)
8	*p*-$FC_6H_4C\equiv CSiMe_3$	606 (5200)	$[Cn^*(CF_3CO_2)Ru^{IV}OC_2(SiMe_3)(FC_6H_4)O]^+$ (**3h**) (609.9, 100%)
9	*p*-$CF_3C_6H_4C\equiv CSiMe_3$	609 (5000)	$[Cn^*(CF_3CO_2)Ru^{IV}OC_2(SiMe_3)(CF_3\text{-}C_6H_4)O]^+$ (**3i**) (659.9, 100%)
10	*p*-$CH_3-C_6H_4C\equiv CSiMe_3$	613 (5400)	$[Cn^*(CF_3CO_2)Ru^{IV}OC_2(SiMe_3)(CH_3\text{-}C_6H_4)O]^+$ (**3j**) (605.9, 100%)
11	*p*-$CH_3O-C_6H_4C\equiv CSiMe_3$	626 (5000)	$[Cn^*(CF_3CO_2)Ru^{IV}OC_2(SiMe_3)(CH_3O\text{-}C_6H_4)O]^+$ (**3k**) (621.9, 100%)
12	$nC_3H_7C\equiv C\text{-}nC_3H_7$	639	$[Cn^*(CF_3CO_2)Ru^{IV}OC_2(C_3H_7)_2O]^+$ (**3l**) (528.2, 20%) $[(Cn^*)(CF_3CO_2)\ Ru^{II}(MeCN)_2]^+$ (468.0, 35%), $[(Cn^*)(CF_3CO_2)Ru^{II}(MeCN)]^+$ (427.1, 100%)
13	$C_6H_5C\equiv CCH_3$	647	$[Cn^*(CF_3CO_2)Ru_{IV}OC_2(CH_3)(C_6H_5)O]^+$ (**3m**) (533.9, 80%), $[(Cn^*)(CF_3CO_2)Ru^{II}\ (MeCN)_2]^+$ (468.0, 45%), $[(Cn^*)(CF_3CO_2)Ru^{II}(MeCN)]^+$ (427.1, 100%)
14	$CH_3C\equiv CCH_3$	649	$[Cn^*(CF_3CO_2)Ru^{IV}OC_2(CH_3)_2O]^+$ (**3n**) (471, 15%), $[(Cn^*)(CF_3CO_2)Ru^{II}(MeCN)_2]^+$ (468.0, 60%), $[(Cn^*)(CF_3CO_2)\ Ru^{II}(MeCN)]^+$ (427.1, 100%)
15	$C_6H_5C\equiv CC_6H_5$	658	$[Cn^*(CF_3CO_2)Ru^{IV}OC_2(C_6H_5)_2O]^+$ (**3o**) (596.1, 100%), $[(Cn^*)(CF_3CO_2)\ Ru^{II}(MeCN)_2]^+$ (468.0, 90%), $[(Cn^*)(CF_3CO_2)Ru^{II}(MeCN]^+$ (427.1, 35%)
16	$MeO_2CC\equiv CCO_2Me$	535 (4900)	$[Cn^*(CF_3CO_2)Ru^{IV}OC_2(CO_2Me)_2O]^+$ (**3p**) (559.9, 100%), $[(Cn^*)(CF_3CO_2)Ru^{II}\ (MeCN)_2]^+$ (468.0, 35%), $[(Cn^*)(CF_3CO_2)Ru^{II}\ (MeCN)]^+$ (427.1, 60%)

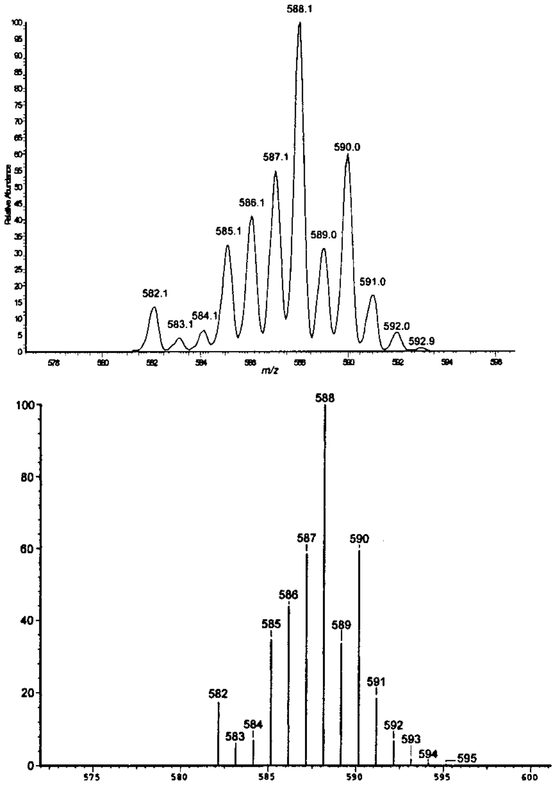

Figure 4. Experimental (top) and calculated (bottom) isotopic distribution pattern of $[(Cn^*)(CF_3CO_2)\overline{Ru^{IV}OC_2(SiMe_3)_2O}]^+$ (**3a**).

In this work, we employed ESI-MS to determine the molecular composition of the metastable dark colored intermediates observed in the stoichiometric alkyne oxidations by **1**.

As shown in Figure 4, the mass spectrum obtained by mixing **1** with excess bis(trimethylsilyl)acetylene in CH_3CN revealed a single prominent ion cluster at $m/z = 588$, which we assign to the $[(Cn^*)(CF_3CO_2)\overline{Ru^{IV}OC_2(SiMe_3)_2O}]^+$ complex cation based on excellent agreement between the experimental and calculated isotopic distribution pattern. Also, the spectral pattern is identical to that obtained with an authentic complex **3a**. The molecular cluster corresponding to the *cis*-$[(Cn^*)(CF_3CO_2)Ru^{VI}O_2]^+$ cation ($m/z = 418$) was not observed, indicating that the ruthenium oxidant had reacted completely. Complex **2** was also found to react with an excess of bis(trimethylsilyl)acetylene in CH_3CN at room temperature to afford a similar cycloadduct that was characterized by UV−vis spectroscopy ($\lambda_{max} = 592$ nm) and ESI-MS [$m/z = 534$ (M^+), 100%].

Similarly, the ESI-MS spectra obtained by reacting **1** with other silylated acetylenes and dimethyl acetylenedicarboxylate in CH_3CN showed a single prominent molecular ion species that is best formulated as a cycloadduct between the alkyne and the ruthenium oxidant. The mass spectral data are listed in Table 3.

For the oxidation of 4-octyne, diphenylacetylene, 1-phenyl-1-propyne, and 2-butyne by **1**, the ESI-MS analyses of the reaction mixtures [conditions: **1** (2 μmol) + alkynes (10 mmol) in CH_3CN (3 mL)] gave three sets of ion cluster peaks. The ESI mass spectrum for the reaction of **1** with diphenylacetylene is shown in Figure 5. The two cluster peaks at $m/z = 468$ (M^+); 427($M^+ - CH_3CN$) are assigned to the $[(Cn^*)(CF_3CO_2)Ru^{II}(CH_3CN)_2]^+$ cation, since the same ESI-MS spectrum has been obtained with an authentic sample of $[(Cn^*)(CF_3CO_2)Ru^{II}(CH_3CN)_2]ClO_4$. On the basis of the mass value and the isotope pattern, the molecular composition of the remaining ion cluster is best formulated as the complex $[(Cn^*)(CF_3CO_2)\overline{Ru^{IV}OC_2R^1R^2O}]^+$ ($R^1 = R^2 = n\text{-}C_3H_7$, $m/z = 527$; $R^1 = R^2 = Ph$, $m/z = 596$; $R^1 = Ph$, $R^2 = Me$, $m/z = 532$; $R^1 = R^2 = Me$, $m/z = 470$, see Table 3). The identities of the two cluster peaks in the region of $m/z = 500−560$ presumably due to fragmentation from the cycloadduct complex remains unknown in this work. Similar mass losses are not observed for the reactions with 4-octyne, 1-phenyl-1-propyne, and 2-butyne.

Kinetic Studies on the [3 + 2] Cycloaddition of *cis*-$[(Cn^*)(CF_3CO_2)Ru^{VI}O_2]ClO_4$ with Some Disubstituted Alkynes. The kinetics of the cycloaddition of **1** with a series of substituted trimethylsilylacetylenes and dimethyl acetylenecarboxylate has been studied by stopped-flow spectrophotometry. These alkynes were chosen for the kinetic studies because the deterioration of their cycloadducts occurred on a time scale much slower than their formation so that the kinetic analysis was feasible. Monitoring the growth of the 535−626 nm absorption band allowed us to establish the rate law $k_2[Ru^{VI}][alkyne]$, where k_2 = second-order rate constant. In the presence of 10- to 50-fold excess alkyne, we observed clean first-order kinetics (Figure 6). The pseudo-first-order rate constants (k_{obs}) were obtained by the nonlinear least-squares fits of the growth curves, and the slopes of the k_{obs} vs [alkyne] plots gave the k_2 values. The results are shown in Table 4. Under the concentrations employed in this work, no rate saturation was observed. For comparison, Table 5 lists some rate constants for the oxidation of alkynes by some other oxidants reported in the literature.

When the diphenylacetylene, 2-octyne and 1-phenyl-1-propyne oxidations were examined by stopped-flow spectrophotometry, the kinetic profiles of the initial cycloadduct formations were kinetically inseparable from a secondary chemical reaction, presumably the decomposition of the initial cycloadducts. The spectral development at ca. 660 nm of these reactions did not conform to first-order kinetics even in the presence of 40-fold excess of alkyne. For this reason these reactions had not been studied in detail.

The temperature dependence of the k_2 values for the reactions of bis(trimethylsilyl)acetylene, 1-trimethylsilylhexan-1-yne, and 1-(4-chlorophenyl)-2-trimethylsilylacetylene with **1** has been examined. The activation parameters were determined from the $\ln(k_2/T)$ vs $1/T$ plots, which are linear over the temperature range studied (286−315 K). The entropies of activation ($\Delta S^‡$) are -18 ± 1.7, -17 ± 1.9, and -15 ± 1.4 cal mol^{-1} K^{-1} and enthalpies of activation ($\Delta H^‡$) are 9.3 ± 0.9, 10.9 ± 1.2, and 11.9 ± 1.4 kcal mol^{-1} for the bis(trimethylsilyl)acetylene, 1-trimethylsilyl-1-hexyne, and 1-(4-chlorophenyl)-2-trimethylsilylacetylene oxidations, respectively. Attempts to determine the k_2 values at $T > 328$ K met with significant decomposition of the cycloadduct complexes, and clean pseudo-first-order kinetic profiles were not obtained. The $\Delta H^‡$ values for the three reactions are comparable to some reported values for the oxidation of propiolic acid (6 kcal mol^{-1}) and phenylpropiolic acid (7 kcal mol^{-1}) by $KMnO_4$.[41] The $\Delta S^‡$ values are large and negative in all cases, consistent with the rate-determining association of the *cis*-dioxoruthenium(VI) oxidant and alkynes. However, these $\Delta S^‡$ values are somewhat smaller than that obtained in the oxidation of propiolic and phenylpropiolic acids (-31 cal mol^{-1} K^{-1}) by $KMnO_4$.[41]

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(40) Simándi, L. I.; Jáky, M. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1481.
(41) Simándi, L. I.; Jáky, M. *J. Chem. Soc., Perkin Trans. 2* **1977**, 630.

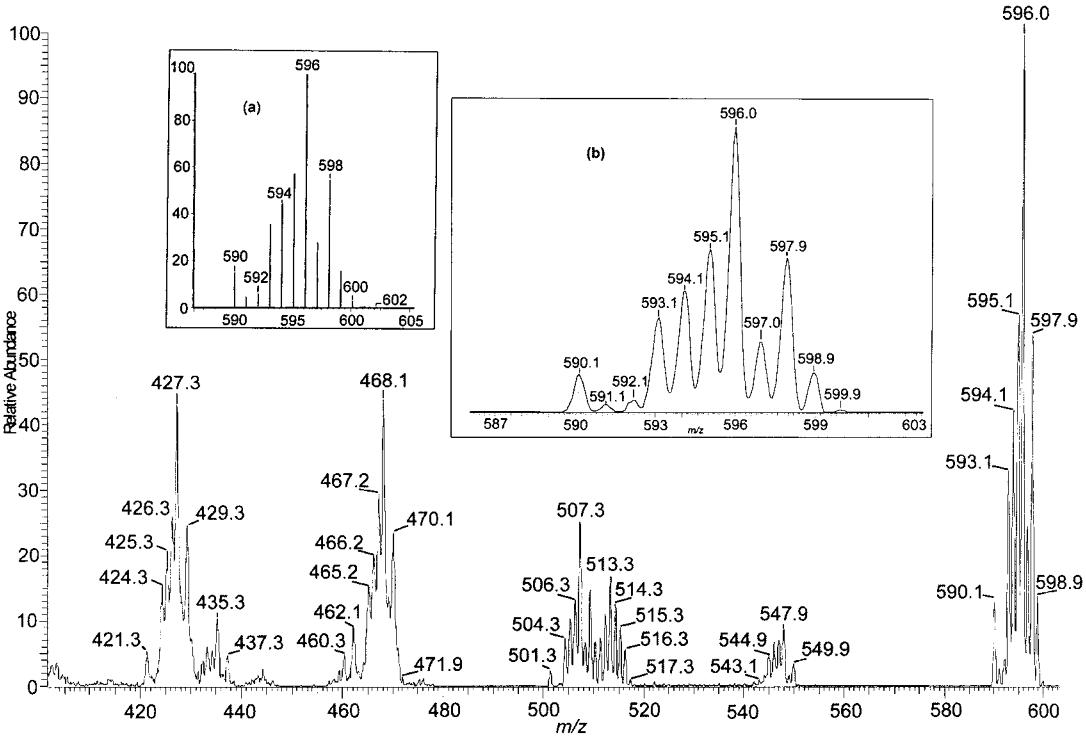


Figure 5. Electrospray ionization mass spectrum obtained from the reactions of diphenylacetylene with **1** in neutral CH_3CN. Insets: (a) Calculated and (b) experimental isotopic distribution pattern for the cycloadduct $[(\mathrm{Cn}^*)(\mathrm{CF_3CO_2})\overline{\mathrm{Ru^{IV}OC_2Ph_2O}}]^+$ complex.

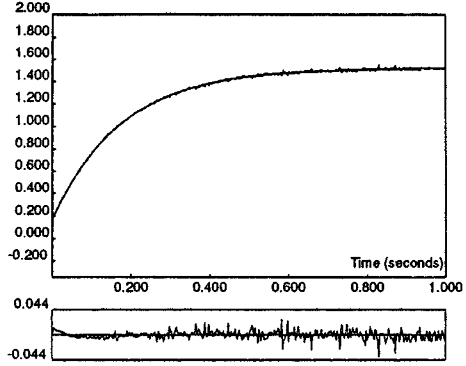
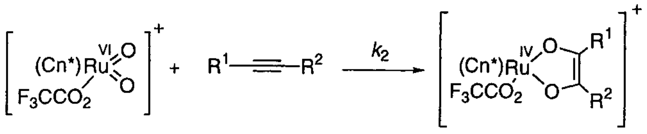


Figure 6. Experimental and calculated absorbance−time curves and residue for the reaction of $Me_3SiC{\equiv}CSiMe_3$ (0.1 M) with **1** (1 mM) in CH_3CN at 296 K.

Table 4. Second-Order Rate Constants for the Cycloaddition of Alkynes with *cis*-Dioxoruthenium(VI) Complex 1[a]



entry	R^1	R^2	k_2/dm^3 mol^{-1} s^{-1}	I_p/eV[b]
1	C_4H_9	$SiMe_3$	10.7 ± 0.4[d]	9.34
2	CH_3	$SiMe_3$	5.7 ± 0.2	9.53
3	EtO_2C	$SiMe_3$	5.1 ± 0.2	9.98
4	$(CH_3)_3C$	$SiMe_3$	3.6 ± 0.2	10.19
5	Me_3Si	$SiMe_3$	103 ± 4[c]	10.5
6	MeO_2C	CO_2Me	1.9 ± 0.1	10.94
7	*p*-$MeOC_6H_4$	$SiMe_3$	18.8 ± 0.8	
8	*p*-MeC_6H_4	$SiMe_3$	8.6 ± 0.4	8.63
9	*p*-FC_6H_4	$SiMe_3$	5.8 ± 0.2	8.87
10	*p*-ClC_6H_4	$SiMe_3$	4.6 ± 0.2[e]	8.93
11	C_6H_5	$SiMe_3$	4.7 ± 0.2	9.06
12	*p*-$CF_3C_6H_4$	$SiMe_3$	2.1 ± 0.1	

[a] $T = 297 \pm 0.1$ K. [b] Calculated ionization potential. [c] $\Delta H^\ddagger = 9.3 \pm 0.9$ kcal mol^{-1}; $\Delta S^\ddagger = -18 \pm 1.7$ cal mol^{-1} K^{-1}. [d] $\Delta H^\ddagger = 10.9 \pm 1.2$ kcal mol-1; $\Delta S^\ddagger = -17 \pm 1.9$ cal mol^{-1} K^{-1}. [e] $\Delta H^\ddagger = 11.9 \pm 1.4$ kcal mol^{-1}; $\Delta S^\ddagger = -15 \pm 1.4$ cal mol^{-1} K^{-1}.

Discussion

Internal alkynes react with M=O oxidants such as OsO_4, $KMnO_4$, or RuO_4 to afford 1,2-diketones, which are synthetically useful intermediates.[45] It has long been postulated that the alkyne oxidations proceed via a putative cyclic diester intermediate generated by a formal [3 + 2] cycloaddition between a MO_2 moiety and C≡C bond, analogous to alkene dihydroxylations.[10] However, in all cases, structural evidence of this cyclic diester/cycloadduct is lacking in the literature. Previously Griffith and co-workers[32b] reported that the reaction of OsO_4 with alkynes in the presence of tertiary bases afforded *trans*-dioxoosmium(VI) ester complexes $[Os_2O_4(O_4C_2RR')L_4]$ (L = isoquinoline or pyridine) with a proposed structure depicted in Scheme 3 (entry 1). These dioxoosmium(VI) complexes were presumably derived from a cyclic diester osmium(VI) intermediate via a [3 + 2] cycloaddition pathway.[12a,32]

While the mechanism of the alkene oxidations by M=O species has been extensively investigated, related studies on the alkyne oxidations are sparse. In the 1970s Simándi and Jáky reported their mechanistic studies on the alkyne oxidation by $KMnO_4$.[39−41] In 1985 Lee and co-workers reported similar studies with $^nBu_4NMnO_4$ as oxidant.[42] In the study by Simándi and Jáky, the oxidation was proposed to be initiated by a nucleophilic attack of MnO_4^- anion on the C≡C bond leading

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(43) Ibne Rasa, K.; Pater, R. H.; Ciabatonni, J.; Edwards, J. O. *J. Am. Chem. Soc.* **1973**, *95*, 7894.

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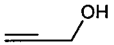
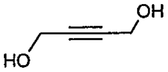
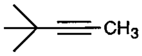
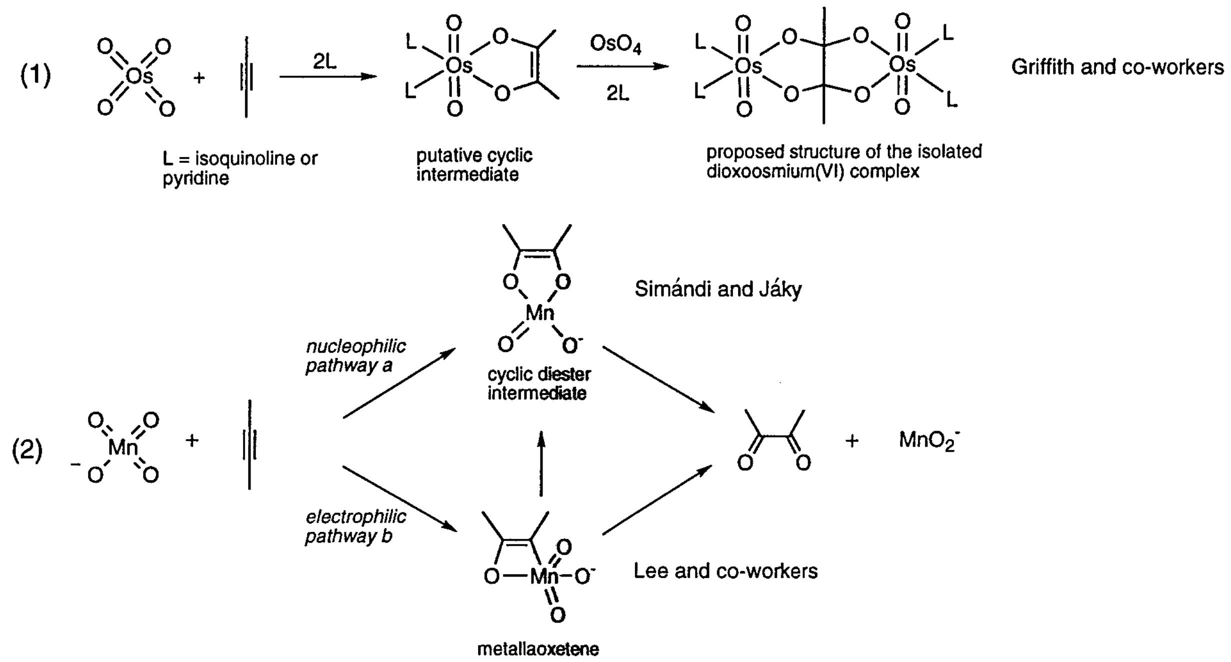
Table 5. Some Reported Kinetic Data for the Alkyne Oxidations by Other Oxidants[a]

entry	alkynes	oxidants	solvent	rate constants, $dm^3 mol^{-1} s^{-1}$	ref
1	$HO_2C-\equiv-CO_2H$	$KMnO_4$	1.5 M $NaClO_4$	$k_1 = 1230$; $k_2 = 520$; $k_3 = 35$ ($\Delta H^{\ddagger} = 6.1$ kcal mol^{-1}; $\Delta S^{\ddagger} = -32$ eu)	39
2		$KMnO_4$	0.3 M $NaClO_4$	10.0 ($\Delta H^{\ddagger} = 6.3$ kcal mol^{-1}; $\Delta S^{\ddagger} = -33$ eu)	40
3		$KMnO_4$	0.3 M $NaClO_4$	12.5 ($\Delta H^{\ddagger} = 5.3$ kcal mol^{-1}; $\Delta S^{\ddagger} = -36$ eu)	40
4	$\equiv-CO_2H$	$KMnO_4$	pH 3.77, ionic strength = 1.5 M	$k_1 = 183$; $k_2 = 43.2$ ($\Delta H^{\ddagger} = 6.2$ kcal mol^{-1}; $\Delta S^{\ddagger} = -31$ eu)	41
5	$Ph-\equiv-CO_2H$	$KMnO_4$	pH 3.77, ionic strength = 1.5 M	$k_1 = 38.8$; $k_2 = 11.6$ ($\Delta H^{\ddagger} = 7.2$ kcal mol^{-1}; $\Delta S^{\ddagger} = -31$ eu)	41
6	$C_4H_9-\equiv-C_4H_9$	Bu_4NMnO_4	CH_2Cl_2	$7.3 \pm 0.7 \times 10^{-4}$	42
7	$Ph-\equiv-Et$	Bu_4NMnO_4	CH_2Cl_2	$30 \pm 5 \times 10^{-4}$	42
8		Bu_4NMnO_4	CH_2Cl_2	$60 \pm 5 \times 10^{-4}$	42
9	$C_3H_7-\equiv-C_3H_7$	mClC$_6$H$_4$CO$_3$H	CH_2Cl_2	21.2×10^{-4}	43
10	$Ph-\equiv-H$	mClC$_6$H$_4$CO$_3$H	C_6H_6	1.65×10^{-5}	44
11	$Ph-\equiv-Ph$	$[O{=}Cr^V(salen)]OTf$	CH_3CN	$4.7 \pm 0.9 \times 10^{-5}$	30

[a] k_1, k_2, and k_3 are rate constants for undissociated (H_2A), monodissociated (HA^-), and double dissociated (A^{2-}) species, respectively.

Scheme 3. Proposed Reaction Schemes for the Alkyne Oxidation by M=O Reagents



to a Mn(V) diester intermediate (Scheme 3, entry 2, pathway a), which subsequently decomposed to 1,2-diketones and Mn(III).[41] However, Lee and co-workers suggested an electrophilic mechanism wherein the Mn(V) diester was derived from a metallaoxetene intermediate (Scheme 3, entry 2, pathway b).[42] A similar metallaoxetene intermediate had also been proposed by Manosi and co-workers in 1993 on the oxidation of diphenylacetylene by oxochromium(V) salen complexes to benzil.[30] Despite these considerable efforts in this field, the mechanism of alkyne oxidations by M=O compounds has remained quite speculative because of the near total absence of experimental information on the nature of the M=O/alkyne intermediate.

In this work, we have found that the *cis*-$[(Cn^*)(CF_3CO_2)Ru^{VI}O_2]ClO_4$ complex (**1**) readily oxidized disubstituted alkynes to give 1,2-diketones in good yields. Using UV−visible and electrospray ionization mass spectroscopies, **1** was found to undergo an initial [3 + 2] cycloaddition reaction with alkynes $[R-C\equiv C-R']$ to give the $[(Cn^*)(CF_3CO_2)\overline{Ru^{IV}OC_2RR'O}]^+$ intermediates. These Ru(IV) cycloadducts are featured by an intense low energy absorption band with λ_{max} in 550−660 nm. One of the cycloadducts, $[(Cn^*)(CF_3CO_2)\overline{Ru^{IV}OC_2(SiMe_3)_2O}]ClO_4$ (**3a**), has been isolated and structurally characterized by X-ray crystallography. These findings are the first experimental evidence for a [3 + 2] cycloaddition between a *cis*-MO_2 unit with a C≡C bond of alkyne in the M=O mediated alkyne oxidations.

Regarding the intense low energy absorption of the cycloadducts, because of their large ϵ_{max} values (ca. 5000 dm^3 mol^{-1} cm^{-1}) the electronic transition involved can be assigned as charge transfer in nature, presumably $\pi(^{-}O{-}CR{=}CR'{-}O^{-}) \rightarrow$ Ru(IV). In accordance with this assignment, the transition energy as reflected by the λ_{max} increases with electron-withdrawing substituents (see Table 3, compare entries 2 and 5 and entries 9 and 11). We note that LMCT transitions in Ru(IV) complexes with reducing auxiliary ligands such as phenoxides and amides, such as $[Ru^{IV}(chbae)(PPh_3)(py)]$ (H_4chbae = 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane; py = pyridine), usually occur in the visible region.[46]

Nature of the Transition State of the [3 + 2] Cycloaddition. When the log k_2 values of the cycloaddition reactions were plotted against the calculated ionization potentials (I_p) of the alkynes, no linear free energy relationship can be established (see Supporting Information). The I_p values were calculated at the MP2(FC)/6−31 + G(2df,p)//HF/6−31 level and have been corrected for zero-point vibrational energies (see Experimental Section for details).

Indeed, except for $Me_3SiC{\equiv}CSiMe_3$, the rate constants vary over a range of less than an order of magnitude, albeit with a change of I_p by 2.3 eV. Apparently electron-rich alkynes (lower I_p values) react faster with **1** than those bearing electron-withdrawing substituents. This is best described by a mechanism involving an electrophilic attack of the *cis*-dioxoruthenium(VI) moiety to the C≡C bond. Among the nine disubstituted acetylenes studied, the aliphatic alkynes appear to be more reactive than the aromatic analogues toward the cycloaddition reaction, since some of the aliphatic alkynes exhibit comparable reactivity to the aromatic analogues despite larger I_p values (see Table 4, compare entries 1 and 8; 2 and 11).

Indeed, the bis(trimethylsilyl)acetylene oxidation is particularly outstanding in the log k_2 vs I_p plot. The k_2 value for this reaction is about 10 times faster than the similar reaction with $C_3H_7C{\equiv}CSiMe_3$ (I_p = 9.34 eV), even though $Me_3SiC{\equiv}CSiMe_3$ has a calculated I_p value of 10.50 eV. As opposed to $Me_3SiC{\equiv}CSiMe_3$, the reaction of $MeO_2CC{\equiv}CCO_2Me$ (calculated I_p = 10.94 eV) with **1** is 5-fold slower than that of $C_3H_7C{\equiv}CSiMe_3$.

For a reaction involving rate-limiting single electron transfer, the slope of the log k_2 vs ΔG plot (ΔG = driving force of the reaction) would equal to $-16.8\ eV^{-1}$; therefore, lowering the ionization potential of the substrate by 1 eV should result in a dramatic rate acceleration.[47] In this work, however, with the exception of $Me_3SiC{\equiv}CSiMe_3$ the k_2 values are rather insensitive to the change of the calculated I_p values of the alkynes, which is incompatible with a single electron-transfer mechanism.

Product Studies. Oxene Insertion. Analogous to the alkene epoxidation by reactive Ru═O complexes,[5a−f,6a,b] the alkyne oxidation by **1** may occur via an oxirene intermediate, i.e., an "epoxide" of alkyne. Theoretical studies have suggested that oxirene is a highly reactive species, energetically similar to a ketocarbene.[48] Oxirene intermediates have been proposed for alkyne oxidations by peracids,[25,43,44] dioxiranes,[28,48] microsomes,[49] and methylrhenium(VIII) trioxide.[50] For example, the oxidation of 2-butyne by dimethyldioxirane was found to produce 2-hydroxy-2-methylpropanoic acid as the major product.[28b] A proposed mechanism is that the reaction is initiated by oxygen atom transfer reaction from the dioxirane to the alkyne to give an oxirene intermediate. The oxirene subsequently rearranges to a ketocarbene, which then converts to the product propanoic acid. It should be noted that no diacetyl was formed in this reaction; other products such as 1-oxiranylethanone and 2,2,5,5-tetramethyl-1,3-dioxolan-4-one were detected only in low yields.

If the alkyne oxidation by **1** takes place via oxene insertion, the corresponding 2-butyne oxidation should result in a similar product profile as the dioxirane-mediated oxidation, i.e., a predominant formation of 2-hydroxy-2-methylpropanoic acid. However, in this work, diacetyl was formed exclusively in 97% yield (see Table 1, entry 4). The absence of rearrangement products does not rigorously exclude the oxirene intermediate since it is possible that the formation of the second C−O bond would precede the Wolff rearrangement within the coordination sphere. Nonetheless, our findings do not warrant a rate-limiting oxirene formation mechanism.

[2 + 2] Cycloaddition. It is well documented that d^0 oxotitanium(IV) and zirconium(IV) complexes undergo [2 + 2] cycloaddition with C≡C bond to furnish metallaoxetene complexes.[51] Some of them with phenylacetylene and diphenylacetylene as substrates have been characterized by X-ray crystal analysis. As noted earlier, metallaoxetene intermediates have been postulated for the oxidation of alkynes by potassium permanganate[42] and oxochromium(V) Schiff-base complexes.[30]

For a [2 + 2] cycloaddition, the presence of a vacant coordination site is desirable. If the metallaoxetene formation is an obligatory pathway, then we anticipate that the reaction of alkynes with coordinatively saturated *cis*-$[(TetMe_6)Ru^{VI}O_2](ClO_4)_2$ (**2**) would not be facile because of the formation of a highly energetic seven-coordinated ruthenium center. However, we found that complex **2** oxidized 2-butyne and 1-trimethylsilyl-1-propyne to their 1,2-diketones in 97% yields. Furthermore, facile cycloaddition reaction of **2** with bis(trimethylsilyl)acetylene similar to complex **1** has been observed based on UV−vis and ESI-MS studies.

Hammett Correlation Studies. Rate-Limiting Vinyl Radical Formation. The effect of para-substituents on the k_2 values of the reactions of $ArC{\equiv}CSiMe_3$ with **1** has been investigated, and the reactivity of the substituted $YC_6H_4C{\equiv}CSiMe_3$ was found to decrease in the order Y = MeO > Me > F > Cl > H > CF_3. Fitting (by least-squares method) the log k_{rel} with Hammett σ^+ constants gave a straight line (R = 0.97) with a ρ^+ value = −0.61. This finding is contrary to the report by Lee and co-workers on the alkyne oxidation using $^nBu_4NMnO_4$ as oxidant, wherein a concave free energy plot was obtained.[42] The small ρ^+ value found in this work indicates little positive charge development at the α-carbon atom consistent with a weakly polar transition state; this also coincides with the small dependence of the k_2 values on the calculated ionization potential of alkynes as noted earlier. By the same token, the participation of carbocation radical is excluded. A vinyl cation intermediate also appears unlikely because the rate-limiting formation of a vinyl cation is always associated with a large ρ^+ value,[52] such as $\rho^+ = -3.84$ (electrophilic addition to C≡C bond)[53a] and ρ^+

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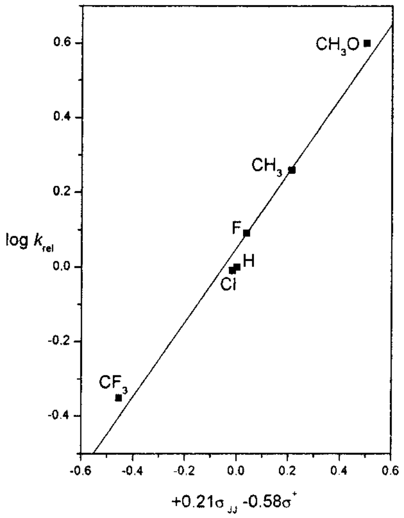

Figure 7. Linear dual-parameter Hammett correlation ($R = 0.99$, slope $= 1.00$) using $\sigma_{JJ}{}^{\bullet}$ and σ^+ for the cycloaddition of **1** with p-Y$-C_6H_4C{\equiv}CSiMe_3$ ($k_{rel} = k_Y/k_H$; Y = OCH_3, CH_3, F, H, Cl, and CF_3).

$= -5.1$ (solvolysis of vinyl tosylates in ethanol).[53b] On the other hand, rate-limiting vinyl radical formation[54a] is known to have small ρ^+ values as reported in the radical addition to substituted phenylacetylenes: $\rho^+ = -0.53$ (for p-Br$-C_6H_4S{\cdot}$)[54b] and -0.64 (for p-Cl$-C_6H_4SO_2{\cdot}$).[54c] Therefore, the small charge dependence observed in this work might be expected for a vinyl radical intermediate formation.

Apart from polar substituent effect, radical reactivity is also influenced by the substituent's ability to delocalize the spin density on the carbon radical center, namely, spin delocalization effect. Previously, we applied a carboradical substituent constant $\sigma_{JJ}{}^{\bullet}$, developed by Jiang and Ji,[55] to our kinetic studies on the styrene epoxidation by Ru═O complexes.[5e−f] With this parameter the epoxidation reaction was rationalized by the rate-limiting formation of benzylic radical intermediate, and both spin delocalization and polar substituent effects would affect the rate of reaction.[5e,f] The $\sigma_{JJ}{}^{\bullet}$ scale was chosen because it measures the spin delocalization effect of the substituent and is relatively free from residual polar effect.[55]

If the cycloaddition reactions of alkynes with *cis*-dioxoruthenium(VI) involve a vinyl radical intermediate, we anticipate similar effects to operate as spin density develops at the α-carbon while advancing to the transition state. Considering spin delocalization effect by employing the $\sigma_{JJ}{}^{\bullet}$ parameters, a dual-parameter Hammett correlation ($\log k_{rel} = \rho_{JJ}{}^{\bullet}\sigma_{JJ}{}^{\bullet} + \rho^+\sigma^+ = +0.21\sigma_{JJ}{}^{\bullet} - 0.58\sigma^+$) afforded a better straight line ($R = 0.99$, slope $= 1.00$) than the single parameter $\log k_{rel}$ vs σ^+ regression (Figure 7). The linear free energy correlation with the spin delocalization and polar effects is a good indication of radical character developed at the α-carbon in the transition state. The positive $\rho_{JJ}{}^{\bullet}$ value implies that the spin delocalization effect stabilizes the radical center and promotes the cycloaddition reaction. The negative ρ^+ value is indicative of the electrophilic nature of the cycloaddition reaction. The magnitude of $|\rho^+/\rho_{JJ}{}^{\bullet}| = 2.8$ suggests that the polar substituent effect is more important in the cycloaddition of the *cis*-dioxoruthenium(VI) to alkynes.[55]

Proposed Mechanism. We conclude that the cycloaddition reaction of aromatic alkynes with *cis*-$[(Cn^*)(CF_3CO_2)Ru^{VI}O_2]ClO_4$ (**1**) involves a rate-limiting formation of a vinyl radical intermediate (Scheme 4), which subsequently collapses at the adjacent Ru═O moiety to form the ruthenium(IV) dioxolene product. A linear (*sp* hybridized) configuration for the vinyl radical is assumed in order to achieve maximum orbital overlap for spin delocalization. Indeed extensive experimental and theoretical investigations have suggested that α-phenyl alkenyl radicals would favor a linear structure.[56]

To account for the extra reactivity of $Me_3SiC{\equiv}CSiMe_3$ toward cycloaddition with **1**, we suggest that the β-silyl group can stabilize the vinyl radical intermediate by hyperconjugation (β-silyl effect, Scheme 5). Although the stabilizing effect of β-silyl substituent in promoting the reactivity of carbocations[57] and vinyl cations[58] has been widely studied, silicon effects on vinyl radical stability are less established. According to a report by Ingold and co-workers,[59] $Et_3SiCH_2CH_3$ was found to be about 5.5 times more reactive than n-C_5H_{12} for β-H atom abstraction by ${}^tBuO{\cdot}$ radical. The higher reactivity of $Et_3SiCH_2CH_3$ was explained by the ability of the β-silyl group to stabilize the incipient radical. Since there is little C−H bond breaking at the transition state, the modest substituent effects observed for the H-atom abstraction is in accord with Hammond's postulate. Recently, Zhang and Bordwell[60] showed that the β-Me_3Si group can exert substantial stabilization effects of 3−5 kcal mol^{-1} on carboradicals based on the C−H bond dissociation energy measurements of Me_3SiCH_2- and $MeCH_2$-substituted thioesters. The effect of the α-$SiMe_3$ group on the reaction of $Me_3SiC{\equiv}CSiMe_3$ with **1** is less clear-cut. Davidson and co-workers have suggested that α- and β-silyl groups can stabilize free radicals to a similar extent (ca. 2.6 kcal mol^{-1}) based on gas kinetic experiments.[61] On the contrary, recent work by Zhang and Bordwell found that α-$SiMe_3$ showed little or no stabilization to carbon-centered radicals.[60]

Experimental Section

Materials. All solvents and alkynes were purified by standard procedures. Diphenylacetylene, 1-phenyl-1-propyne, bis(trimethylsilyl)-acetylene, 1-trimethylsilyl-1-propyne, ethyl 3-(trimethylsilyl)propynoate, 4-octyne, 2-butyne, 1-trimethylsilyl-3,3-dimethylbutyne, 1-trimethylsilylhexayne, dimethyl acetylenedicarboxylate, trimethylsilylacetylene, iodobenzene, 1-chloro-4-iodobenzene, 1-fluoro-4-iodobenzene, 4-iodotoluene, dichlorobis(triphenylphosphine)palladium(II), and copper(I) iodide were obtained commercially. Triethylamine was distilled over CaH_2 before use. Acetonitrile (AR, Lab-scan) for stoichiometric reactions and kinetic studies was first distilled over $KMnO_4$ and then CaH_2 before used. The alkyne substrates were purified by distillation after passage through a neutral aluminum oxide column. $[(Cn^*)Ru^{III}(CF_3CO_2)_3]{\cdot}H_2O$ was prepared by the previously reported procedure.[22b]

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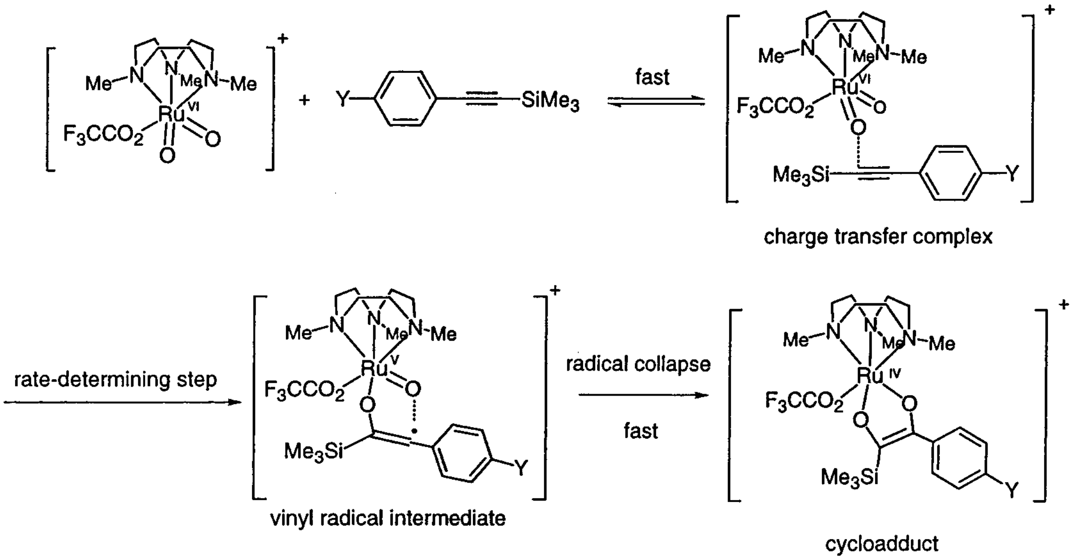
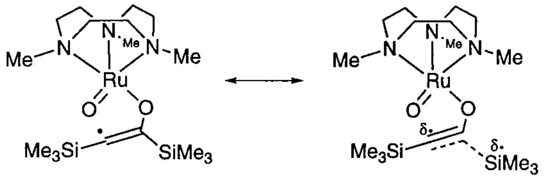
Scheme 4. Proposed Mechanism for the Cycloaddition of Alkynes to *cis*-Dioxoruthenium(VI)



Scheme 5. Resonance Structures Representing the β-Silyl Effect



Instrumentation. Electrospray ionization mass spectra were acquired with a Finningan MAT LCQ spectrometer. The sheath (compressed air) and auxiliary (nitrogen) gases were operated at 100 and 40 psi, respectively. Typical operating voltages were 3.0 V capillary voltage and 3.5 kV spray voltage. All the spectra were collected at 22 °C capillary temperature.

UV–visible kinetic measurements for rapid reaction were performed on an Applied Photophysics Ltd. SX.18MV sequential stopped-flow spectrofluorimeter by using Applied Photophysics Ltd. SX.18 MV kinetic spectrometer workstation software (version 4.24) on a Acorn Risc PC computer. Kinetic runs were initiated by mixing an equivalent volume of alkynes solution with the ruthenium solution. The temperature of solutions was maintained to within ±0.2 °C using a RET-100 (NESLAB Instruments Inc.) circulating water bath. Product analyses were performed on a G1800C GCD Series II spectrometer equipped with an electron ionization detector, connected with a HP Vectra XA computer containing an 82341C HP-IB card.

General Procedure for the Preparation of Substituted 1-Phenyl-2-trimethylsilylacetylenes. To a mixture of substituted iodobenzene (3.55 g, 16 mmol) and trimethylsilylacetylene (1.57 g, 16 mmol) in dry triethylamine (20 mL) was added with $Pd(PPh_3)_2Cl_2$ (0.112 g, 1 mol %) and CuI (0.15 g, 5 mol %) under a nitrogen atmosphere. The mixture was heated at 70 °C overnight. After cooling the mixture to room temperature, diethyl ether (50 mL) was added, and the suspension was filtered. The filtrate was collected and evaporated to dryness by rotory evaporation. The liquid residue was then purified on an alumina column using hexanes as the eluant. After solvent evaporation, the product was further purified by vacuum distillation.

1-(4-Fluorophenyl)-2-trimethylsilylacetylene. Yield: 2.37 g, 77%. Anal. Calcd for $C_{11}H_{13}FSi$ (M_r = 192.31): C, 68.07; H, 6.81. Found: C, 68.11; H, 6.77. IR (Nujol, cm^{-1}): 3025, 3010, 2890, 2100, 1595. ^1H NMR (300 MHz, 298 K, $CDCl_3$): δ 0.24 (s, 9 H), 6.97 (t, 2 H, J = 6.8 Hz), 7.44 (dd, 2 H, J = 8.85, 5.45 Hz). ^{13}C NMR (75.47 MHz, 298 K, $CDCl_3$): δ 0.00, 93.89, 104.07, 115.69, 117.96, 119.37, 134.01, 1390.1, 164.30. EI-MS: m/z 192 (M^+).

1-Phenyl-2-trimethylsilylacetylene. Yield: 2.45 g, 88%. Anal. Calcd for $C_{11}H_{14}Si$ (M_r = 174.32): C, 75.79; H, 8.10. Found: C, 75.67; H, 8.23. IR (Nujol, cm^{-1}): 3010, 2885, 2095, 1595. ^1H NMR (300 MHz, 298 K, $CDCl_3$): δ 0.25 (s, 9 H), 7.28 (m, 3 H), 745 (m, 2 H). ^{13}C NMR (75.47 MHz, 298 K, $CDCl_3$): δ 0.00, 95.29, 105.22, 115.77, 117.98, 119.37, 136.41, 143.45, 146.30. EI-MS: m/z 174 (M^+).

1-(4-Chlorophenyl)-2-trimethylsilylacetylene. Yield: 2.77 g, 83%. Anal. Calcd for $C_{11}H_{13}SiCl$ (M_r = 208.76): C, 63.29; H, 6.28. Found: C, 63.33; H, 6.32. IR (Nujol, cm^{-1}): 3012, 2895, 2098, 1595. ^1H NMR (300 MHz, 298 K, $CDCl_3$): δ 0.25 (s, 9 H), 7.26 (d, 2 H, J = 6.8 Hz), 7.39 (d, 2 H, J = 6.8 Hz). ^{13}C NMR (75.47 MHz, 298 K, $CDCl_3$): δ 0.00, 95.29, 105.22, 115.77, 117.98, 119.37, 136.41, 143.45, 146.30. EI-MS: m/z 208 (M^+).

1-(4-Toluene)-2-trimethylsilylacetylene. Yield: 2.56 g, 85%. Anal. Calcd for $C_{12}H_{16}Si$ (M_r = 188.34): C, 76.53; H, 8.56. Found: C, 76.33; H, 8.58. IR (Nujol, cm^{-1}): 3015, 2890, 2098, 1595. ^1H NMR (300 MHz, 298 K, $CDCl_3$): δ 0.24 (s, 9 H), 2.31 (s, 3 H), 7.07 (d, 2 H, J = 7.9 Hz), 7.34 (d, 2 H, J = 7.9 Hz). ^{13}C NMR (75.47 MHz, 298 K, $CDCl_3$): δ 0.00, 20.98, 90.16, 93.17, 105.31, 119.98, 128.90, 131.15, 138.55. EI-MS: m/z 188 (M^+).

1-(4-Anisole)-2-trimethylsilylacetylene. Yield: 2.58 g, 79%. Anal. Calcd for $C_{12}H_{16}OSi$ (M_r = 204.34): C, 70.53; H, 7.89. Found: C, 70.54; H, 7.88. IR (Nujol, cm^{-1}): 3013, 2990, 2100, 1595. ^1H NMR (300 MHz, 298 K, $CDCl_3$): δ 0.24 (s, 9 H), 3.78 (s, 3 H), 6.80 (d, 2 H, J = 8.9 Hz), 7.40 (d, 2 H, J = 8.9 Hz). ^{13}C NMR (75.47 MHz, 298 K, $CDCl_3$): δ 0.00, 55.18, 82.58, 92.32, 105.11, 113.71, 115.14, 116.25, 133.37, 138.09. EI-MS: m/z 204 (M^+).

Preparation of *cis*-$[(Cn^*)(CF_3CO_2)Ru^{VI}O_2]ClO_4$ (1). To ice-cooled 0.2 M CF_3CO_2H (10 mL) containing $[(Cn^*)Ru^{III}(CF_3CO_2)_3]\cdot H_2O$ (0.12 g) was added a saturated solution of $(NH_4)_2Ce^{IV}(NO_3)_6$ (1 g in 2 mL of deionized water). An immediate color change from light yellow to dark green was observed. Addition of $NaClO_4$ to the green solution induced precipitation of the desired complex. The solid was collected on a frit and air-dried. Yield: 55%. UV–vis in 0.2 M CF_3CO_2H [λ_{max}/nm (ϵ_{max}/dm^3 mol^{-1} cm^{-1})]: 329 (2400), 675 (50). IR (Nujol, cm^{-1}): 1647 ($\nu_{C=O}$), 842 (ν_{asym} RuO_2), 856 (ν_{sym} RuO_2). ESI-MS (CH_3CN) calcd for $C_{11}H_{21}N_3O_4F_3Ru$: m/z 418 (M^+). Anal. Calcd For $C_{11}H_{21}N_3O_8ClF_3Ru$: C, 25.56; H, 4.10; N, 8.13. Found: C, 25.86; H, 4.07; N, 8.21.

Caution! Transition metal perchlorates are potentially explosive, particular care should be exercised in preparation and handling.

General Procedure for the Stoichiometric Oxidation of Alkynes. To a 0.2 M CF_3CO_2H/CH_3CN (10 mL) solution of alkynes (30 mmol) was added **1** (10 μmol) under a nitrogen atmosphere. The reaction mixture was stirred for 5 h at room temperature. The solvent was removed by vacuum, and the residue was extracted by diethyl ether (2 × 10 mL). The combined organic extracts were washed with 0.1 M $NaHCO_3$ (2 × 10 mL) and then concentrated to about 3 mL by reduced pressure. Aliquots were taken for GC-MS analyses.

For all the stoichiometric reactions, *cis*-$[(Cn^*)(CF_3CO_2)Ru^{II}(CH_3CN)_2]ClO_4$ complex was isolated and purified by recrystallization from a CH_3CN/diethyl ether mixture (92% yield). Anal. Calcd for $C_{15}H_{27}F_3N_5ClO_6Ru$ ($M_r = 566.93$): C, 31.78; H, 4.80; N, 12.35. Found: C, 31.51; H, 5.03; N, 12.07. IR (Nujol, cm^{-1}): 2275, 2011 ($\nu_{C\equiv N}$), 1091 (ν_{Cl-O}). UV−vis (CH_3CN) [λ_{max} (ϵ/cm^{-1} mol^{-1} dm^3)]: 328 nm (210). ^1H NMR (300 MHz, 298 K, CD_3CN): 2.12 (s, 3 H), 2.25 (m, 6 H), 2.83 (s, 6 H), 2.94−3.21 (m, 6 H). ^{13}C NMR (75.47 MHz, 298 K, CD_3CN): δ 50.24, 55.28, 55.50, 62.95, 63.76, 64.33, 65.13, 239.10. ESI-MS (CH_3CN) calcd as $C_{15}H_{27}F_3N_5O_2Ru$ cation: *m/z* 468 (M^+), 427 ($M^+ - CH_3CN$).

Reaction of Complex 1 with Bis(trimethylsilyl)acetylene. Isolation of $[(Cn^*)(CF_3CO_2)\overline{Ru^{IV}OC_2(SiMe_3)_2O}]ClO_4$ (3a). To an excess of bis(trimethylsilyl)acetylene (2 mmol) in CH_3CN (10 mL) *cis*-$[(Cn^*)(CF_3CO_2)Ru^{VI}O_2]ClO_4$ (0.1 g, 0.2 mmol) was added under an argon atmosphere. A deep purple coloration instantaneously developed. The reaction mixture was vigorously stirred for 1 h. Solvent was then removed under vacuum, and the residue was redissolved in 80% aqueous acetone. Addition of $LiClO_4$ (0.05 g, 0.47 mmol) and slow evaporation of solvent afforded a purple microcrystalline solid. The solid was collected on a frit, washed with water and then dried in vacuo. Yield: 0.13 g, 98%. Anal. Calcd for $C_{19}H_{39}Si_2N_3O_8F_3ClRu$ ($M_r = 687.22$): C, 33.21; H, 5.72; N, 6.11. Found: C, 33.23; H, 5.68; N, 6.22. IR (Nujol, cm^{-1}): 3013, 1698 ($\nu_{C=O}$), 1256 (ν_{C-O}), 1091. UV−vis (CH_3CN) [λ_{max} (ϵ/cm^{-1} mol^{-1} dm^3)]: 566 nm (5100). ^1H NMR (300 MHz, 298 K, $CDCl_3$): δ 0.11 (s, 18 H), 2.12 (s, 3 H), 2.25 (m, 6 H), 2.83 (s, 6 H), 2.94−3.21 (m, 6 H). ^{13}C NMR (75.47 MHz, 298 K, $CDCl_3$): δ 3.11, 3.25, 3.41, 3.58, 3.74, 3.91, 50.24, 55.28, 55.50, 62.95, 63.76, 64.33, 65.13, 239.10. ESI-MS (CH_3CN) calcd as $C_{19}H_{39}F_3N_3O_4Si_2Ru$ cation: *m/z* 588 (M^+).

Electrospray Ionization Mass Spectroscopic Analyses of the Reaction of $R^1-C\equiv C-R^2$ and *cis*-$[Ru^{VI}(Cn^*)(CF_3CO_2)O_2]ClO_4$. Alkynes ($R^1$ = alkyl or aryl, R^2 = alkyl, aryl, or TMS) (10 mmol) dissolved in distilled CH_3CN (3 mL) were treated with *cis*-$[(Cn^*)(CF_3CO_2)Ru^{VI}O_2]ClO_4$ (2 μmol) at room temperature. The mixtures were stirred vigorously and a blue/purple color immediately developed. The reaction mixture was then filtered through a 0.5 μm syringe filter before analyses. An average of 20 scans of mass spectra was obtained. For all reactions, the base peak can be formulated as the cycloadduct $[Cn^*(CF_3CO_2)\overline{Ru^{IV}OCR^1CR^2O}]^+$ cation complexes. For the reactions of diphenylacetylene, 4-octyne, and 1-phenyl-1-propyne, ion clusters [*m/z* = 468 (M^+) and 427 ($M^+ - CH_3CN$)] arising from $[(Cn^*)(CF_3CO_2)Ru^{II}(CH_3CN)_2]^+$ cation were detected along with the ion cluster corresponding to the cycloadduct complexes.

Kinetic Measurements. The oxidations of alkynes by *cis*-$[(Cn^*)(CF_3CO_2)Ru^{VI}O_2]ClO_4$ were monitored by the increase in absorbance of the absorption band at 553−615 nm under pseudo-first-order conditions where the alkyne concentration is at least 20-fold in excess of the ruthenium oxidant. Pseudo-first-order rate constants, k_{obs}, were obtained by nonlinear least-squares fits of A_t to time t according to the equation below:

$$A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs}t)$$

where A_0 and A_∞ are the initial and final absorbances and A_t is the absorbance at time t. The k_{obs} is the observed first-order rate constant. Kinetic data over four half-lives were used for the fits. The second-order rate constants (k_2) were obtained from linear fits of k_{obs} to the concentration of alkynes.

Activation enthalpy ($\Delta H^\ddagger$) and activation entropy ($\Delta S^\ddagger$) values were obtained from the slope and intercept of plots of $\ln(k_2/T)$ vs $1/T$ using the following equation:

$$\ln(k_2/T) = \ln(R/Nh) + \Delta S^\ddagger/R - \Delta H^\ddagger/RT$$

where N = Avogadro's number, R = universal gas constant, and h = Planck's constant.

Computational Methods and Results for the Calculation of the Ionization Potential (I_p) of the Disubstituted Acetylenes. The geometries of all the acetylenic molecules as well as their cations were optimized at the levels of HF/6-31G(d) and MP2(Full)/6-31G(d). The only exception was $[MeO_2CC\equiv CCO_2Me]^+$ cation, for which the MP2 geometry optimization was not successful. Hence the structure of this cation was determined only at the HF/6-31G(d). In addition, to characterize all the stationary points as minima and to include zero-point vibrational energy (ZPVE) corrections in the calculations of the ionization potentials, harmonic vibrational frequency calculations at HF/6-31G(d) for all species were also carried out. Based on the MP2 optimized geometries, we performed single-point energy calculations at the level of MP2(FC)/6-31+G(2df,p)//MP2(Full)/6-31G(d), plus a ZPVE (scaled by 0.8929) correction. All the calculations were performed with the Gaussian 98 package of programs.[62]

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Supporting Information Available: ORTEP diagram and table of crystal data, atomic coordinates, calculated hydrogen coordinates, anisotopic displacement parameters, and bond distances and bond angles for **3a**; the ^1H and ^{13}C NMR spectra of **3a**; UV−vis and ESI-MS spectra for the reactions of **1** with selected disubstituted acetylenes, listing of energies and zero-point vibrational energies (ZPVE) of all the acetylenic compounds and their cations and ionization potentials of the neutrals, and the free-energy plot of log(second-order rate constant, k_2, of the cycloaddition) vs the calculated ionization potentials of alkynes. This material is available free of charge via the Internet at http://pubs.acs.org.

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