

Electron-Transfer-Induced Interconversion of Alkyne and Vinylidene Chromium Complexes: A Quantitative Study

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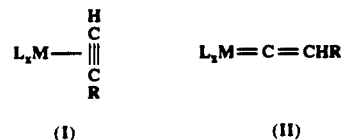
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Abstract: UV irradiation of $[\text{Cr}(\text{CO})_3(\eta\text{-C}_6\text{Me}_6)]$ with $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ in THF gives the orange vinylidene complex $[\text{Cr}(\text{CO})_2\{\eta\text{-C}=\text{C}(\text{SiMe}_3)_2\}(\eta\text{-C}_6\text{Me}_6)]$ (**V**) which undergoes oxidative isomerization to the alkyne cation $[\text{Cr}(\text{CO})_2\text{-}(\eta\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)(\eta\text{-C}_6\text{Me}_6)]^+$ (**A**⁺), isolable as the orange $[\text{PF}_6]^-$ salt. The temperature dependence (from 228 to 295 K) of the rate of isomerization of $[\text{Cr}(\text{CO})_2\{\eta\text{-C}=\text{C}(\text{SiMe}_3)_2\}(\eta\text{-C}_6\text{Me}_6)]^+$ (**V**⁺) to **A**⁺, determined by cyclic voltammetry, gives $\Delta S^\ddagger = -6 \pm 13 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta H^\ddagger = 61 \pm 3 \text{ kJ mol}^{-1}$. The vinylidene cation (**V**⁺) has been generated at low temperature, by reacting **V** with $[\text{FeCp}_2]^+$, and characterized by ESR spectroscopy. Paramagnetic cation **A**⁺ undergoes reductive isomerization to **V**; the rate of isomerization **A** to **V**, determined by cyclic voltammetry (from 279 to 293 K) and spectroelectrochemistry (at 242 K), gives $\Delta S^\ddagger = 84 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta H^\ddagger = 97 \pm 1 \text{ kJ mol}^{-1}$. At temperatures above 233 K, the isomerization of **A** to **V** is catalyzed by **V**⁺, via the cross reaction $\text{V}^+ + \text{A} \rightleftharpoons \text{V} + \text{A}^+$. The thermodynamic and kinetic parameters are in accord with a mechanism for the isomerization of **A** to **V** in which the alkyne ligand slips to η^1 -coordination prior to the transition state. Accordingly, the isomerization of **V**⁺ to **A**⁺ resembles the 1,2-sigmatropic shift of a SiMe_3 group in a purely organic system.

Introduction

Free vinylidenes, the simplest of the unsaturated carbenes, are highly reactive tautomers of alkynes.¹ When stabilized by coordination to a transition metal, however, they are useful in both stoichiometric² and catalyzed³ organic and organometallic syntheses. Vinylidene complexes, which can be mono-, bi- or polynuclear, are known for most transition metals⁴ and may be prepared by a variety of methods. In terms of the work described herein, the most pertinent route to mononuclear species involves the reaction of an alkyne with a transition metal substrate. This method usually relies on the use of terminal alkynes as precursors,⁴ but of late it has also been successful with internal alkynes having alkyl/aryl⁵ or silyl substituents.⁶

The mechanism by which a coordinated terminal alkyne complex, $\text{L}_x\text{M}(\eta^2\text{-HC}\equiv\text{CR})$ (**I**), is converted into the corresponding vinylidene, $\text{L}_x\text{M}=\text{C}=\text{CHR}$ (**II**),



was studied theoretically by Silvestre and Hoffmann⁷ using the model compound $[\text{Mn}(\text{CO})_2(\text{HC}\equiv\text{CH})\text{Cp}]$. Slippage of the C_2 fragment toward η^1 -coordination is energetically favored over formal oxidative addition to the metal center to give the hydrido acetylide derivative $\text{MH}(\text{C}\equiv\text{CR})$ as the first step in the mechanism; such a mechanism is also thought likely for the SiMe_3 migration required in the formation of $[\text{RhCl}\{\text{C}=\text{C}(\text{SiMe}_3)\text{R}\}(\text{PPr}^i_3)_2]$ ($\text{R} = \text{SiMe}_3, \text{Pr}^n, \text{Bu}^n, \text{Bu}^t$) from $\text{Me}_3\text{-SiC}\equiv\text{CR}$ and $[\text{RhCl}(\text{PPr}^i_3)_2]$ ⁸ and for the alkyl or aryl migration⁵ necessary when $[\text{Fe}(\text{CO})_2(\text{C}=\text{CR}^1\text{R}^2)\text{Cp}]^+$ is converted into $[\text{Fe}(\text{CO})_2(\eta\text{-R}^1\text{C}=\text{CR}^2)\text{Cp}]^+$ ($\text{R}^1 = \text{R}^2 = \text{Me}$ or Ph ; $\text{R}^1 = \text{Me}, \text{R}^2 = \text{Ph}$).

The relative stabilities of metal–alkyne and metal–vinylidene isomers is highly dependent on the metal d-configuration. For example, for d^4 metal centers vinylidene complexes are rarely favored⁸ over the analogous two-electron alkyne derivative.⁹ For d^6 complexes, however, the vinylidene complex is generally preferred, and alkyne-to-vinylidene isomerization occurs in order to alleviate the repulsive interactions between the filled d orbitals

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of the metal [e.g. the "t_{2g}" (d_{xy}, d_{xz}, d_{yz}) set of an octahedral complex] and the nonbonding π -orbital (filled, and orthogonal to the bonding π -donor orbital) of the alkyne.^{4,10} However, this repulsion is reduced as the metal center becomes less electron-rich so that [Fe(CO)₂(C=CRR')Cp]⁺ isomerizes to [Fe(CO)₂(η -RC=CRR')Cp]⁺ (R = R' = Me or Ph; R = Me, R' = Ph) even at 223 K {cf. the stable vinylidene complexes [FeL₂(C=CRR')Cp]⁺ (L = P-donor)}.⁵ In this case, vinylidene-to-alkyne isomerization is favored by the presence of the strong π -accepting carbonyl ligands which not only reduce electron density at iron but also lead to a highly electrophilic vinylidene α -carbon atom thereby favoring migration of one of the β -carbon substituents to give the alkyne.

In terms of the isomerization of d⁶ alkyne and vinylidene complexes, the isolation of both [Cr(CO)₂(C=CR₂)(η -arene)] (R = Me or Ph, arene = C₆H₆, 1,3,5-C₆H₃Me₃, or C₆Me₆)¹¹ and [Cr(CO)₂(η -RC=CRR')(η -C₆Me₆)]¹² and their stability to interconversion is remarkable. As surprising, however, was our initial observation¹³ not only that UV photolysis of Me₃-SiC≡CSiMe₃ and [Cr(CO)₃(η -C₆Me₆)] afforded the vinylidene complex [Cr(CO)₂{ η -C=C(SiMe₃)₂}(η -C₆Me₆)] (V) but that its one-electron oxidation gave the 17-electron alkyne cation [Cr(CO)₂(η^2 -Me₃SiC≡CSiMe₃)(η -C₆Me₆)]⁺ (A⁺) in an unprecedented, redox-induced vinylidene-to-alkyne isomerization. We have subsequently studied this isomerization in detail and now present electrochemical, spectroscopic, and kinetic studies which define a square scheme encompassing the oxidative isomerization of the 18-electron vinylidene complex (V) to the 17-electron alkyne cation (A⁺), and the reductive isomerization of the latter to the former. Moreover, we have isolated or spectroscopically characterized all four members of the square scheme, quantified the kinetics of the two isomerization processes, and shown that the conversion of the 18-electron alkyne complex into the vinylidene isomer is electron-transfer catalyzed.

Experimental Section

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen using dried, distilled, and deoxygenated solvents. Unless stated otherwise, the complexes are air-stable in the solid state and dissolve in polar solvents such as CH₂Cl₂ or THF to give solutions which only slowly decompose in air. The complexes [Cr(CO)₃(η -C₆Me₆)]¹⁴ and [FeCp₂][PF₆]¹⁵ were prepared by published methods. Routine infrared spectra were recorded on Nicolet MX5 or 5ZDX FT spectrometers; IR spectroelectrochemical experiments used a Mattson Polaris FTIR spectrometer. ¹H and ¹³C NMR spectra, calibrated against TMS as an internal standard, were recorded on Jeol GX-270 and GX-400 instruments, respectively. X-band ESR spectra were recorded at the University of Bristol on a Bruker ESP-300E spectrometer equipped with a Bruker variable-temperature accessory and a Hewlett Packard 5350B microwave frequency contour. The field calibration was checked by measuring the resonance of the diphenylpicrylhydrazyl (DPPH) radical before each series of spectra. Microanalyses were carried out by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

[Cr(CO)₂{ η -C=C(SiMe₃)₂}(η -C₆Me₆)] (V). A mixture of [Cr(CO)₃(η -C₆Me₆)] (0.51 g, 1.71 mmol) and Me₃SiC≡CSiMe₃ (2 mL, 8.80 mmol) in THF (50 mL) was irradiated under UV light for 7 h. The orange solution was filtered through alumina and then evaporated to dryness *in vacuo*. Extraction of the residue into boiling hexane (130

mL) and cooling the extract to -20 °C gave the product as fine orange needles, yield 0.50 g (66%). The compound is air-stable in the solid state for prolonged periods (it darkens after ca. 1 year) and dissolves in organic solvents to give orange solutions which slowly decompose in air. ¹H NMR (270 MHz, 295 K, benzene-d₆): δ 1.81 (18H, s, C₆Me₆), 0.35 (18H, s, SiMe₃). ¹³C NMR (100 MHz, 294 K, benzene-d₆): δ 347.9 (C α), 240.3 (CO), 109.6 (C-Me), 106.0 (C β), 16.7 (C-Me), 2.9 (SiMe₃). IR (in *n*-hexane, cm⁻¹): 1925 (s, CO), 1872 (s, CO), 1567 (m, C=C). Anal. Calcd for CrC₂₂H₂₄O₂Si₂: C, 60.0; H, 8.2. Found: C, 59.9; H, 8.4.

[Cr(CO)₂(η -Me₃SiC≡CSiMe₃)(η -C₆Me₆)] [PF₆]⁻·CH₂Cl₂ (A⁺[PF₆]⁻·CH₂Cl₂). To a stirred solution of [Cr(CO)₂{ η -C=C(SiMe₃)₂}(η -C₆Me₆)] (V) (228 mg, 0.52 mmol) in CH₂Cl₂ (50 mL) at 0 °C was added [FeCp₂][PF₆] (171 mg, 0.52 mmol). After 3 min the dark orange solution was reduced in volume *in vacuo*, to ca. 30 mL, and *n*-hexane (20 mL) was added. After filtration the solution was cooled to -78 °C to give a dark orange solid; reduction of the volume of the mother liquors *in vacuo* gave a second fraction, total yield (as a 1:1 solvate) 240 mg (69%). The solid complex decomposes slowly in air at room temperature. IR (in CH₂Cl₂, cm⁻¹): 2017 (s, CO), 1951 (s, CO), 1763 (mw, C=C). Anal. Calcd for CrC₂₂H₂₄O₂Si₂PF₆·CH₂Cl₂: C, 41.2; H, 5.7. Found: C, 41.7; H, 5.9.

Generation of [Cr(CO)₂{ η -C=C(SiMe₃)₂}(η -C₆Me₆)]⁺ (V⁺) for ESR Spectroscopy. A solution of [Cr(CO)₂{ η -C=C(SiMe₃)₂}(η -C₆Me₆)] (V) in CH₂Cl₂ (ca. 0.01 M, ca., 0.5 mL) was degassed in an ESR tube by the freeze-pump-thaw method. A few crystals of solid [FeCp₂][PF₆] (ca. 1.0 mg) were then added to the frozen solution at 77 K. The tube was then evacuated at 77 K and transferred to the cavity of the ESR spectrometer cooled to 150 K. The fluid solution ESR spectrum of the radical cation (V⁺) was recorded when the mixture was warmed to 180 K.

The anisotropic, frozen solution ESR spectrum of (V⁺) was recorded in CH₂Cl₂/THF (2:1). In this solvent mixture the cation, prepared as above, was formed at 150 K; when a sufficient concentration of the cation had been generated the sample was cooled to 77 K and the spectrum recorded.

Spectroelectrochemistry. The IR spectroelectrochemical thin-layer cell was operated in the transmission mode.¹⁶ In a typical experiment, a solution of [Cr(CO)₂{ η -C=C(SiMe₃)₂}(η -C₆Me₆)] (V) (10.0 mL, 1.0 × 10⁻³ M in CH₂Cl₂ and 0.5 M in [NBuⁿ]₄[PF₆]) was drawn into the spectroelectrochemical cell. This temperature in the cell was lowered to 218 K whereupon an IR spectrum of the solution was recorded [ν (CO) = 1901 and 1834 cm⁻¹]. Exhaustive electrolysis of this solution at 0.8 V *vs* Ag/AgCl produced a solution which displayed bands only at 2015 (s), 1950 (s), and 1764 (mw) cm⁻¹ [due to A⁺]. This solution was then exhaustively reduced at -0.5 V *vs* Ag/AgCl whereupon the IR spectrum displayed bands only at 1874 and 1799 cm⁻¹ (with a shoulder at 1811 cm⁻¹) [due to A]. This solution remained unchanged for 1 h at 218 K. The cell was then warmed to 242 K with no change in the IR spectrum except for a sharpening of the shoulder on the band at 1799 cm⁻¹. At 242 K, bands at 1901 and 1834 cm⁻¹, due to V, slowly grew at the expense of the bands at 1874 and 1799 cm⁻¹. The isomerization reaction was monitored for a further 90 min.

Experiments at higher temperatures proceeded similarly to the point where A⁺ was rereduced. At 261 K, this solution was electrolyzed at -0.5 V for 15 s, thereby resulting in less than 10% conversion to A. IR bands due to V were present in the first spectrum acquired and these bands completely replaced those due to A within 30 s. Similarly, at 253 and 234 K weak bands due to V were evident even after only 1 min of electrolysis (>10% conversion), in addition to the expected bands due to A. The latter were monitored for 30 min as they converted into those of V.

Cyclic Voltammetry. The oxidative conversion of V to A⁺ was typically studied in the following manner. A vacuum cell equipped with a sidearm, a Pt disk working electrode, a Ag/AgCl reference electrode, and a coiled Pt wire auxiliary electrode was charged with [NBuⁿ]₄[PF₆] (0.40 g 1.0 mmol) in the working electrode compartment. The sidearm was charged with [Cr(CO)₂{ η -C=C(SiMe₃)₂}(η -C₆Me₆)] (V) (4.5 mg, 0.01 mmol). Dry CH₂Cl₂ (10 mL) was then vacuum

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transferred into the working electrode compartment and a CV recorded of the solvent/electrolyte background at ambient temperature. Compound **V** was then added to the solution by tilting the sidearm. CV's were subsequently recorded at four different temperatures. Temperature control was achieved by immersion of the vacuum cell into a constant temperature bath. The lowest temperature achieved was 228 K, using a saturated aqueous CaCl_2 -dry ice bath. A temperature of 258 K was achieved with an aqueous NaCl -dry ice bath. CV's were also recorded at 273 and 295 K.

Rate constants were determined from individual CV's by the method of Nicholson. For the transformation of V^+ to A^+ the peak current ratio i_{pc}/i_{pa} for the V/V^+ couple was measured for each scan rate.¹⁷ From these data, the switching potentials and the working curves,¹⁸ the rate constants for the forward reaction were determined.

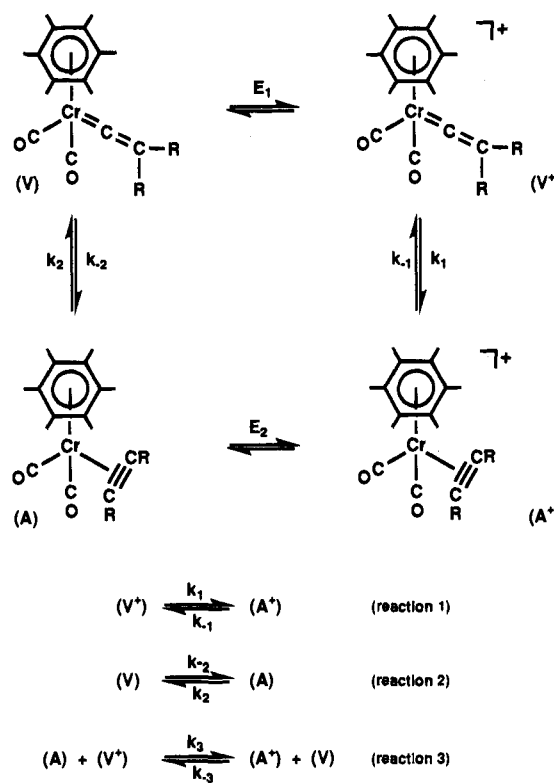
The voltammograms monitoring the conversion of **A** to **V** were obtained in an H-cell after bulk electrolysis under drybox conditions. In a typical experiment, $[\text{NBu}_4][\text{PF}_6]$ (1.2 g, 3.0 mmol) was dissolved in CH_2Cl_2 (30 mL), and the solution transferred into the working electrode compartment of an H-cell equipped with a Ag/AgCl reference electrode, a coiled Pt wire auxiliary electrode, and a large Pt basket working electrode. The solvent levels in the three compartments were allowed to equilibrate. A Pt disk electrode was immersed in the working electrode compartment to record CV's of the solvent/electrolyte background. Compound $[\text{Cr}(\text{CO})_2\{\eta\text{-C}\equiv\text{C}(\text{SiMe}_3)_2\}(\eta\text{-C}_6\text{Me}_6)]$ (**V**) (19 mg, 0.043 mmol) was added to the working electrode compartment, which contained 17 mL of base electrolyte solution, and the CV and RPE were recorded. The solution was then anodically electrolyzed at 0.1 V (*vs* $[\text{FeCp}_2]/[\text{FeCp}_2]^+$), thereby generating a solution of A^+ ; the CV and RPE were recorded to confirm that exhaustive electrolysis had been achieved. The rate constants for the transformation of **A** to **V** at several different temperatures were determined from the ratios i_{pa}/i_{pc} for the A/A^+ couple, using the procedure outlined above.

Results

The Synthesis of $[\text{Cr}(\text{CO})_2\{\eta\text{-C}\equiv\text{C}(\text{SiMe}_3)_2\}(\eta\text{-C}_6\text{Me}_6)]$ (V**).** UV irradiation of a mixture of $[\text{Cr}(\text{CO})_3(\eta\text{-C}_6\text{Me}_6)]$ and $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ in THF for 7 h gave an orange solution from which fine orange needles were obtained after evaporation of the reaction mixture to dryness *in vacuo*, extraction of the residue into boiling *n*-hexane, and cooling the extract to room temperature. Similar photolysis reactions with $\text{RC}\equiv\text{CR}'$ ($\text{R} = \text{R}' = \text{Ph}$, $\text{C}_6\text{H}_4\text{OMe-}p$, CO_2Me ; $\text{R} = \text{H}$, $\text{R}' = \text{Ph}$) give^{13,19} the alkyne complexes $[\text{Cr}(\text{CO})_2(\eta\text{-RC}\equiv\text{CR}')(\eta\text{-C}_6\text{Me}_6)]$ which show fully reversible oxidation waves in the cyclic voltammograms and from which the 17-electron cations $[\text{Cr}(\text{CO})_2(\eta\text{-RC}\equiv\text{CR}')(\eta\text{-C}_6\text{Me}_6)]^+$ can be generated and, in some cases, isolated.¹⁹ The elemental analysis (C and H), mass spectrum (parent ion, *m/e* 440), and ¹H NMR spectrum of the orange needles were in agreement with the expected alkyne complex $[\text{Cr}(\text{CO})_2(\eta\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)(\eta\text{-C}_6\text{Me}_6)]$ (**A**). However, the CV (see below) and the IR and ¹³C NMR spectra revealed the orange needles to be the vinylidene complex $[\text{Cr}(\text{CO})_2\{\text{C}=\text{C}(\text{SiMe}_3)_2\}(\eta\text{-C}_6\text{Me}_6)]$ (**V**). Thus, the IR spectrum in hexane showed $\nu(\text{C}=\text{C})$ at 1567 cm^{-1} (in addition to the two carbonyl absorptions at 1925 and 1872 cm^{-1}) and the ¹³C NMR spectrum showed peaks at 347.9 and 106.0 ppm, in regions associated with the α and β carbon atoms of other vinylidene ligands (258 – 382 and 87 – 143 ppm, respectively)⁴ {*cf.* $[\text{Cr}(\text{CO})_2(\text{C}=\text{CMe}_2)(\eta\text{-C}_6\text{H}_6)]$ (312.5 , C_α : 133.7 , C_β)¹¹}.

Electrochemical Studies. The electrochemical behavior of **V** is very different from that of alkyne complexes such as $[\text{Cr}(\text{CO})_2(\eta\text{-PhC}\equiv\text{CPh})(\eta\text{-C}_6\text{Me}_6)]$.^{13,19} At room temperature, or at slow scan rates at low temperatures, the CV of **V** shows an incompletely reversible oxidation wave ($E_{1/2} = -0.31\text{ V vs}$

Scheme 1



$[\text{FeCp}_2]/[\text{FeCp}_2]^+$) accompanied by a product wave ($E_{1/2} = -0.70\text{ V}$) which shows evidence of reversibility on the second scan even at slow scan rates. This behavior is shown by detailed electrochemical, spectroscopic, and synthetic studies to involve the unprecedented oxidative isomerization of the vinylidene complex (**V**) to the alkyne complex cation (A^+).

The interconversion of **V** and **A** in two different oxidation states may be represented by a square scheme (Scheme 1). The behavior of such a system depends on the relative potentials of the two couples V^+/V and A^+/A (E_1 and E_2 , respectively), the rates of the two isomeric interconversions (reactions 1 and 2 of Scheme 1) and the cross reaction involving complexes in different oxidation states (reaction 3 of Scheme 1), and the equilibrium constants for the three reactions, given by eqs 1–3. The heterogeneous electron-transfer kinetics are sufficiently rapid in the present case to eliminate any apparent need to take them into account in describing the voltammetric results.

$$K_1 = \frac{k_1}{k_{-1}} = \frac{[\text{A}^+]}{[\text{V}^+]} \quad (1)$$

$$K_2 = \frac{k_2}{k_{-2}} = \frac{[\text{V}]}{[\text{A}]} \quad (2)$$

$$K_3 = \frac{k_3}{k_{-3}} = \frac{[\text{V}][\text{A}^+]}{[\text{V}^+][\text{A}]} = \exp \frac{F(E_1 - E_2)}{RT} \quad (3)$$

The thermodynamically favored isomers are A^+ in the case of the 17-electron cations and **V** in the case of the neutral 18-electron complexes. The potential difference, $E_1 - E_2 = 393 \pm 2\text{ mV}$, independent of temperature over the range 253 – 295 K , corresponds to $\Delta H_3^\circ = -37.9 \pm 0.2\text{ kJ mol}^{-1}$, $\Delta S_3^\circ = 0 \pm 6\text{ J mol}^{-1}\text{ K}^{-1}$, and $K_3 = 4.4 \times 10^6$ at 298 K . The interconversions of the two pairs of isomers proceed at rates which can be outrun in CV experiments at moderate scan rates. At room temperature, partial chemical reversibility is observed

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Table 1. Rate Constants for the Isomerization of $[\text{Cr}(\text{CO})_2\{\eta\text{-C}=\text{C}(\text{SiMe}_3)_2\}(\eta\text{-C}_6\text{Me}_6)]^+$ (V^+) to $[\text{Cr}(\text{CO})_2(\eta\text{-Me}_3\text{SiC}=\text{CSiMe}_3)(\eta\text{-C}_6\text{Me}_6)]^+$ (A^+) from Cyclic Voltammograms of 0.9 mM $[\text{Cr}(\text{CO})_2\{\eta\text{-C}=\text{C}(\text{SiMe}_3)_2\}(\eta\text{-C}_6\text{Me}_6)]$ (V) in CH_2Cl_2

T/K	$\nu/\text{V s}^{-1}$	k_1/s^{-1}	T/K	$\nu/\text{V s}^{-1}$	k_1/s^{-1}
228	0.050	0.027	295	5.00	55
	0.10	0.023		6.00	54
258	0.10	0.74	7.00	57	
	0.20	0.82	8.00	50	
	0.40	0.73	9.00	51	
	0.80	0.71	10.00	52	
	1.00	0.77	12.00	47	
273	1.60	0.69	5.00	51 ^a	
	2.00	0.63	10.00	54 ^a	
	0.80	4.7	5.00	45 ^b	
	1.00	4.9	10.00	51 ^b	
	1.60	5.1	5.00	51 ^c	
	2.00	5.2	10.00	49 ^c	
	2.70	4.9			
3.20	4.7				

^a $[\text{V}] = 1.9 \text{ mM}$. ^b $[\text{V}] = 2.3 \text{ mM}$. ^c $[\text{V}] = 2.8 \text{ mM}$.

for the V/V^+ couple at sweep rates above 5 V s^{-1} . The ratios of reverse to forward currents were used to derive rate constants for the conversion of V^+ to A^+ (Table 1). From the rate constant at room temperature a half-life of $1.4 \times 10^{-2} \text{ s}$ is calculated for V^+ . Full chemical reversibility is observed at lower sweep rates (*ca.* 1 V s^{-1}) for the A/A^+ couple since A has a significantly longer half-life (*ca.* 0.9 s) than V^+ . The variation of chemical reversibility with scan rate permits several independent measurements of the isomerization rates.¹⁷ Thus, the value of k_1 can be determined from CV scans of the V/V^+ wave and the value of k_2 is similarly accessible from studies of the A/A^+ wave. This strategy for measuring the isomerization kinetics of Scheme 1 presupposes (i) that the two isomerization reactions are direct and without significant formation of side products and (ii) that $K_1, K_2 \gg 1$, *i.e.* thermodynamically equilibrated solutions of a single oxidation state contain significant amounts of only one isomer. The experimental data support both assumptions. Solutions of pure V are available, of course, upon dissolution of the original sample; solutions of A^+ were prepared by exhaustive anodic electrolysis of V .

The two thermodynamically unstable isomers, namely V^+ and A , were detected spectroscopically as well as by voltammetry. The former was observed by ESR spectroscopy and the latter by IR spectroscopy. In the spectroscopic experiments, evidence for the cross reaction (reaction 3 of Scheme 1) was obtained at 234 K, and estimates of the rate constants k_{-1} and k_{-2} were made. It was therefore possible to estimate K_1 and K_2 . Details of the electrochemical and spectroscopic experiments follow.

The Oxidatively Induced Vinylidene-to-Alkyne Isomerization. As depicted in Scheme 1, oxidation of the vinylidene complex (V) is followed by rapid isomerization to form the cationic alkyne complex (A^+). Rate constants for this reaction in CH_2Cl_2 were obtained by cyclic voltammetry. Representative CVs are shown in Figure 1 and the resulting values of k_1 are given in Table 1. Note that the rate constants obtained by this method are independent of the initial concentration of V , indicating that the isomerization of V^+ to A^+ is uncomplicated by the cross reaction.²⁰

The rate constant k_1 varies from 0.025 to 51 s^{-1} in the temperature range 228–295 K. A linear Eyring plot ($R^2 = 0.994$) of these data, shown in Figure 2a, yields the activation parameters for the isomerization process: $\Delta S_1^\ddagger = -6 \pm 13 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta H_1^\ddagger = 62 \pm 3 \text{ kJ mol}^{-1}$.

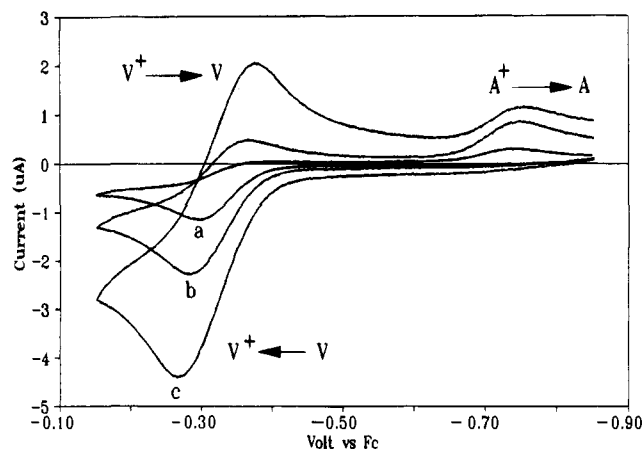


Figure 1. Cyclic voltammograms of 1.0 mM $[\text{Cr}(\text{CO})_2\{\eta\text{-C}=\text{C}(\text{SiMe}_3)_2\}(\eta\text{-C}_6\text{Me}_6)]$ (V) at 50, 200, and 800 mV s^{-1} , recorded at 255 K in $\text{CH}_2\text{Cl}_2/0.1 \text{ M}$ $[\text{NBu}_4][\text{PF}_6]$ vs the $[\text{FeCp}_2]/[\text{FeCp}_2]^+$ couple.

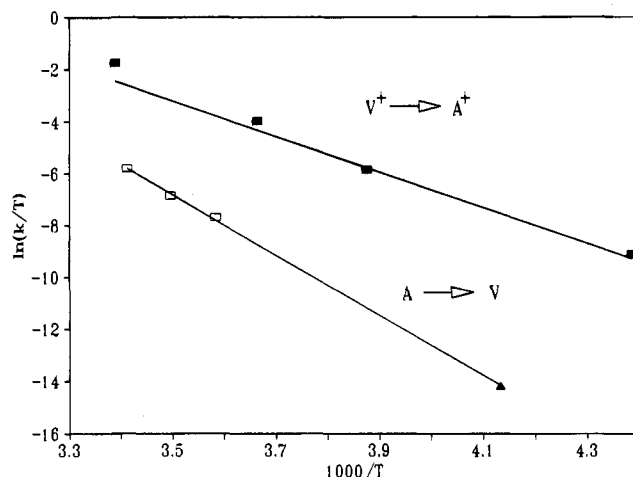


Figure 2. Eyring plots of kinetic data for the isomerizations of (a) $[\text{Cr}(\text{CO})_2\{\eta\text{-C}=\text{C}(\text{SiMe}_3)_2\}(\eta\text{-C}_6\text{Me}_6)]^+$ (V^+) to $[\text{Cr}(\text{CO})_2(\eta\text{-Me}_3\text{SiC}=\text{CSiMe}_3)(\eta\text{-C}_6\text{Me}_6)]^+$ (A^+) and (b) $[\text{Cr}(\text{CO})_2(\eta\text{-Me}_3\text{SiC}=\text{CSiMe}_3)(\eta\text{-C}_6\text{Me}_6)]$ (A) to $[\text{Cr}(\text{CO})_2\{\eta\text{-C}=\text{C}(\text{SiMe}_3)_2\}(\eta\text{-C}_6\text{Me}_6)]$ (V). All data were derived from voltammetric data except the triangular point, which was derived from IR data.

While electrochemistry is a valuable technique for quantifying chemical reactions, structural details (geometric and electronic) are better probed by other physical techniques. Accordingly, the transformations noted above were also examined by IR and ESR spectroscopy.

Exhaustive anodic electrolysis of V in CH_2Cl_2 at 261 K ($E = 0.20 \text{ V vs } [\text{FeCp}_2]/[\text{FeCp}_2]^+$) resulted in the passage of 0.9 F equiv^{-1} as the solution became only slightly darker yellow. Cyclic voltammetry showed that the original oxidation wave ($E_{1/2} = -0.34 \text{ V}$) was almost quantitatively replaced by a wave at $E_{1/2} = -0.70 \text{ V}$.²¹ The room temperature ESR spectrum of this solution displays a singlet with ^{53}Cr satellites, ($g = 1.998$, $\langle a^{\text{Cr}} \rangle = 16.5 \text{ G}$). The same product was also generated by bulk electrolysis in an optically transparent thin-layer electrolysis (OTTLE) cell. Upon exhaustive anodic electrolysis at low temperature ($< 261 \text{ K}$), the IR bands associated with V were replaced by carbonyl bands at 2015 and 1950 cm^{-1} and a weaker band at 1764 cm^{-1} (Figure 3) assigned to $\nu(\text{C}=\text{C})$ (see below).

The assignment of these spectra to A^+ was confirmed by the chemical synthesis, isolation, and characterization of the $[\text{PF}_6]^-$ salt of the alkyne-containing cation. Thus, treatment of V with $[\text{FeCp}_2][\text{PF}_6]$ in CH_2Cl_2 at 0°C , filtration of the resulting orange

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(21) The diffusion coefficient of A^+ ($D_A = 5.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) was determined by comparing the RPE limiting current with that of ferrocene.

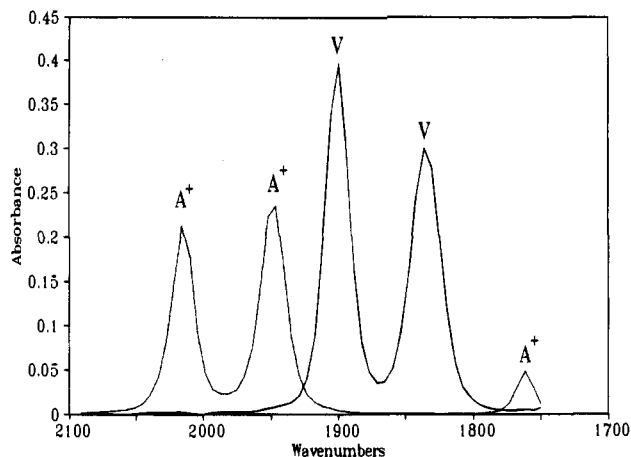


Figure 3. OTTLE cell IR spectra of (a) 2.0 mM $[\text{Cr}(\text{CO})_2(\eta\text{-C}\equiv\text{C}(\text{SiMe}_3)_2)(\eta\text{-C}_6\text{Me}_6)]$ (V) and (b) 2.0 mM $[\text{Cr}(\text{CO})_2(\eta\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)(\eta\text{-C}_6\text{Me}_6)]^+$ (A^+) in $\text{CH}_2\text{Cl}_2/0.5 \text{ M } [\text{NBu}^n_4][\text{PF}_6]$.

solution, and addition of *n*-hexane gave the orange $[\text{PF}_6]^-$ salt of A^+ , as a CH_2Cl_2 (1:1) solvate, in 69% yield. The salt was characterized by elemental analysis (C and H), by ESR and IR spectroscopy, and by CV. The ESR spectrum is not only identical to that noted above but is also very similar to those formed on reversible one-electron oxidation of the alkyne complexes $[\text{Cr}(\text{CO})_2(\eta\text{-RC}\equiv\text{CR}')(\eta\text{-C}_6\text{Me}_6)]$ ($\text{R} = \text{R}' = \text{Ph}$, CO_2Me ; $\text{R} = \text{H}$, $\text{R}' = \text{Ph}$).^{13,19} The IR band at 1764 cm^{-1} is assigned to $\nu(\text{C}\equiv\text{C})$ on the basis of similar bands observed for alkyne complexes such as $[\text{Nb}(\eta\text{-PhC}\equiv\text{CPh})(\eta\text{-C}_5\text{Me}_4\text{SiMe}_3)_2]$ (1710 cm^{-1})²² and $[\text{V}(\text{NAr})(\text{PMe}_3)(\eta\text{-PhC}\equiv\text{CPh})\text{Cp}]$ (1778 cm^{-1}).²³ Surprisingly, bands assignable to $\nu(\text{C}\equiv\text{C})$ have not been previously noted for $[\text{Cr}(\text{CO})_2(\eta\text{-RC}\equiv\text{CR}')(\eta\text{-C}_6\text{Me}_6)]^+$ ($\text{R} = \text{R}' = \text{Ph}$, CO_2Me ; $\text{R} = \text{H}$, $\text{R}' = \text{Ph}$).

No features attributable to V^+ were observed in the IR OTTLE cell even when the oxidation of V was carried out at 234 K. This is in accord with the CV experiments which indicate that the half-life of V^+ should be of the order of 30 s at this temperature. Because it takes at least 10 min to electrolyze the solution exhaustively at 253 K, the concentration of V^+ is never great enough to be detected [or V^+ is totally obscured by spectral features due to A^+]. Nevertheless, V^+ has been detected by ESR spectroscopy. Treatment of V in CH_2Cl_2 at 77 K with solid $[\text{FeCp}_2][\text{PF}_6]$ followed by warming the mixture to 180 K resulted in the observation of a single line in the ESR spectrum at $\langle g \rangle = 2.0145$. Similar treatment of such a mixture in $\text{CH}_2\text{Cl}_2\text{-THF}$ (2:1) and subsequent re-cooling to 77 K gave a well-resolved rhombic spectrum (Figure 4) with $g_1 = 2.030$, $g_2 = 2.020$, $g_3 = 1.993$ ($g_{\text{av}} = 2.014$), a much larger *g*-anisotropy than exhibited by A^+ and other alkyne cations.¹³ These parameters are consistent with the assignment of a low-spin d^5 configuration to V^+ .²⁴ On warming the samples described above, the signal due to V^+ is replaced by the isotropic spectrum of A^+ , *i.e.* by a single line flanked by ^{53}Cr satellites, ($\langle g \rangle = 1.998$, $\langle a^{\text{Cr}} \rangle = 16.5 \text{ G}$).

The Reductively-Induced Alkyne-to-Vinylidene Isomerization. The rate of the isomerization of A to V was measured by cyclic voltammetry in a manner similar to that described above except that the alkyne complex (A^+) was generated *in situ* by bulk anodic electrolysis of V. The rate constant, k_2 , was found to vary from 0.13 to 0.88 s^{-1} in the temperature range 279–293 K (Table 2). At lower temperatures, the rate

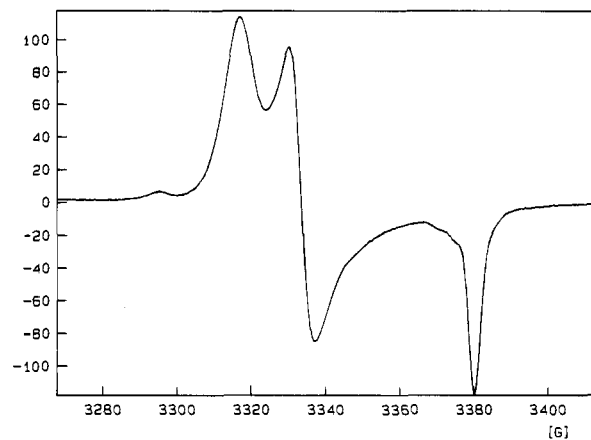


Figure 4. ESR spectrum of $[\text{Cr}(\text{CO})_2(\eta\text{-C}\equiv\text{C}(\text{SiMe}_3)_2)(\eta\text{-C}_6\text{Me}_6)]^+$ (V^+) at 77 K in $\text{CH}_2\text{Cl}_2\text{-THF}$ (2:1).

Table 2. Rate Constants for the Isomerization of $[\text{Cr}(\text{CO})_2(\eta\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)(\eta\text{-C}_6\text{Me}_6)]$ (A) to $[\text{Cr}(\text{CO})_2(\eta\text{-C}\equiv\text{C}(\text{SiMe}_3)_2)(\eta\text{-C}_6\text{Me}_6)]$ (V) from Cyclic Voltammograms of 2.1 mM $[\text{Cr}(\text{CO})_2(\eta\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)(\eta\text{-C}_6\text{Me}_6)]^+$ (A^+) in CH_2Cl_2

<i>T</i> /K	$\nu/\text{V s}^{-1}$	k_2/s^{-1}	<i>T</i> /K	$\nu/\text{V s}^{-1}$	k_2/s^{-1}
279	0.140	0.12	286	0.090	0.29
	0.120	0.13		0.080	0.30
	0.100	0.14		0.070	0.30
	0.090	0.13		0.060	0.29
	0.080	0.13		0.050	0.30
	0.070	0.12		293	0.400
0.060	0.11	0.300	0.95		
0.050	0.13	0.250	0.84		
286	0.160	0.31	0.200	0.85	
	0.140	0.28	0.150	0.81	
	0.120	0.30	0.100	0.89	
	0.100	0.37			

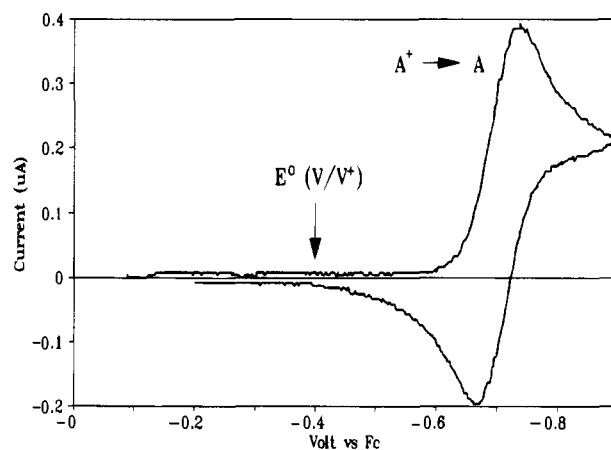


Figure 5. Cyclic voltammogram of $[\text{Cr}(\text{CO})_2(\eta\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)(\eta\text{-C}_6\text{Me}_6)]^+$ (A^+) at 100 mV s^{-1} , recorded at 243 K in $\text{CH}_2\text{Cl}_2/0.1 \text{ M } [\text{NBu}^n_4][\text{PF}_6]$ vs the $[\text{FeCp}_2]/[\text{FeCp}_2]^+$ couple.

of isomerization is too slow to be measured reliably by CV; at higher temperatures, A^+ slowly decomposes.

Complex A was generated by bulk electrolysis of A^+ at 228 K after room temperature CV experiments had been performed on the latter. Only 2.94 C was required for complete oxidation, two thirds the charge expected from the original concentration of V, further evidence for the thermal sensitivity of A^+ . Repeated CV scans at various temperatures revealed no significant concentration of V below 243 K (Figure 5). Above this temperature, the concentration of V steadily increased with time, but no attempt was made to follow the kinetics in this experiment.

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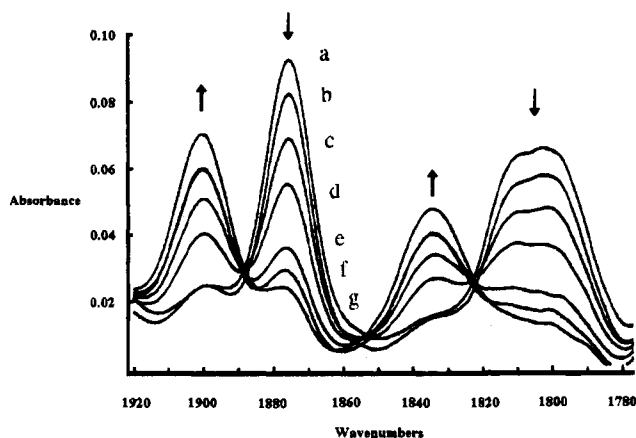


Figure 6. OTTLE cell IR spectral monitoring of the conversion of $[\text{Cr}(\text{CO})_2(\eta\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)(\eta\text{-C}_6\text{Me}_6)]$ (**A**) to $[\text{Cr}(\text{CO})_2\{\eta\text{-C}=\text{C}(\text{SiMe}_3)_2\}(\eta\text{-C}_6\text{Me}_6)]$ (**V**) at 234 K in $\text{CH}_2\text{Cl}_2/0.5 \text{ M } [\text{NBu}_4][\text{PF}_6]$: (a) immediately after electrolytic formation of **A** and (b) 2 min, (c) 7 min, (d) 11 min, (e) 19 min, (f) 22 min, and (g) 25 min later.

The identity of **A** as an alkyne complex is further verified by noting that the values of $\nu(\text{CO})$ (1874 and 1799 cm^{-1}) and E_2 [the potential for the oxidation of (**A**) to (**A**⁺)] agree with those for other alkyne complexes $[\text{Cr}(\text{CO})_2(\eta\text{-RC}\equiv\text{CR}')(\eta\text{-C}_6\text{Me}_6)]$ ($\text{R} = \text{R}' = \text{Ph}, \text{CO}_2\text{Me}, \text{CO}_2\text{Et}, \text{C}_6\text{H}_4\text{OMe}$; $\text{R} = \text{H}, \text{R}' = \text{Ph}$) for which a linear correlation has been noted between $\nu(\text{CO})$ and E . It is noteworthy that at lower temperatures the IR band at 1799 cm^{-1} displays a shoulder at 1811 cm^{-1} (Figure 6). The origin of this shoulder is unclear and has not been noted previously for related alkyne complexes. It may arise from the overlap of $\nu_{\text{asym}}(\text{CO})$ with a $\nu(\text{C}\equiv\text{C})$ stretch {which would be expected to occur at a higher wavenumber than that of cation **A**⁺ (1764 cm^{-1}) on the basis of the bonding scheme previously proposed for $[\text{Cr}(\text{CO})_2(\eta\text{-alkyne})(\eta\text{-arene})]^{13}$. Alternatively, it may result from rotational isomerism.

The isomerization of **A** to **V** was also monitored by IR spectroelectrochemistry. When a solution of **V** is exhaustively oxidized and then exhaustively re-reduced at 223 K, it displays only IR bands due to **A**. On warming the solution, the IR spectrum does not change noticeably below about 242 K. Monitoring the decay of the carbonyl bands of **A** with time at 242 K gives $k_2 = 1.7 \times 10^{-4} \text{ s}^{-1}$ ($t_{1/2} = 67 \text{ min}$). This value was obtained by subtracting the contribution of **V** from the spectrum and by measuring the intensity of the higher-energy band of **A** in the difference spectrum. Under these conditions, there should be no significant amount of **V**⁺ or **A**⁺ left in solution and thus no contribution from the cross-reaction (reaction 3 of Scheme 1).

The value for k_2 obtained from the spectroelectrochemical study agrees well with the data from the CV experiments. The Eyring plot (Figure 2b) is linear ($R^2 = 0.999$) and leads to activation parameters: $\Delta H_2^\ddagger = 97 \pm 1 \text{ kJ mol}^{-1}$, $\Delta S_2^\ddagger = 84 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1}$.

Alkyne-to-Vinylidene Isomerization via the Cross Reaction. When a solution of **A**⁺ is reduced at temperatures above 233 K, the rate of isomerization of **A** to **V** is faster than expected from the rate data of Figure 2b. In fact, at higher temperatures the isomerization of **A** is complete by the time exhaustive cathodic electrolysis of **A**⁺ has been achieved. This rate enhancement is attributed to the effect of the cross reaction. To obtain rate data for this catalyzed isomerization process, the solution of **A**⁺ was only partially electrolyzed under conditions where bands due to **A** are observable without bands due to **V**. Thus a 2.0 mM solution of **A**⁺ was reduced for 1 min at 234 K to obtain 15% ($\pm 5\%$) conversion of **A**⁺ to **A**. Subsequent

Table 3. Summary of Equilibrium and Rate Parameters (Values in Parentheses Are Estimates; See Text)

reaction	K_{234}	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\Delta S^\circ/\text{J mol}^{-1} \text{ K}^{-1}$
$\text{V}^+ \rightleftharpoons \text{A}^+$	170 ± 50	(-31)	(-90)
$\text{A} \rightleftharpoons \text{V}$	$(1.7 \pm 0.5) \times 10^6$	(-7)	(90)
$\text{V}^+ + \text{A} \rightleftharpoons \text{A}^+ + \text{V}$	$(2.9 \pm 0.3) \times 10^8$	-37.9 ± 0.2	0 ± 6
reaction	k_{234}/s^{-1}	ΔH^\ddagger	ΔS^\ddagger
$\text{V}^+ \rightarrow \text{A}^+$	0.049 ± 0.015	62 ± 3	-6 ± 13
$\text{A}^+ \rightarrow \text{V}^+$	$(2.9 \pm 0.2) \times 10^{-4}$	(93)	(84)
$\text{A} \rightarrow \text{V}$	$(3.2 \pm 0.3) \times 10^{-5}$	97 ± 1	84 ± 4
$\text{V} \rightarrow \text{A}$	$(1.9 \pm 0.6) \times 10^{-11}$	(104)	(-6)

monitoring of the IR absorptions (Figure 6) revealed a zero-order decay of **A** with $k_{\text{obs}} = (5.0 \pm 0.2) \times 10^{-7} \text{ M s}^{-1}$ ($t_{1/2} = 13 \text{ min}$, compared with 6 h expected for the k_2 isomerization at this temperature). Since solutions of pure **A** generated at 223 K can persist without apparent change for at least an hour at 234 K, this result indicates that under conditions where there is a significant concentration of **A**⁺, and hence a finite concentration of **V**⁺, the cross reaction is significant.

If we assume that the first-order isomerization reaction characterized by k_2 can be neglected under these circumstances, the isomerization of **A** to **V** must occur *via* reactions 3 and 1 of Scheme 1. The rate equations for [**A**] and [**V**⁺] can be written as in eqs 4 and 5. If [**V**⁺] is small,

$$d[\text{A}]/dt = -k_3[\text{A}][\text{V}^+] + k_{-3}[\text{V}][\text{A}^+] \quad (4)$$

$$d[\text{V}^+]/dt = -k_3[\text{A}][\text{V}^+] + k_{-3}[\text{V}][\text{A}^+] - k_1[\text{V}^+] + k_{-1}[\text{A}^+] \quad (5)$$

the steady-state approximation can be applied to give eq 6, which, if $k_1[\text{V}^+] \ll k_{-1}[\text{A}^+]$, further simplifies to eq 7. Thus the observed zero-order rate constant is $k_{\text{obs}} = k_{-1}[\text{A}^+]$.

$$d[\text{A}]/dt = k_1[\text{V}^+] - k_{-1}[\text{A}^+] \quad (6)$$

$$d[\text{A}]/dt = -k_{-1}[\text{A}^+] \quad (7)$$

Since $[\text{A}^+] = 1.7 \pm 0.1 \text{ mM}$, we have $k_{-1} = (2.9 \pm 0.2) \times 10^{-4} \text{ s}^{-1}$ at 234 K.

Discussion

With values of ΔH_3° , ΔS_3° , k_1 , k_2 , and k_{-1} , the values of K_1 , K_2 , K_3 , and k_{-2} at 234 K can be computed. These are listed, together with the other experimentally determined parameters, in Table 3.

Since $\Delta S_1^\circ + \Delta S_2^\circ = \Delta S_3^\circ$, we see that $\Delta S_1^\circ = -\Delta S_2^\circ$, *i.e.*, the entropy change for the vinylidene-to-alkyne isomerization reaction is independent of oxidation state. If we assume that the entropies of activation for the isomerization reactions are also independent of oxidation state, *i.e.*, that the transition state occurs at approximately the same point along the reaction coordinate for both oxidation states, we have $\Delta S_1^\ddagger = \Delta S_1^\ddagger - \Delta S_{-1}^\ddagger \approx -90 \text{ J mol}^{-1} \text{ K}^{-1}$. These values and the equilibrium constants at 234 K give $\Delta H_1^\circ = -31 \text{ kJ mol}^{-1}$, $\Delta H_2^\circ = -7 \text{ kJ mol}^{-1}$, and $\Delta H_{-1}^\ddagger = \Delta H_1^\ddagger - \Delta H_1^\circ \approx 93 \text{ kJ mol}^{-1}$, $\Delta H_{-2}^\ddagger = \Delta H_2^\ddagger - \Delta H_2^\circ \approx 104 \text{ kJ mol}^{-1}$. These estimates are also given in Table 3.

The isomerization of **V**⁺ to **A**⁺ is enthalpy-driven against an unfavorable entropy whereas the isomerization of **A** to **V** is driven largely by the increase in entropy. The enthalpies can be understood in terms of the EHMO results of Hoffmann and Silvestre.⁷ The alkyne complex MO's are generally lower in

energy than the corresponding MO's for the vinylidene complex. The HOMO, on the other hand, is at significantly higher energy in the alkyne complex. Apparently, the vinylidene complex is slightly more stable when the HOMO is doubly occupied, whereas for single occupation, the alkyne complex is considerably more stable. The lower entropy of the alkyne complex is presumably related to steric inhibition of internal motion; moving the bulky SiMe₃ groups further away from the metal center allows for greater freedom of motion for the C₆Me₆ ring.

Since the entropies of activation for the alkyne-to-vinylidene isomerizations are large and positive, nearly the same as ΔS^\ddagger for these reactions, the transition states resemble the vinylidene product, at least with respect to entropy. This is precisely the result expected from Hoffmann and Silvestre's theoretical study of the alkyne-to-vinylidene isomerization reaction⁷ which concluded that the most likely reaction pathway was slippage of the alkyne to η^1 -coordination, followed by the 1,2-sigmatropic shift of the alkyne substituent. The reverse vinylidene-to-alkyne isomerization would then be expected to involve mostly migration of the SiMe₃ group with little motion of the C₂ fragment relative to the metal center, and indeed the activation parameters for the conversion of V⁺ into A⁺ are in good

qualitative agreement with those for 1,2-sigmatropic shifts in purely organic systems.²⁵ *e.g.*, $\Delta H^\ddagger = 88 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -33 \text{ J mol}^{-1} \text{ K}^{-1}$ for the conversion of 1-(trimethylsilyl)indene to 2-(trimethylsilyl)isoindene.²⁶ ESR spectroscopic results¹³ suggest that the HOMO in A⁺ has a significant contribution from an alkyne π orbital whereas in V⁺ the SOMO appears to be a more typical metal-based orbital. Thus we might have expected a larger effect of oxidation state on the alkyne-to-vinylidene isomerizations than on the reverse processes. The apparent opposite result, $\Delta H_1^\ddagger < \Delta H_{-2}^\ddagger$, may relate to the observation that organic sigmatropic rearrangements can be facilitated by removal of electron density.²⁷

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