High-resolution electron impact spectra were obtained on a Kratos MS-50 by using a direct insertion probe. Instrument conditions were as follows: ionizing energy, 70 eV; accelerating potential, 8 KeV; source temperature, 250 °C. Fast atom bombardment spectra were obtained on a Kratos MS-50TA.[15] An Ion Tech atom gun and a standard Kratos FAB source were used. The samples were dissolved in thioglycerol, and a small drop of the sample solution was placed on the copper target of the FAB direct insertion probe. The sample was bombarded with 8 keV xenon atoms, and the ions produced were accelerated through 8 keV.

Reduction with Sodium Borohydride or Sodium Borodeuteride (Procedure a). BTX-B or BTX-A (5 mg) was dissolved in methanol (1 mL) and allowed to stand with slight excess of sodium borohydride or sodium borodeuteride for 15 min at room temperature. Reaction mixture was treated with Dowex 50 W × 8 (H$^+$), filtrated, and evaporated to dryness. The residue was twice evaporated with methanol.

Catalytic Hydrogenation (Procedure b). The compound to be hydrogenated (5 mg) was dissolved in THF (1 mL) and hydrogenated (4 h, room temperature) over 10% Pd/C (2 mg) under a slight hydrogen pressure. The catalyst was centrifuged, and the supernatant was evaporated to dryness.

Methylation (Procedure c). The compound to be methylated (4 mg) was dissolved in THF (1 mL) and stirred with sodium hydride for 20 min. Methyl iodide (0.05 mL) was then added. After 16 h *n*-hexane (5 mL) was added, the mixture was centrifuged, and the supernatant was evaporated to dryness.

1,5,37,42-Tetra-*O*-methyldodecahydrobrevetoxin-B (3) and Its 1,1,42-Trideuterio Analogue (3-*d*$_3$). BTX-B (5 mg) was hydrogenated by procedure b, reduced with sodium borohydride or sodium borodeuteride by procedure a, and finally methylated by procedure c. The product obtained (3 and 3-*d*$_3$) was purified by flash chromatography with benzene-ethyl acetate (1:1) and analyzed by EIMS.

1,4,39,44-Tetra-*O*-methyldodecahydrobrevetoxin-A (4). BTX-A (5 mg) was reduced with sodium borohydride by procedure a, hydrogenated by procedure b, and finally methylated by procedure c. The product obtained (5) was purified by flash chromatography with benzene-ethyl acetate (1:1) and analyzed by EIMS.

BTX-A Ozonolysis Derivative 5. BTX-A (5 mg) was reduced with sodium borohydride by procedure a. The product obtained was dissolved in methanol (1 mL) and ozonized at −78 °C for 20 min. The solution was then purged by argon for 1 h. The ozonides formed were reduced with sodium borohydride by procedure a. The product obtained was methylated by procedure c and purified by flash chromatography with benzene-ethyl acetate 1:1.

Acknowledgment. We are grateful to Dr. John C. James for discussions and Joseph C. Cesarelli for technical assistance. The studies were supported in part by NIH Grant AI 10187 (to K.N.) and NSF Grant No. CHE-8211164 (to MCMS, an NSF Regional Instrumentation Facility).

Supplementary Material Available: Table of mass spectral data (7 pages). Ordering information is given on any current masthead page.

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Kinetics, Stereochemistry, and Mechanism of Interaction of Vaska's Complex with Ethynylvinyl Triflates. Formation of Novel σ-Butatrienyl-Iridium Compounds

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Received August 15, 1986

Abstract: The reaction of Vaska's complex [$(Ph_3P)_2Ir(CO)(Cl)$, **3**] with a variety of substituted enynyl triflates [$RCH{=}CH(OTf)C{\equiv}CR'$, **4** and **5**] was investigated. Oxidative addition readily occurs in benzene or toluene at room temperature to give novel, isolable, crystalline hexacoordinate iridium(III) butatrienyl complexes **8**. Rate studies indicate steric inhibition by bulky substituents on the terminal acetylenic carbon and give high negative entropies of activation. A careful stereochemical investigation showed that reaction occurs with complete (or nearly complete) *retention* of olefin stereochemistry. A two-step S_N2' process with syn approach of the incoming Ir nucleophile is proposed to account for these observations.

Oxidative addition reactions are among the most ubiquitous and well-investigated processes in organometallic chemistry.[2] Particularly important and valuable oxidative additions are carbon-metal σ-bond-forming reactions, for they generally represent an obligatory step in the multitude of metal-mediated catalytic carbon coupling processes. A great variety of organic substrates such as alkyl,[2a,f] benzyl,[2f,3] allyl,[4] propargyl,[5] acyl,[2a,3] vinyl,[3,6] and aryl[2e,3] systems (usually halides) undergo oxidative additions, most often with d^8 and d^{10} metal complexes, with the metal generally serving as a nucleophile.

A good deal is known about the nature and mechanism of these reactions with alkyl, benzyl, allyl, acyl, and aryl halides, whereas the vinylic systems are much less investigated and understood.[2-7] This parallels the state of affairs in organic chemistry where aliphatic and aromatic nucleophilic substitutions (S_N1, S_N2, S_NAr, etc.) are well understood but until recently nucleophilic vinylic substitutions (S_NV) were generally ignored.[8] The reasons for this apparent anomaly are usually ascribed to the inertness of simple alkylvinyl halides to S_NV processes even with powerful nucleophiles or under forcing solvolytic conditions.[8]

The introduction of the perfluorosulfonate leaving groups, with a $k_{CF_3SO_3^-}/k_{X^-}$ reactivity ratio of 10^6–10^8, and the ready availability of vinyl triflates[9] ameliorates this difficulty, as illustrated by the easy generation of both simple alkylvinyl cations[10] and alkylide-

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[1] (a) Utah. (b) Abstracted in part from: Dixit, V. *Ph.D. Dissertation* University of Utah, 1985. (c) William & Mary.

[2] (a) Collman, J. P. *Acc. Chem. Res.* **1968**, *1*, 136. (b) Cramer, R. *Ibid.* **1968**, *1*, 186. (c) Vaska, L. *Ibid.* **1968**, *1*, 335. (d) Heck, R. F. *Ibid.* **1969**, *2*, 10. (e) Parchall, G. W. *Ibid.* **1970**, *3*, 139. (f) Halpern, J. *Ibid.* **1970**, *3*, 386.

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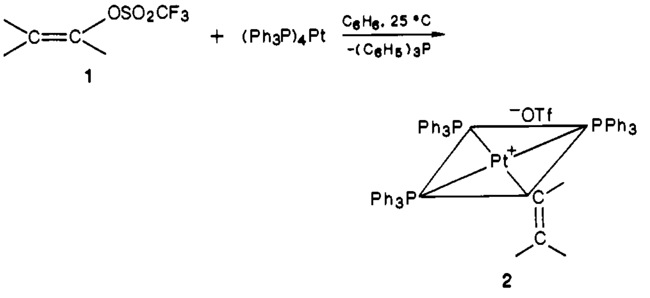
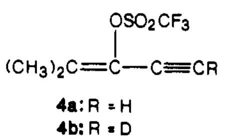
0002-7863/87/1509-1150$01.50/0

necarbenes[11] by S_NV processes.[8] Despite the high reactivity of vinyl triflates in organic S_NV processes, little is known about their reactions with organometallic systems and in particular possible oxidative additions with d^8–d^{10} metal complexes. Recently, we reported[12] on the ready oxidative addition, under very mild conditions, of a series of alkylvinyl triflates, **1**, to $(Ph_3P)_4Pt$ to give novel, stable σ-vinyl Pt complexes, **2**. In this paper we wish to report a detailed kinetic and stereochemical investigation of the interaction of Vaska's complex, **3**, with a series of ethynylvinyl triflates **4**.



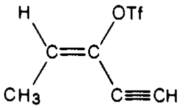
Results and Discussion

The ethynylvinyl triflates **4** and **5** and chloride **6** were prepared[13] from the corresponding known acetylenic ketones.

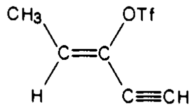


$(CH_3)_2C{=}C(OSO_2CF_3){-}C{\equiv}CR$

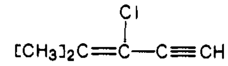
- **4a**: R = H
- **4b**: R = D
- **4c**: R = CH3
- **4d**: R = C6H5
- **4e**: R = SiMe3
- **4f**: R = *t*-Bu



5E



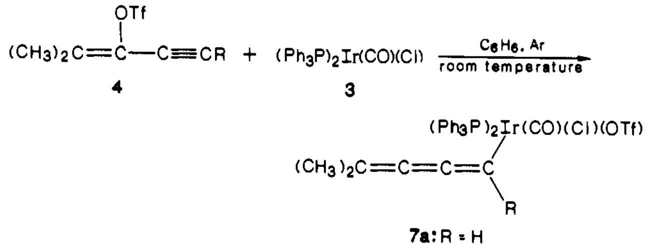
5Z



$[CH_3]_2C{=}C(Cl){-}C{\equiv}CH$

6

Interaction of a 2-fold excess of enynyl triflates **4a–e** and **5** with Vaska's complex, **3**, in carefully degassed benzene or toluene under argon at room temperature occurred over several minutes to 72 h depending upon the substituent R, yielding pale-yellow (off-white) microcrystalline butatriene adducts **7** quantitatively.[14] The extent of reaction could be followed qualitatively by the color change of the solution from the bright, intense, yellow of Vaska's complex to a pale, lemon yellow color upon reaction and quantitatively by the disappearance of the strong CO absorption at 1950 cm^{-1} and the appearance of a new band at 2040–2060 cm^{-1}. Vinyl triflate **4f** and chloride **6** did not react even after several weeks at room temperature and under forcing conditions (refluxing benzene) gave only dark decomposition products.

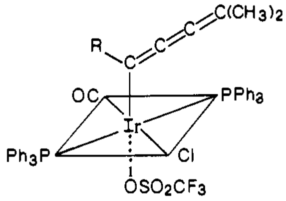


- **7a**: R = H
- **7b**: R = D
- **7c**: R = CH3
- **7d**: R = C6H5
- **7e**: R = SiMe3

The butatriene products **7** are isolable, reasonably stable, microcrystalline solids (but decompose over several hours in solution particularly in chlorinated solvents) and represent only the second known examples[15] of a σ-bonded cumulene transition-metal complex. To date we have been unable to obtain suitable crystals for X-ray determination, and hence structure determination is established by careful spectral analyses.[16]

FAB-mass spectra clearly indicated a 1:1 adduct.[17] The infrared spectra of all complexes show the expected shift of the carbonyl stretch from 1950 cm^{-1} in the tetracoordinated Ir(I) of Vaska's compound, **3** to a region of 2040–2060 cm^{-1}, highly characteristic of hexacoordinate Ir(III) species.[2c] In addition all spectra displayed a shoulder between 2020 and 2040 cm^{-1}, strongly indicative of a cumulene.[18] The presence of triflate is indicated by the characteristic symmetric and asymmetric SO_2 stretches at 1150–1225 cm^{-1} and confirmed by ^{19}F NMR. Equally significant is the *absence* of any absorption, in all IR, in the 1700–1800-cm^{-1} region, characteristic of π-bound acetylene complexes,[19] and the *absence* of a C≡C—H absorption above 3100 cm^{-1} in the complexes from **4a** and **5**. The ^1H NMR are consistent with 1:1 adducts, and the proposed structures and the ^1H NMR (vide infra) of adducts **10E** and **10Z** from **5E** and **5Z**, respectively, are particularly characteristic of the cumulene ligand. The presence of two central, sp-hybridized, cumulenic carbons is confirmed by the two highly characteristic[18] low-field signals in the 150–170 ppm region in the ^{13}C NMR spectrum and the *absence* of any signals in the characteristic acetylenic region[20] of 60–80 ppm.

The stereochemistry around iridium in the octahedral complex is established by ^{13}C NMR and far-infrared spectroscopies. Specifically, in the ^{13}C NMR the apparent triplets in the phenyl region of the spectrum (in the broad-band proton-decoupled mode), due to virtual coupling[21] with the two ^{31}P nuclei, establish the two triphenylphosphine ligands as trans.[22] Jenkins and Shaw[23] have demonstrated that the Ir–Cl stretching in the far infrared in octahedral Ir(III) complexes depends primarily on the nature of the ligands trans to the chlorine and is insensitive to the cis ligands. Moreover, Collman and Sears[24] have shown that the absorption for chlorine trans to a carbonyl is in the region of 302–315 cm^{-1} and the band is always very strong, whereas electron-releasing groups (alkyl, etc.) trans to Cl cause a decrease in the Ir–Cl stretching frequency. A strong band at 312 cm^{-1} in the adducts from **5** establish the CO and Cl as trans. Hence, the structure of adducts **7** is clearly established as a *trans*-σ-butatrienyl, hexacoordinate, octahedral Ir(III) complex, **8**.



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[14] No other products were detected by spectroscopic means. Isolated yields on a 0.1 mmol scale were 75–95%.

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[16] Because of solubility and stability problems (in solution), not all spectra were obtained for all the adducts. Only key adducts from **4a,c** and **5** were *fully* characterized. However, the similarity of properties, behavior, and spectra (particularly IR and ^1H NMR) leaves no doubt about the identity of all adducts. See text and Experimental Section.

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Table I. Second-Order Rate Constants, Activation Parameters, and Relative Rates of Reaction of Enyne Triflates **4** and **5**

compd	temp, °C	k_2, $M^{-1}\ s^{-1}$	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	E_a, kcal/mol	K_{rel}
4a, $(CH_3)_2C{=}C(OTf)C{\equiv}CH$	5.0^{a}	43.0×10^{-3}	12.7	−19.2	13.8	21.2^{b}
	25.4	216.0×10^{-3}				
	35.1	448.0×10^{-3}				
4c, $(CH_3)_2C{=}C(OTf)C{\equiv}CCH_3$	5.0^{a}	10.2×10^{-3}	6.2	−45.4	6.8	5.36^{b}
	14.0	15.49×10^{-3}				
	25.3	22.01×10^{-3}				
	34.8	34.23×10^{-3}				
4d, $(CH_3)_2C{=}C(OTf)CC{\equiv}CC_6H_5$	5.0^{a}	1.95×10^{-3}	6.5	−74.7	7.1	1.02^{b}
	25.4	4.41×10^{-3}				
	35.1	6.83×10^{-3}				
	44.7	9.04×10^{-3}				
4e, $(CH_3)_2C{=}C(OTf)C{\equiv}CSiMe_3$	5.0^{a}	1.90×10^{-3}	5.4	−51.6	6.1	1.00^{b}
	45.04	7.54×10^{-3}				
	54.62	9.98×10^{-3}				
5E, $CH_3CH{=}C(OTf)C{\equiv}CH$	5.0	2.46				1.65^{c}
5Z	5.0	1.49				1.00^{c}

^{a}Extrapolated. ^{b}For **4** relative to $SiMe_3$ = 1.00. ^{c}For **5** relative to each other.

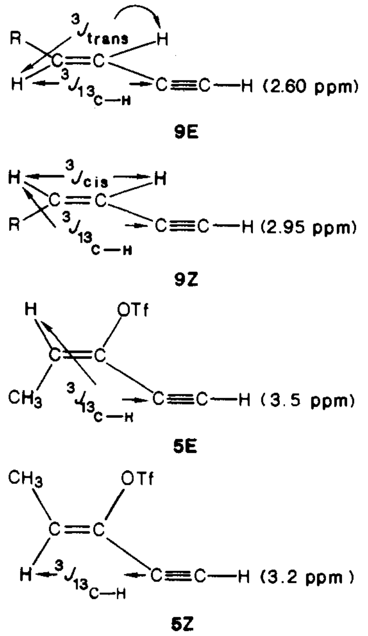
Kinetic Investigations. The rates of reaction of enynyl triflates **4** and **5** with Vaska's complex, **3**, were determined in carefully degassed, freshly distilled toluene. With a large excess (15–35-fold) of triflate, rates were measured in duplicate, by standard spectrophotometric techniques, as pseudo-first-order rates, by following the disappearance of Vaska's compound at 387 nm. Excellent pseudo-first-order rates were observed for over 90% reaction, and the second-order rate constants, activation parameters, and relative rates are listed in Table I. As indicated above, the *t*-Bu compound **4f** and the chloride **6** did not react under measurable conditions, whereas **5** reacted too rapidly to measure rates at other temperatures and determine activation parameters.

A careful kinetic isotope effect study was also carried out with **4a** and **4b**. Side by side runs, in quadruplicate at 25.3 ± 0.05 °C, with a triflate concentration of 8.40×10^{-3} mol and a 2.40×10^{-4} M **3** gave k_2 ($M^{-1}\ s^{-1}$) = 0.217 ± 0.007 for **4a** and 0.211 ± 0.005 for **4b**, respectively, and hence a secondary kinetic isotope effect of k_H/k_D = 1.03 ± 0.03.

Stereochemical Studies. One of the most important mechanistic tools is stereochemistry. Hence, we undertook a careful stereochemical investigation of the reaction of isomeric vinyl triflates **5**. Preparative GC allowed separation of the two geometric isomers **5E** and **5Z** in better than 99% purity. Their stereochemistry was assigned on the basis of NMR shown in Chart I.

Kingsbury and co-workers[25] have investigated the long-range ^{13}C–H coupling, $^3J_{C-H}$, between the olefinic proton and the acetylenic carbon in a series of disubstituted enynes whose stereochemistry is well established by the standard vicinal olefinic proton couplings[26] as shown in Chart I. In all cases the trans couplings in **9Z** were found to be larger, $^3J_{C-H}$ (trans, **9Z**) > $^3J_{C-H}$ (cis, **9E**), than the cis couplings in **9E**. A similar relationship was observed[25] for a series of trisubstituted enynes whose geometry was known by various H–H and ^{13}C–H couplings.[27,28] For enyne triflate **5E**, a $^3J_{C-H}$ = 9.15 Hz was observed, while for **5Z** the value was $^3J_{C-H}$ = 2.06 Hz in accord with the above observations. Furthermore, Rosenberg and Drenth[29] have shown that the C≡CH in the ^1H NMR for **9Z** is at a lower field than for **9E** (R = CH_3). Likewise we found the C≡CH of **5E** [where the CH_3 and C≡CH are in the same relationship as is **9Z** (R = CH_3)] at a lower field of 3.5 ppm vs. 3.2 ppm for the **5Z** isomer. Hence, the geometry of the pure isomeric starting enynes **5** is firmly established.

Chart I



Likewise, the stereochemistry of the isomeric product adducts **10Z** and **10E** was determined by ^1H NMR chemical shifts and long-range coupling constants, with the aid of model compounds **11–13** listed in Table II. The coupling constants for **10Z** and **10E**, respectively, were obtained at 7 °C in C_6D_6 by appropriate decoupling procedures of the mutually coupled protons. The α-proton H attached to the carbon bearing the Ir could not be directly observed as it is shifted under the aromatic protons of the Ph_3P.

Considerable data are available on the long-range couplings in cumulenes. The $^4J_{HC=C=CH}$ couplings in allenes are known to be negative and of the order of −5.8 to −6.8 Hz.[26,30] The $^5J_{HC=C=C=CH}$ in butatrienes is predicted[31] to be positive. $^5J_{cis}$ couplings in **11Z**[32] and **12Z**[33] are smaller in magnitude than the corresponding $^5J_{trans}$ in their respective isomers. Likewise, the $^6J_{trans}$ couplings between the δ-CH_3 and α-cumulenic C–H are larger in **11Z**[32] and **13E**[34] than the corresponding $^6J_{cis}$ couplings in the isomers **11E** and **13Z**. In exact analogy we observe $^5J_{trans}$ = 7.1 Hz for **10E** but only $^5J_{cis}$ = 6.6 Hz for **10Z** and $^6J_{trans}$ = 1.6 Hz

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Table II. Long-Range Coupling Constants for Adducts **10Z** and **10E** and Model Compounds

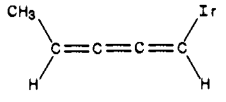
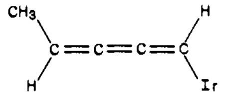
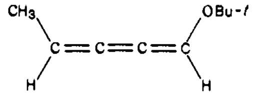
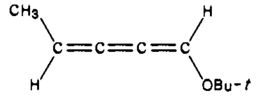
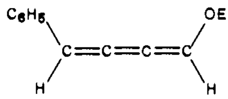
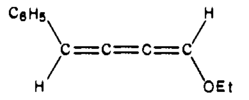
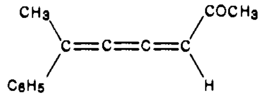
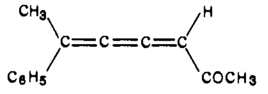
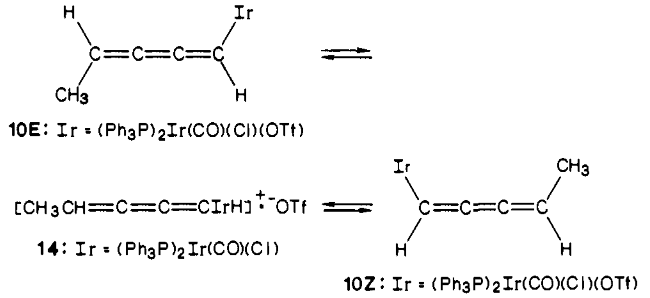
compound	$^5J_{cis}$, Hz	$^5J_{trans}$, Hz	$^6J_{cis}$, Hz	$^6J_{trans}$, Hz
 **10Z**	6.6			1.6
 **10E**		7.1	1.4	
 **11Z**	5.5			1.5
 **11E**		5.8	1.4	
 **12Z**	5.5			
 **12E**	6.0			
 **13E**				1.2
 **13Z**			0.95	

Table III. Stereochemistry of Reaction of **5** with **3**

enyne triflate	temp, °C	reaction time, min	adducts[a] **10Z**	adducts[a] **10E**
5Z	25	15	60	40
5Z	7	60	75	25
5Z	7	40	90	10
5E	25	15	37	63
5E	7	60	18	82
5E	7	40	2	98

[a] Determined by multiple integration of the CH_3 signals in the ^1H NMR.

Scheme I



for **10Z** but only $^6J_{cis}$ = 1.4 Hz for the isomeric **10E**.

Moreover, the chemical shifts of the respective δ-CH_3's and δ-H's are in accord with expectations and analogies. Specifically the CH_3 in **10Z**, on the same side as the bulky iridium, is at a lower field of 1.38 ppm than the 1.30 ppm in the isomeric **10E**, whereas in accord with expectations the δ-H in **10E** at 5.63 ppm is lower than the observed 5.00 ppm for the isomeric **10Z**. Hence, the geometry of the isomeric product adducts **10E** and **10Z** is rigorously established. Furthermore, the long-range couplings in **10** provide additional support for the cumulenic nature of the ligands in **7** as no such long-range ^5J and ^6J couplings are observable in the isomeric starting enynes **5** or related enyne compounds **9**. This is due to the more favorable σ–π overlap within the rigid geometry of the cumulenic framework and hence better through-bond transmission of spin couplings in **10–13** than the less favorable arrangement of the enynes.

Stereochemical experiments were carried out in C_6D_6 and monitored by ^1H NMR.

The results (Table III) indicate that the oxidative addition reaction of Vaska's complex (**3**) with the isomeric enyne triflates **5** is stereospecific. Stereospecificity is both time and temperature dependent. Reisolation of unreacted starting compounds **5E** and **5Z** indicated no interconversion of the starting substrate. Geometric isomerization of **10E** and **10Z** occurs via a new species **14** readily observable in the ^1H NMR with time (Scheme I). Although isolation of pure **14** proved to be difficult, the following NMR data suggest a cationic iridium hydride as a likely structure for **14**. Specifically new signals appeared in the NMR at 1.48 (CH_3, dt, J = 7.2, 3.0 Hz), 3.2 (IrH, *t*, J = 4.8 Hz), 4.65 (CH=C, m), and 7.0–8.0 ppm (m, Ph_3P). Decoupling experiments indicate that the triplet splittings of the CH_3 and CH=C are due to virtual coupling with the two ^{31}P nuclei and that they are also mutually coupled. Irradiation of the 1.48 ppm (CH_3) signal or the 4.65 ppm (CH=C) signal did not affect the 3.2 ppm triplet. The small J_{P-H} = 4.8 Hz and its downfield location (metal hydride chemical shifts vary from −20 to +5 ppm) of 3.2 ppm suggest a possible *cis*-triphenylphosphine orientation and the Ir–H trans to a ligand of high trans influence,[35] in the hexacoordinate octahedral cationic Ir(III) intermediate **14**. The IR of **14** with a 2060-cm^{-1} CO absorption and the characteristic 2020-cm^{-1} cumulene stretch along with the OTf bands at 1150–1225 cm^{-1} provide further support to its identity.

Complete equilibration of nearly pure **10E** or **10Z**, via **14**, was not observed, as once formed some **14** always remained and was also accompanied by some decomposition. In any event, as a consequence of the slow interconversion of **10E** and **10Z**, presumably via **14**, the 9:1 *retention* of olefin stereochemistry in the reaction of **5Z** with Vaska's complex (**3**) and the 98:2 *retention* of stereochemistry with **5E** are *lower* limits to the stereospecificity of this reaction. In fact it is highly likely that the reaction is totally *stereospecific* with *retention* of olefin stereochemistry.

Mechanistic Considerations. Oxidative additions to low-valent group 8 transition-metal complexes generally fall into four main categories:[36] (a) S_N2-type process with the metal acting as nucleophile; (b) free-radical pathways; (c) concerted, three-centered additions; (d) single-electron-transfer (SET) processes. The latter three processes can be ruled out as possible mechanisms for the reaction of Vaska's complex (**3**) with enyne triflates **4** and **5**. SET processes are usually observed with halides. There are no known examples of SET processes with sulfonate esters (and in particular triflate).[37] In the present case the unreactivity of enyne chloride **6** is also consistent with the absence of SET and radical processes. Radical processes can also be ruled out by the lack of inhibition with radical traps, such as galvinoxyl, and by the high degree of

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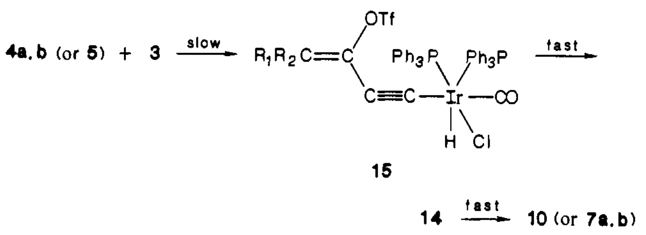
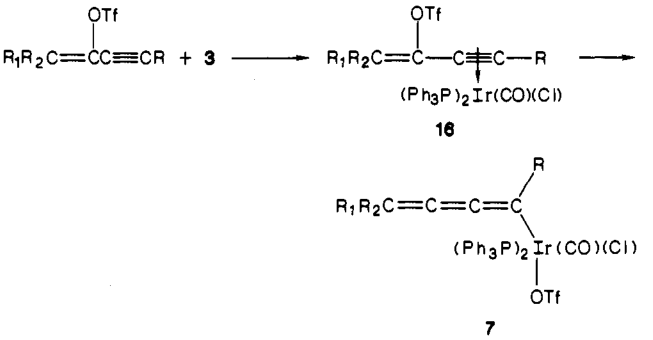
Scheme II



Scheme III



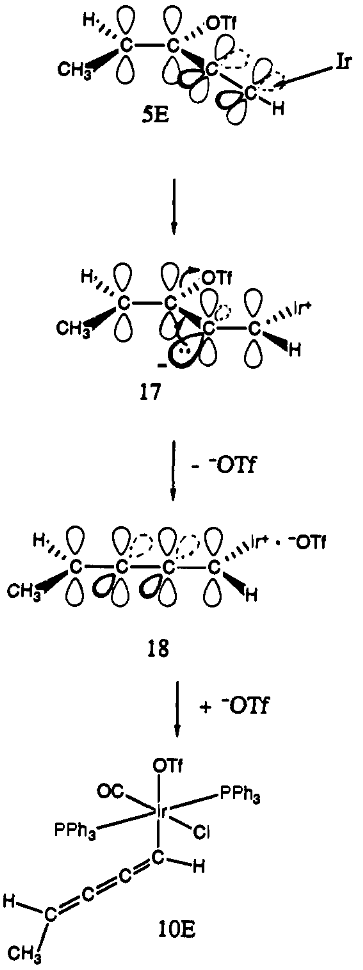
stereospecificity observed in the reaction of **3** with **5**. Although a few concerted, three-centered additions with alkyl halides are known,[38] they generally occur with homonuclear substrates such as oxygen and hydrogen.[2f] In fact, "three-centered additions" are incompatible with enyne substrates and butatriene product formation for reasons of geometric constraints.

However, an S_N2-like process may not be the sole pathway for interaction of **3** and **5** and formation of butatrienyl adducts **7**. Due to the presence of the acetylenic linkage in **4** and **5**, at least two other possibilities exist. In the case of terminal alkynes **4a,b** and **5**, a direct C≡C—H insertion is possible (Scheme II). After the initial rate-determining formation of an (alkynyl) hydridoiridium complex **15**, a rapid rearrangement via **14** to **10** (or **7a,b**) can follow. Analogous terminally bonded acetylide–IrH complexes, via insertion of Vaska's complex (**3**) into RC≡CH, are known.[19,39] However, in the present case this can be easily ruled out by both the high stereospecificity of the observed reactions between **3** and **5** and the kinetic isotope effect data with **4a,b**. The absence of a (or at best very small secondary effect) kinetic isotope effect k_H/k_D = 1.03 ± 0.03 for **4a,b** rules out such a direct rate-determining C–H insertion as this process should have been accompanied by a large $k_H/k_D \geq 3$ *primary* kinetic deuterium isotope effect.[40] Prior C–H insertion is of course not possible with the terminally substituted enyne substrates **4c–f**.

A second possibility involves initial π-complex formation **16** and subsequent rearrangement to **7** (Scheme III). Numerous π-acetylene complexes with group 8 and other transition metals, including Ir, are of course well-known.[41] Moreover, Collman and co-workers[5] have shown that $CH_3C{\equiv}CCH_2Cl$ yields an unstable π-acetylene complex with Vaska's compound (**3**), rather than an allenyl or propargyl displacement product.

We propose that the mechanism for the reaction of Vaska's complex (**3**) with enyne triflates **4** and **5** that best accommodates all of our data is a two-step syn S_N2' process (Scheme IV). Specifically, the large negative entropies of activation (−19 to −51 eu) suggest a highly ordered transition state. Analogous large negative activation entropies were observed for the S_N2 reaction of methyl and benzyl halides with **3**.[42] The linearity of the $\Delta H^{\ddagger}$ vs. $\Delta S^{\ddagger}$ plot (r = 0.998 for **4a–e**) strongly suggests that *all* enynes, the alkyl- and aryl-substituted ones **4c–e** as well as the terminal ones **4a** and **5**, react by the same mechanism.[43] The relative rate data are in accord with such an S_N2' process (as well as perhaps prior π-complexation). The sterically most hindered *t*-Bu substrate **4f** does not react at all, and decreasing steric hindrance results in an increasing rate of reaction, with the least hindered terminal alkynyl **4a** reacting 21 times faster than the hindered **4e**.

Scheme IV



That Vaska's complex (**3**) is sufficiently nucleophilic to carry out an S_N2-type displacement has been elegantly demonstrated by Pearson and Figdore,[43] along with the relative nucleophilicities of a large diverse number of organometallic systems. Moreover, extensive studies have demonstrated that allyl halides[44,45] and sulfonates,[45] $CH_2{=}CRCH_2X$, readily undergo oxidative additions to a variety of iridium(I) $L_2Ir(CO)(Cl)$ species, including Vaska's complex (**3**), to give both *cis*-**19a** and *trans*-**19b**, hexacoordinate, Ir(III) products depending upon substrate structure, the nature of L, and the solvent polarity. Pearson and Poulos[45] proposed a two-step S_N2 mechanism with some double-bond coordination to Ir to account for their observations. Likewise, propargyl and allenyl halides are known[5] to oxidatively add to Vaska's complex (**3**), via an S_N2-like process, resulting in hexacoordinate allenyl–Ir(III) complexes **20**.

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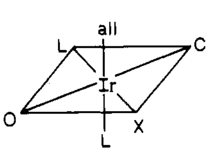
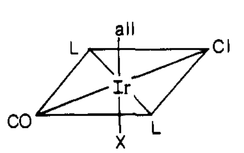
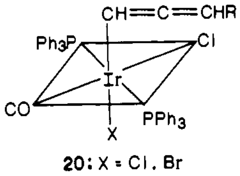


19a: all = $CH_2{=}CRCH_2$
R = H, Cl, CH_3
X = Cl, Br, CH_3SO_3
L = PMe_2Ph, Ph_3



19b



20: X = Cl, Br

Undoubtedly, our strongest support for the mechanism proposed in Scheme IV is the high degree of stereoselectivity of reactions of **5E** and **5Z** with virtually complete retention of olefin geometry. Retention of olefin stereochemistry demands a syn attack, as an anti approach would have resulted in inversion of olefin stereochemistry. Syn as well as anti additions to acetylenes are known,[47,48] depending on substrate, nucleophile, and solvent.

Recent theoretical calculations indicate that syn nucleophilic addition to acetylenes leading to an anti zwitterionic transition state (TS), such as **17**, is favored over the anti approach, resulting in a syn zwitterionic TS.[49,50] Furthermore, in the anti zwitterionic TS, **17**, resulting from syn approach, the insipient "anion" is also anti and therefore in a proper orientation, with respect to the leaving group OTf, and hence its concomitant displacement results in the ionic intermediate or product **18**. Since all of our reactions were carried out in nonpolar benzene or toluene, this initially formed product **18** may well have a cis orientation around the metal as in **19a** analogous to the behavior of the allylic substrates in nonpolar solvents.[44,45] However, no evidence was obtained for such cis adducts in the reaction of **3** with **4** or **5**. This may be ascribed to the very poor and weak coordinating ability of fluorosulfonates,[51] and hence ready dissociation of this ligand (even in nonpolar solvents) could result in the rapid isomerization of any initially formed cis phosphine isomers to the thermodynamically more stable trans adducts. The proposed syn approach nicely accounts not only for the retention of olefin stereochemistry but also for the faster reaction of the **5E** isomer vs. the **5Z** one: **5E**/**5Z** = 1.65.

As seen in Scheme IV, any nucleophile must approach the terminal carbon of the acetylene in the same plane as the β-substituents in the olefin. A syn approach in **5E** (Scheme IV) places the incoming Ir nucleophile on the side *opposite* to the β-CH_3 on the olefin, whereas of course the same syn approach (required by the stereochemical results) in the **5Z** isomer places the Ir on the *same* side as the β-CH_3 and hence causes a steric retardation of reactivity. Indeed, **4a**, where approach on either side is hindered by a methyl group, reacts considerably slower than **5**.

Finally, the possibility of the prior involvement of some kind of a π-acetylene complex as in **16**, analogous to the proposed double-bond involvement of Pearson and Poulos[45] with allylic substrates, cannot be ruled out. The kinetic as well as stereochemical data (assuming π-complexation occurs preferentially on the less hindered face of the acetylene) are compatible with such a possibility. In fact the kinetic isotope effect of $k_H/k_D = 1.03 \pm 0.03$ for **4a**,**b** might support this possibility. Complete rehybridization of an sp carbon to an sp^2 carbon (as required in the reactions of **4** and **5** to give butatrienyl products **8**) should give an *inverse* secondary isotope effect[52] of about $k_H/k_D = 0.78$. Hence, the observed $k_H/k_D = 1.03 \pm 0.03$ indicate either a very early transition state with little rehybridization at the terminal carbon or possible π-complex formation with little affect on the $C{\equiv}CH(D)$ vibrations.

Conclusion. Enyne triflates readily undergo facile oxidative addition to Vaska's complex, to give novel, stable, trans-hexacoordinate butatrienyl complexes **8**. Stereochemical studies indicate complete (or nearly complete) retention of olefin stereochemistry. Relative rate studies indicate steric inhibition by bulky substituents on the terminal acetylenic carbon. A secondary kinetic isotope effect of $k_H/k_D = 1.03 \pm 0.03$ was observed for deuterium substitution on the alkyne. A two-step S_N2' process, with syn approach (i.e., the same side as the departing OTf) of the Ir nucleophile, is proposed as the most likely mechanism for this oxidative addition reaction. The chemistry of these new cumulenyliridium complexes as well as the interaction of other coordinatively unsaturated group 8 metal systems with vinyl triflates is under active investigation and will be the subject of future reports.

Experimental Section

General. All boiling and melting points are uncorrected; IR spectra were recorded on either a Perkin-Elmer 298 or a Nicolet 600 FT spectrophotometer. NMR were recorded on a Varian EM-360 or 390, FT80A, or SC-300 spectrometer and are reported in parts per million (ppm) relative to internal Me_4Si (0.00); for ^{13}C the locks were on deuteriated solvents. Mass spectra were obtained on a Varian MAT112 or a VG Micromass spectrometer. Analytical GC was carried out with a HP-5710A flame ionization GC with a HP-3380-A integrator. Preparative GC utilized a Varian-Aerograph 90P chromatograph. Solvents and reagents were purified and dried by standard procedures immediately prior to use.

Starting Materials. Vaska's complex, **3**, $(Ph_3P)_2Ir(CO)(Cl)$, was purchased from Alfa, recrystallized from benzene, and activated by standard procedures prior to use. Alkynylvinyl triflates **4a–f** are known compounds and were prepared as previously described.[9,13,54]

3-Penten-1-yn-3-yl Triflate (5). The isomeric triflates were prepared[13] from 1-(trimethylsilyl)pentyn-3-one, **21**. The ketone was prepared from 17.1 g (0.1 mol) of commercial $Me_3SiC{\equiv}CSiMe_3$, 9.25 g (0.1 mol) of propionyl chloride, and 13.33 g (0.1 mol) of anhydrous $AlCl_3$ in 350 mL of CH_2Cl_2.[13] An 80.5% yield (12.4 g) of **21** was obtained: bp 65–67 °C (25 mm); IR (neat) 2150 ($C{\equiv}C$), 1670 ($C{=}O$), 850 cm^{-1} ($SiMe_3$); ^1H NMR ($CDCl_3$) δ 0.2 (s, 9 H, $SiMe_3$), 1.0 (t, 3 H, CH_3), 2.5 (q, 2 H, CH_2). Ketone **21** 3.85 g (12.5 mmol) and 10.6 g (37.5 mmol) of $(CF_3SO_2)_2O$ along with 7.7 g (37.5 mmol) of 2.6-di-*tert*-butyl-4-methylpyridine in 300 mL of CH_2Cl_2 gave 5.5 g (77%) of a mixture of 55% **5Z** and 45% **5E**: bp 55–58 °C (1.0 mm). The two isomers were completely separated by preparative GC on a 0.25-in. × 15-ft 15% QF-1 on 60/80 Chromosorb W aluminum column at 110 °C. **5Z**: IR (neat) 3300 ($C{\equiv}CH$), 3050, 2920, 2860, 2110 ($C{\equiv}C$), 1660 ($C{=}C$), 1420, 1220, 1130 (OSO_2CF_3), 960, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.8 (d, 3 H), 3.2 (s, 1 H), 6.05 (q, 1 H); ^{13}C NMR δ ($CDCl_3$) 130.01 (s), 128.86 (:), 118.24 (q, CF_3), 80.59 (d), 74.94 (d), 12.02 (q); MS, *m/z* (relative intensity) 214 (M^+, 35%), 159 (19.2), 83 (14.7), 81 (15.5), 65 (40.3), 64 (51.5) 63 (12.0), 53 (100). **5E**: IR (neat) 3300 ($C{\equiv}CH$), 3050, 2920, 2860, 2110 ($C{\equiv}C$), 1660 ($C{=}C$), 1420, 1220, 1130 (OSO_2CF_3), 960, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.9 (d, 3 H), 3.50 (s, 1 H), 6.2 (q, 1 H); ^{13}C NMR ($CDCl_3$) δ 130.33 (s), 129.50 (d), 118.39 (q), 85.80 (d), 73.12 (d), 13.21 (q); MS, *m/z* (relative intensity) 214 (M^+, 31%), 159 (22), 83 (17), 81 (14.0), 65 (41), 64 (49.5), 63 (21.1), 53 (100). For isomer assignments, see text.

4-Methyl-3-penten-1-yn-3-yl Chloride (6). Hydrolysis of 130 mg (0.7 mmol) of 1-(trimethylsilyl)-4-methyl-3-penten-1-yn-3-yl chloride (**22**) with 196 mg (2.0 mmol) of $KF{\cdot}2H_2O$ in 20 mL of methanol, after column chromatography on silica gel (pentane eluent), gave 60 mg (75%) of **6** as a colorless oil: IR (neat) 3300 ($C{\equiv}CH$), 2150 ($C{\equiv}C$), 1665

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cm^{-1} ($C{=}C$); ^{1}H NMR ($CDCl_3$) δ 1.85 (s, 3 H), 1.90 (s, 3 H), 3.20 (s, 1 H).

1-(Trimethylsilyl)-4-methyl-3-penten-1-yn-3-yl Chloride. Into a 100-mL, three-neck, round-bottomed flask equipped with a reflux condensor, an oil bath, and magnetic stirrer were placed 1.0 g (6.0 mmol) of known[13] ketone $(CH_3)_2CHC(O)C{\equiv}CSiMe_3$, 20 mL of benzene, and 4.12 g (30.0 mmol) of anhydrous K_2CO_3. The stirred mixture was heated to 50 °C, and 1.24 g (6.0 mmol) of PCl_5 was added over a period of 10 min. The reaction was followed by GC using a 0.125-in. × 6-ft 10% UCW-928 on 80/100 Chromosorb W column A at 150 °C, and after 12 h at reflux, 40% of the starting ketone was still seen with a mixture of several other compounds. The solution was cooled to room temperature, filtered, and extracted with 2 × 50 mL of water and 2 × 50 mL of saturated $NaHCO_3$ followed by 2 × 50 mL of water and dried over anhydrous $MgSO_4$. The solvent was removed by distillation, and the remaining residue was purified by column chromatography on silica gel (pentane as the eluent) to yield 133 mg (12%) of the desired compound as a colorless oil: IR (neat) 2960, 2920, 2860, 2150 ($C{\equiv}C$), 850 cm^{-1} ($SiMe_3$); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.2 (s, 9 H), 1.85 (s, 3 H), 1.95 (s, 3 H); MS, *m/z* (relative intensity) 189 (M^+ + 3, 2.1) 188.0 (M^+ + 2, 10.2), 187.0 (M^+ + 1, 5.8), 186.0 (M^+, 28.5), 174 (2.1), 173 (16.8), 172 (73), 171 (49.4), 135 (5.1), 130.9 (5.2), 121 (5.0), 118.9 (36.5), 117 (100), 95.0 (17.1), 93.0 (48.2).

1-Deuterio-4-methyl-3-penten-1-yn-yl Triflate (4b). This compound was made by hydrolyzing 1.51 g (5.0 mmol) of triflate $(CH_3)_2C{=}C(OTf)C{\equiv}CSiMe_3$ with 1.51 g (16.0 mmol) of anhydrous KF and 1.51 g of D_2O in 20 mL of C_2H_5OD.[54] The compound obtained was further treated with D_2O and freshly distilled triethylamine for 5 h, followed by solvent removal and quick filtration through a silica gel plug, yielding 576.5 mg (50%) of pure deuterio compound **4b**. The deuterium incorporation was shown to be 92.61% by mass spectroscopy: IR (neat) 3000, 2980, 2920, 2860, 2590 ($C{\equiv}C{-}D$), 1950 ($C{\equiv}CD$), 1650, 1420, 1210, 1160, 1140, 940, 840 cm^{-1}; MS, *m/z* (relative intensity) 230.9 (M^+ + 2, 2.2), 229.9 (M^+ + 1, 2.8), 228.9 (M^+, 35.1), 227.9 (1.6), 149.9 (4.1), 96.1 (28.3), 79.9 (17.5), 78.9 (18.5), 78 (19.9), 54.1 (100).

General Procedure for the Formation of Butatriene–Iridium Complexes. Bis(triphenylphosphine)chlorocarbonyl(1,4-dimethyl-1,2,3-pentatriene)iridium Triflate (7c). Into a dry 50-mL, round-bottomed flask equipped with a stirring bar was placed 0.31 g (0.4 mmol) of Vaska's complex (**3**) in the drybox, under argon. The flask was stoppered with a serum cap, and the septum was secured. The flask was removed from the drybox, and argon was introduced into the flask by a needle inlet and outlet, attached to a bubbler. The system was purged with argon, and 20 mL of dry degassed benzene was added to the flask via a syringe. To the rapidly stirring reaction mixture, 0.19 g (0.8 mmol) of triflate **4c** in 2 mL of benzene was injected via a syringe. The progress of the reaction was followed by monitoring the disappearance of the band at 1950 cm^{-1} and the appearance of a new band at 2000–2060 cm^{-1} due to the hexacoordinated iridium carbonyl stretching. This particular system required 45 h at room temperature to go to completion. After 24 h 20% more triflate was added to the mixture. When the reaction was completed, the whole mixture was injected into 250 mL of degassed pentane and stored in the refrigerator for a few hours to get the maximum precipitation of the product. The complex was recrystallized by dissolving in warm benzene and then adding hexanes until the solution became cloudy. The mixture was then set aside at room temperature overnight, and the crystals were filtered under argon and vacuum dried to yield 0.30 g (73%) of complex **7c**, as pale-yellow crystals: mp 146–150 °C dec; IR (KBr pellet) 2040 (s, $C{\equiv}O$), 2030 (w, $C{=}C{=}C{=}C$), 1150–1225 cm^{-1} (s, OSO_2); ^{1}H NMR (C_6D_6) δ 1.06 (s, 3 H), 1.60 (s, 3 H), 1.95 (s, 3), 7.1–7.9 (m, 30 H; ^{13}C NMR (CD_3NO_2) δ 167.1 160.2, 138.5, 137.0, 135.0, 123.5, 117.0, 86.0, 40.44, 29.86, 26.32.

Bis(triphenylphosphine)chlorocarbonyl(1-phenyl-4-methyl-1,2,3-pentatriene)iridium Triflate (7d). This complex was prepared from 0.31 g (0.4 mmol) of **3** and 0.23 g (0.75 mmol) of triflate **4d** according to the general procedure to yield 390 mg (91%) of a yellow–orange solid: mp 205–212 °C dec. The reaction time was 66 h: IR (KBr pellet) 2050 (s, $C{\equiv}O$), 2040 (w, $C{=}C{=}C{=}C$), 1150–1225 cm^{-1} (OSO_2); ^{1}H NMR (C_6D_6) δ 1.1 (s, 3 H), 1.6 (s, 3 H), 7.1–7.8 (m, 35 H).

Reaction of Triflate 5Z with Vaska's Complex (3) at 25 °C. Pure triflate **5Z** (0.4 mmol) was reacted with 0.2 mmol (0.155 g) of Vaska's complex (**3**) in 10 mL of benzene at 25 °C. The heterogeneous mixture became clear after 5 min. The clear solution was quenched with 100 mL of pentane after 15 min to give a 60:40 mixture of adducts **10Z** and **10E**, as determined by repeated integration of the methyl signals in the ^{1}H NMR.

Reaction of Triflate 5E with Vaska's Complex (3) at 25 °C. The reaction of pure triflate **5E** (0.4 mmol) in the same manner as **5Z** produced a 37:63 mixture of adducts **10Z** and **10E**, respectively.

Reaction of Triflate 5Z with Vaska's Complex (3) at 7 °C To Give Bis(triphenylphosphine)chlorocarbonyl[(*Z*)-1,2,3-pentatriene]iridium Triflate (10Z). The reaction of 0.4 mmol of triflate **5Z** with 0.2 mmol of **3** in 10 mL of benzene was performed at 7 °C. The mixture became homogeneous after 40 min and was quenched immediately to yield 160 mg (81%) of **10Z** as the major compound (90:10): mp 147–152 °C dec; IR (KBr pellet) 2060 (s, $C{\equiv}O$), 2020 (w, $C{=}C{=}C{=}C$), 1150–1250 (s, OSO_2), 312 cm^{-1} (s, polyethylene pellet, FT-IR); ^{1}H NMR (C_6D_6) δ 1.38 (dd, 3 H, *J* = 7.2, 1.6 Hz), 5.00 (m, 1 H), 7.0–8.0 (m, 31 H); ^{13}C NMR (C_6D_6, mixture of **10Z** and **10E**) δ 163.9, 160.5, 158.8, 151.8, 135.2, 134.82, 134.77, 134.69, 134.53, 134.43, 134.33, 131.74, 131.52, 129.3, 128.92, 128.77, 128.68, 128.60, 128.53, 128.41, 128.34, 128.27, 128.17, 127.97, 100.7, 80.2, 77.2, 18.02, 14.14.

Reaction of Triflate 5E with Vaska's Complex (3) at 7 °C To Give Bis(triphenylphosphine)chlorocarbonyl[(*E*)-1,2,3-pentatriene]iridium Triflate (10E). The reaction of pure triflate **5E** (0.4 mmol) in the same manner as **5Z** at 7 °C produced 150 mg (76%) of adduct **10E** with 2% of the adduct **10Z**: mp 145–148 °C dec; IR (KBr pellet) 2060 (s, $C{\equiv}O$), 2020 (w, $C{=}C{=}C{=}C$), 1150–1225 (s, OSO_2), 312.5 cm^{-1} (polyethylene pellet, FT-IR); ^{1}H NMR (C_6D_6) δ 1.30 (dd, 3 H, *J* = 7.2, 1.44 Hz), 5.63 (m, 1 H), 7.0–8.0 (m, 31 H); ^{13}C NMR, same as above for mixture of **10E** and **10Z**.

Reaction of Enyne Triflate 4f and Enyne Chloride 6 with Vaska's Complex. Reaction of 0.23 mmol (0.18 g) of **3** with 0.46 mmol (0.053 g) of enyne chloride **6** in 5 mL of benzene showed, after 12 days of reflux, mostly unreacted starting materials as determined by IR and NMR and decomposition products. Likewise, reaction of *tert*-butyl triflate **4f**, even after several days of reflux in benzene, showed no sign of product formation and only unreacted starting materials, and some decomposition products were observed by IR and NMR.

Isomerization of Complexes 10Z and 10E. The reaction mixture of **5Z** and **3** in C_6D_6 at 7 °C, resulting in a 90:10 mixture of **10Z** and **10E**, was allowed to warm to room temperature and the ^{1}H NMR retaken after 2 h. Integration of the methyl signals at 1.38, 1.30, and 1.48 ppm, respectively, showed a 3:2:1 ratio of **10Z**:**10E**:**14**, along with minor impurities. After 24 h at room temperature more impurities and larger amounts of **14** were observed along with **10Z** and **10E**. Likewise, the original **98**:**2** mixture of **10E** and **10Z** from reaction of **5E** with **3** at 7 °C in C_6D_6 showed an **80**:**20** ratio of **10E** and **10Z** after 24 h at room temperature along with small amounts of **14**. After 48 h at room temperature mostly decomposition products along with **14** and small amounts of **10E** and **10Z** were observed.

Reaction of Triflates 5E and 5Z with Vaska's Complex (3) at Room Temperature (Formation of Complex 14). A mixture (45% *Z* and 55% *E*) of triflates **5** (0.4 mmol) was reacted with (0.2 mmol) **3** at room temperature to give a mixture of the complexes **10E**, **10Z**, and iridium hydride **14**, detected by the upfield signals (1.38, 1.30, and 1.48 ppm, respectively) in the ^{1}H NMR spectrum. However, the recrystallization of the mixture produced almost pure iridium hydride complex **14**. The recrystallization was performed by dissolving the complexes in a small amount of warm benzene and then adding hexanes until the solution became cloudy. The mixture was set aside at room temperature for 12 h, and off-white crystals were collected and vacuum dried: mp 145–158 °C dec; IR (KBr pellet) 2065 (s, $C{\equiv}O$), 2025 (w, $C{=}C{=}C{=}C$), 1150–1225 cm^{-1} (s, OSO_2); ^{1}H NMR (C_6D_6) 1.48 (dt, 3 H, *J* = 7.2, 3.0 Hz), 3.2 (t, IrH, *J* = 4.8 Hz), 4.65 (m, 1 H), 7.0–8.0 (m, 30 H).

Acknowledgment. Financial support by the NSF (CHE-84-19099) at Utah, the Petroleum Research Fund, administered by the American Chemical Society, and the NSF 2- and 4-year College Research Equipment Program, at William and Mary, is gratefully acknowledged. We are also grateful to Johnson Matthey for a generous loan of $IrCl_3$ and to Dr. Lars Wistrand for the preliminary study of the reaction of **4a** with **3**.