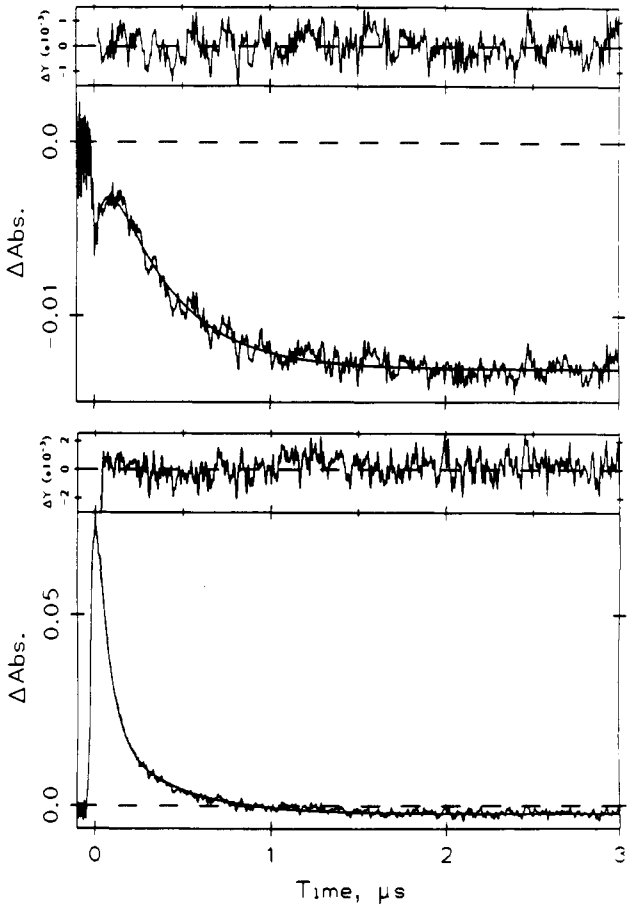

Figure 1. Transient kinetics following laser flash excitation (480 nm, 25 ns, 4 mJ) of a mixture of $Ru(bpy)_2(im)(His\text{-}33)^{2+}$-$Fe^{II}$-cyt c (18 μM) and Ru_a^{3+} (7 mM). Smooth lines are fits to a biexponential decay function. The faster component corresponds to decay of the excited Ru complex (k_{obsd} = 1.6 (1) × 10^7 s^{-1}); the slower component arises from the intramolecular ET reaction (k_{obsd} = 2.6 (3) × 10^6 s^{-1}). Top: Kinetics recorded at 550 nm. Bottom: Kinetics recorded at 306 nm.

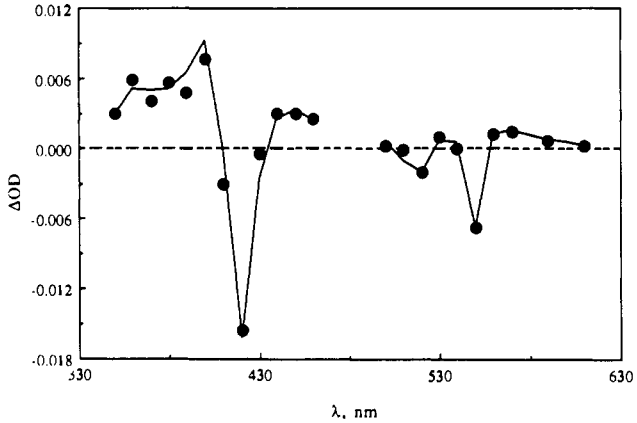

Figure 2. Difference spectrum (●) of the product of the intramolecular ET reaction. The solid line is the [Fe^{III}]-[Fe^{II}] cytochrome c difference spectrum (ref 17).

systems) is that the inverted region for ET (i.e., $-\Delta G° > \lambda$) is more accessible.

Up to this time, high-driving-force intramolecular ET rates in proteins and protein-protein complexes have been extracted mainly from studies of excited-state reactions.[2,6,7,19-21] Extremely fast ET rates can be measured by this technique, but the lower limit is always determined by the intrinsic excited-state lifetime (~1 μs for transition-metal complexes; ~10 ms for metalloporphyrins). This limit restricts the range of donor-acceptor distances that can be probed, as well as the nature of the proteins that can be examined (heme proteins substituted with unnatural metals). The flash-quench approach opens the way for studies of intramolecular ET at high driving forces over a wide range of distances in *both heme and nonheme proteins in which the natural metal is still in place.*

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Supplementary Material Available: Chromatograms from the preparation and purification of $Ru(bpy)_2(im)(His\text{-}33)$-Fe-cyt c, absorption spectra of $Ru(bpy)_2(im)(His\text{-}33)$-Fe-cyt c, and spectra from the reactions of Fe-cyt c and $Ru(bpy)_2(im)(His\text{-}33)$-Fe-cyt c with diethyl pyrocarbonate (5 pages). Ordering information is given on any current masthead page.

(19) (a) Peterson-Kennedy, S. E.; McGourty, J. L.; Kalweit, J. A.; Hoffman, B. M. *J. Am. Chem. Soc.* **1986**, *108*, 1739-1746. (b) McGourty, J. L.; Peterson-Kennedy, S. E.; Ruo, W. Y.; Hoffman, B. M. *Biochemistry* **1987**, *26*, 8302-8312. (c) Natan, M. J.; Hoffman, B. M. *J. Am. Chem. Soc.* **1989**, *111*, 6468-6470. (d) Kuila, D.; Baxter, W. W.; Natan, M. J.; Hoffman, B. M. *J. Phys. Chem.* **1991**, *95*, 1-3.

(20) (a) Liang, N.; Pielak, G. J.; Mauk, A. G.; Smith, M.; Hoffman, B. M. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 1249-1252. (b) Nocek, J. M.; Liang, N.; Wallin, S. A.; Mauk, A. G.; Hoffman, B. M. *J. Am. Chem. Soc.* **1990**, *112*, 1623-1625. (c) Wallin, S. A.; Stemp, E. D. A.; Everest, A. M.; Nocek, J. M.; Netzel, T. L.; Hoffman, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 1842-1844.

(21) McLendon, G. *Acc. Chem. Res.* **1988**, *21*, 160-167.

Metallacyclobutanes from Kinetic Nucleophilic Addition to η^3-Allyl Ethylene Complexes of Iridium. Regioselectivity Dependence on Nucleophile and Allyl Orientation

James B. Wakefield and Jeffrey M. Stryker*

Department of Chemistry, Indiana University
Bloomington, Indiana 47405

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The addition of nucleophiles to transition metal complexes of unsaturated hydrocarbons has been extensively investigated, leading to a number of synthetically useful organic reactions.[1] For unsaturated organometallic systems that possess several potentially reactive electrophilic sites, Davies, Green, and Mingos have developed a series of rules governing the regioselectivity of kinetic nucleophilic additions.[2] For complexes coordinating both η^2-alkene and η^3-allyl ligands, these rules predict addition preferentially to the olefin functionality. This prediction is supported both on theoretical grounds[2] and in many systems by experimental results.[2,3] Possible exceptions have, however, been noted for geometrically constrained complexes of the form $(C_5R_5)M[(1\text{-}3)\text{-}\eta^3\text{:}(5,6)\text{-}\eta^2\text{-cycloalkadienyl}]^+X^-$ (**1**, R = Me, H; M = Co, Rh,

(1) (a) Hegedus, L. In *The Chemistry of the Carbon-Carbon Bond, Volume 2*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1985; Chapter 6, pp 401-512. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, University Science: Mill Valley, CA, 1987; Chapter 7, pp 401-431.

(2) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047. Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. In *Reactions of Coordinated Ligands, Volume 1*; Braterman, P. S., Ed.; Plenum: New York, 1986; pp 897-937.

(3) (a) Mechanistically unambiguous studies: Domingos, A. J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974**, 145. Charles, A. D.; Diversi, P.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1981**, 1906. (b) Other systems: Cooke, M.; Draggett, P. T.; Green, M.; Johnson, B. F. G., Lewis, J.; Yarrow, D. J. *J. Chem. Soc., Chem. Commun.* **1971**, 621. Cotton, F. A.; Deeming, A. J.; Josty, P. L.; Ullah, S. S.; Domingos, A. J. P.; Johnson, B. F. G.; Lewis, J. *J. Am. Chem. Soc.* **1971**, *93*, 4624. Cotton, F. A.; LaPrade, M. D. *J. Organomet. Chem.* **1972**, *39*, 345. Eisenstadt, A. *J. Organomet. Chem.* **1973**, *60*, 335; **1976**, *113*, 147. Deeming, A. J.; Ullah, S. S.; Domingos, A. J. P.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974**, 2093. Schiavon, G.; Paradisi, C.; Boanini, C. *Inorg. Chim. Acta* **1975**, *14*, L5. Aumann, R. *Chem. Ber.* **1975**, *108*, 1974.

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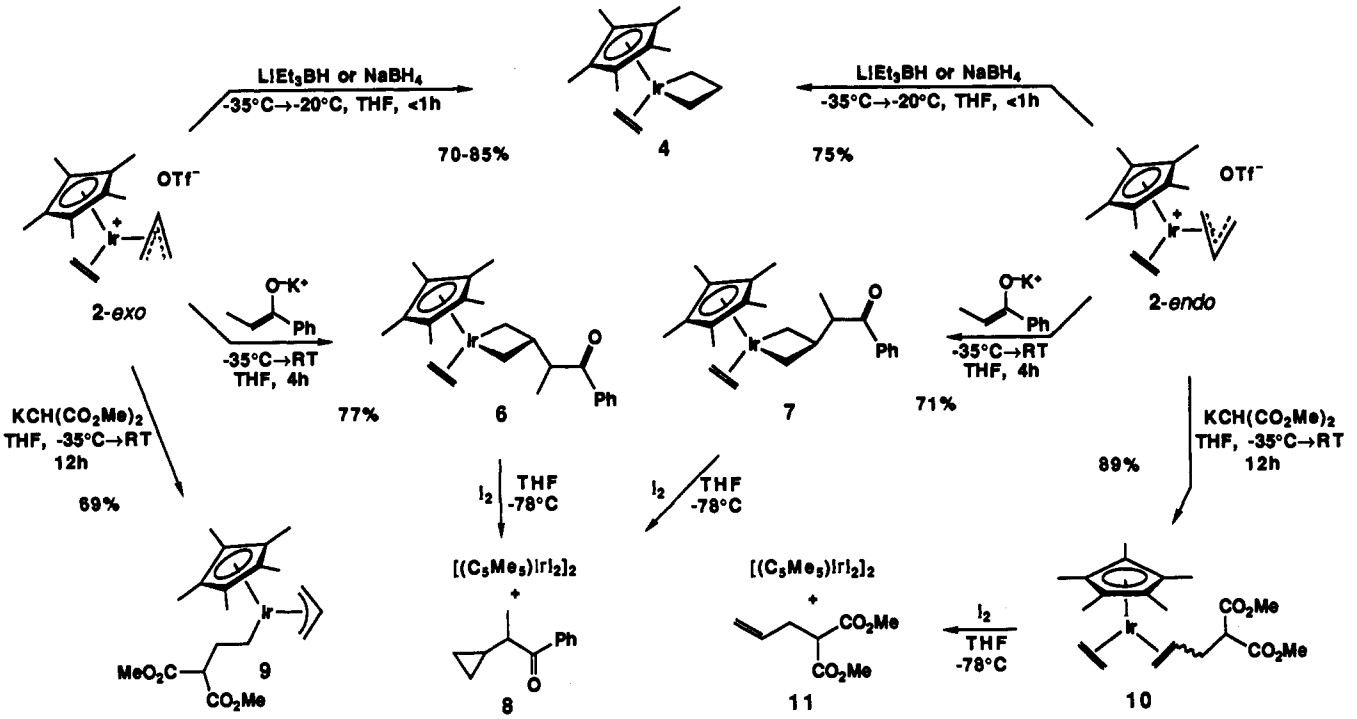
Scheme I



Ir), which yield nonconjugated diene derivatives from nucleophilic addition to the allyl terminal position.[4,5]

The endo and exo isomers of η^3-allyl ethylene complex **2**[6,7] (Scheme I) are closely analogous to the previously investigated cycloalkadienyl complexes **1** (R = Me, M = Ir);[5c] except that the allyl and olefin ligands are unconstrained by linkage. Very few such complexes have been prepared,[8] and no experimental studies of nucleophilic additions in these systems have been reported. Complex **2**-*exo* is isostructural with phosphine complexes $(C_5Me_5)(Me_3P)M(\eta^3\text{-allyl})^+X^-$ (**3**, M = Ir, Rh; X = BF_4, OTf),[9] known to undergo addition of strong nucleophiles selectively at the *central* allyl position.[10-12] The investigation of nucleophilic addition in this system thus provides a structurally unbiased test of the selectivity rules, a determination of the effects of allyl configuration on the regioselectivity of nucleophilic addition, and an evaluation of the effects of replacing a strong donor ligand with a π-acidic ethylene. The hydride, enolate, and malonate anions selected for this study encompass the range of nucleophilicity typically associated both with irreversible, "kinetic" addition and potentially reversible addition.[11] Hydride addition also raises the possibility of intramolecular rearrangements subsequent to formation of a kinetic adduct.

We report that, despite predictions to the contrary, the addition of "kinetic" nucleophiles to both *exo* and *endo* isomers of complex **2** leads to the formation of metallacyclobutane complexes via selective addition to the η^3-allyl central carbon (Scheme I). Furthermore, weaker nucleophiles are directed to *different* electrophilic sites, depending on the configuration of the allyl ligand. These results also show that, contrary to other allyl systems,[13] the nucleophile does not induce endo–exo isomerization competitively with adduct formation.

Treatment of complexes **2**-*exo* and **2**-*endo* with either $LiEt_3BH$ or $NaBH_4$ at low temperature each leads exclusively to the formation of metallacyclobutane ethylene complex **4** in isolated yields above 70%.[14-16] The spectroscopic data for this complex are fully consistent with the metallacyclobutane formulation, particularly the characteristic high field chemical shift (δ −31.7) of the metallacycle α-carbons in the ^{13}C NMR spectrum.[10,11] The complex is stable in the solid state but decomposes in solution over several days at room temperature, apparently (by ^1H NMR spectroscopy) without release of ethylene. Kinetic metallacyclobutane formation is supported both by labeling studies and by independent synthesis of the alkyl complex anticipated from hydride addition to the ethylene ligand. Thus, the reactions of isomerically homogeneous **2**-*exo* and **2**-*endo* with $NaBD_4$ give *different* metallacyclobutane

(4) Care should be taken in interpreting these reports as well as some of the studies in ref 3; it has frequently not been established that the observed products are indeed *kinetic* reaction products.

(5) (a) Lewis, J.; Parkins, A. W. *J. Chem. Soc. (A)* **1967**, 1150. See, also: Lewis, J.; Parkins, A. W. *J. Chem. Soc. (A)* **1969**, 953. (b) Evans, J.; Johnson, B. F. G.; Lewis, J.; Yarrow, D. J. *J. Chem. Soc., Dalton Trans.* **1974**, 2375. (c) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 1305. Bennett, M. A.; Nicholls, J. C.; Fazlur Rahman, A. K.; Redhouse, A. D.; Spencer, J. L.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1989**, 1328.

(6) Wakefield, J. B.; Stryker, J. M. *Organometallics* **1990**, *9*, 2428.

(7) In the conventional nomenclature for η^3-allyl complexes of this type, *exo* refers to the allyl orientation "point up" toward the C_5Me_5 ligand and *endo* to the corresponding "point down" configuration.

(8) (a) Pt: Miki, K.; Yamatoya, K.; Kasai, N.; Kurosawa, H.; Urabe, A.; Emoto, M.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1988**, *110*, 3191, and references therein. (b) Ir: Kaska, W. C.; Reichelderfer, R. F. *J. Organomet. Chem.* **1974**, *78*, C47.

(9) Although the allyl orientation in phosphine complexes **3** has been assigned the *endo* orientation,[10] difference NOE spectroscopy on these complexes and X-ray crystallography of the metallacyclobutane formed after nucleophilic addition indicate that the allyl ligand is in fact *exo*: Schwiebert, K. E.; Tjaden, E. B.; Wakefield, J. B.; Stryker, J. M., unpublished results.

(10) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7346. McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3388.

(11) Tjaden, E. B.; Stryker, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 6420.

(12) Other η^3-allyl complexes that react with nucleophiles at the central carbon: (a) Mo, W: Ephritikhine, M.; Francis, B. R.; Green, M. L. H.; MacKenzie, R. E.; Smith, M. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1131, and references therein. (b) Pd: Hegedus, L. S.; Darlington, W. H.; Russell, C. E. *J. Org. Chem.* **1980**, *45*, 5193. (c) Pt: Benyunes, S. A.; Brandt, L.; Green, M.; Parkins, A. W. *Organometallics* **1991**, *10*, 57.

(13) (a) Faller, J. W.; Chao, K. H.; Murray, H. H. *Organometallics* **1984**, *3*, 1231, and references therein. (b) VanArsdale, W. E.; Winter, R. E. K.; Kochi, J. K. *Organometallics* **1986**, *5*, 645.

(14) Highest yields and cleanest crude reaction mixtures were obtained at short reaction times. Crude product mixtures contained (by ^1H NMR) no other significant products.

(15) Full spectroscopic and analytical data are provided as supplementary material.

(16) Colorless crystals from pentane at −35 °C. Partial data for **4**: ^1H NMR (C_6D_6) δ 4.14 (m, 1 H, H_β-*syn* to the C_5Me_5 ligand[17]), 2.80 (m, 1 H, H_β-syn to ethylene[17]), 2.37 (br s, 4 H, C_2H_4), 1.44 (s, 15 H, C_5Me_5), 0.96 (m, 4 H, H_α); ^{13}C NMR (gated decoupling, C_6D_6) δ 95.0 (s, C_5Me_5), 36.9 (t, J = 156 Hz, C_2H_4), 31.3 (t, J = 126 Hz, C_β), 7.8 (q, J = 126 Hz, C_5Me_5), −31.7 (t, J = 137 Hz, C_α). Anal. Calcd for $C_{15}H_{25}Ir$: C, 45.32; H, 6.34. Found: C, 45.05; H, 6.35.

complexes, each with deuterium incorporated exclusively in the β-position of the ring.[17] The ethyl complex $(C_5Me_5)Ir(\eta^3\text{-allyl})Et$ (**5**), prepared by treatment of $(C_5Me_5)Ir(\eta^3\text{-allyl})Cl$ with EtMgCl,[18] does not rearrange to metallacyclobutane complex **4** under any conditions; this complex cannot be intermediate in the metallacyclobutane formation.

Enolates also add selectively to the central allyl position, producing stable metallacyclobutane complexes epimeric at the metallacycle β-carbon. The reactions of **2-exo** and **2-endo** with the potassium enolate of propiophenone (THF, −35 °C → room temperature), for example, yield metallacyclobutane stereoisomers **6**[15] and **7**,[15] respectively (Scheme I). By ^1H NMR spectroscopy, the crude reaction mixtures reveal no trace of isomeric "leakage" in the addition reaction. Both complexes display the characteristic upfield ^{13}C NMR signals for the α-carbons, now diastereotopic due to the chiral center on the addend. Iodinolysis (THF, −78 °C) of complexes **6** and **7** each gives the cyclopropanated organic **8**[19] and $[(C_5Me_5)IrI_2]_2$,[5b] which can be converted back to the starting allyl complex **2-exo** in a single step.[6]

Stabilized nucleophiles, in contrast, do not give metallacyclobutane products. The addition of potassium dimethylmalonate to **2-exo** proceeds regioselectively to the ethylene ligand, giving neutral alkyl allyl complex **9**.[15,18] The reaction of malonate anion with **2-endo** is equally selective but gives only terminal *allyl* addition, affording bis(olefin) complex **10** as an approximately 3:1 mixture of isomers.[15] Iodinolysis of this mixture at low temperature quantitatively produces $[(C_5Me_5)IrI_2]_2$[5b] and the free allylated malonate **11**, identified by comparison to an authentic sample. While the origin of this selectivity is not readily apparent, in the absence of steric effects,[20] this observation suggests that the electrophilicity of the coordinated ethylene may vary considerably with the allyl configuration.[21] The absence of metallacyclobutane formation may reflect a change in the kinetic selectivity for stabilized nucleophiles (due to a "later" transition state) or the rapid reversibility of initial nucleophilic attack. The formation of unstable intermediates and the possibility for interconversion of complexes **9** and **10** are under investigation.

On an empirical basis, the selectivity rules of Davies, Green, and Mingos[2] continue to be remarkably successful in predicting the outcome of nucleophilic additions. Nonetheless, the addition of strong nucleophiles to the η^3-allyl rather than ethylene ligand in this geometrically unconstrained system clearly violates these rules. Equally importantly, the preference for attack at the η^3-allyl central carbon rather than the terminal carbon is maintained in this system, despite replacing the strongly donating phosphine with the π-acidic ethylene ligand. Taken together, these results suggest that the coordination geometry of the complex may be more important than the degree of electron richness in determining the regiochemistry of nucleophilic addition to the η^3-allyl ligand, supporting alternative theoretical interpretations of the regioselectivity issue.[22] These results also suggest that the selectivity for terminal allyl addition observed in the $(1\text{-}3)\text{-}\eta^3\text{:}(5,6)\text{-}\eta^2$-cycloalkadienyl systems[5] may arise from geometrical constraints that change the relative ordering of the frontier orbitals, render the transition state for metallacyclobutane formation energetically inaccessible, or promote rapid rearrangement of a metallacyclobutane intermediate too strained to be isolated.

Acknowledgment. Financial assistance from the NIH-BRSG program and a Union Carbide Innovation Recognition Award is gratefully acknowledged. We also thank Dr. William Tamblyn and Johnson Matthey, Inc. for a generous loan of precious metals.

Supplementary Material Available: Spectroscopic and analytical data for compounds **4**, **6**, **7**, **9**, and **10** and spectroscopic data for complex **5** (2 pages). Ordering information is given on any current masthead page.

(17) From analysis of both ^1H and ^2H NMR spectroscopy, on addition of $NaBD_4$, **2-exo** yields complex **4-d_1** with deuterium incorporated specifically at the position corresponding to the ^1H NMR signal at δ 2.80. Complex **2-endo** gives **4-d_1** with the label exclusively at δ 4.14.

(18) Several closely analogous complexes have been prepared: McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 4246. The allyl configuration in these complexes has yet to be unambiguously assigned.

(19) Perkins, M. J.; Peynircioglu, N. B.; Smith, B. V. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1025.

(20) From inspection of the X-ray crystal structures of both *exo* and *endo* allyl ethylene complexes[6] and with standard trajectory analysis for the incoming nucleophile, there is no obvious steric argument accounting for the malonate positional selectivity or, in the case of strong nucleophiles, for the kinetic selectivity leading to metallacyclobutane complexes.

(21) The ethylene ligand in **2-exo** is fluxional at room temperature, while that in **2-endo** is rigid,[6] suggestive of greater backbonding, higher electron density, and lower electrophilicity for the ethylene in the latter complex.

(22) (a) η^3-Allyl complexes: Curtis, M. D.; Eisenstein, O. *Organometallics* **1984**, *3*, 887. (b) η^4-Diene complexes: Sautet, P.; Eisenstein, O.; Nicholas, K. M. *Organometallics* **1987**, *6*, 1845.

Inversion of Configuration in Nucleophilic Vinylic Substitutions of (*E*)-β-Alkylvinyliodonium Tetrafluoroborates with Halides

Masahito Ochiai,* Kunio Oshima, and Yukio Masaki

Gifu Pharmaceutical University
5-6-1 Mitahora Higashi, Gifu 502, Japan

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Nucleophilic substitutions at vinylic carbons of moderately activated olefins usually proceed with predominant retention of configuration thought to proceed via addition–elimination in most cases.[1] Alternatively, highly activated olefins afford products with partial or complete stereoconvergence via a multistep process. Exclusive inversion in nucleophilic vinylic substitutions, however, has not been observed for simple systems.[1c,2] Nucleophilic vinylic substitution generally requires activating substituents at the β-position of vinylic substrates (usually vinyl halides), and nucleophilic substitutions of simple alkylvinylic substrates are very uncommon.[3] We report herein a nucleophilic vinylic substitution of (*E*)-β-alkylvinyliodonium tetrafluoroborates with halides, *which proceeds with exclusive inversion of configuration at room temperature.*

Alkenyl(phenyl)iodonium tetrafluoroborates serve as the highly activated species of alkenyl halides in nucleophilic substitutions, mostly because of the superleaving ability of the phenyliodonio group.[4] However, little is known about the stereochemical course of the substitutions. Substitution of (*E*)-β-alkylvinyliodonium tetrafluoroborates **1a**,**b** with *n*-Bu_4NX, which competes with an alkyne-forming elimination, affords alkenyl halides of (*Z*) stereochemistry in completely stereoselective manner (Table I).[5] Treatment of (*E*)-1-decenyliodonium salt **1a** with *n*-Bu_4NCl (10 equiv) in CH_2Cl_2 at room temperature for 10 h gave the inverted chloride (*Z*)-**2a**[6] (X = Cl, 83%) and 1-decyne (14%), along with the concomitant formation of iodobenzene. In CH_3CN, more than 90% selectivity for the substitution over the elimination was achieved. Substitutions with *n*-Bu_4NBr and *n*-Bu_4NI similarly gave the corresponding (*Z*)-alkenyl halides with complete inversion. On the other hand, *n*-Bu_4NF afforded only 1-decyne. Note that the selectivity for substitution over elimination decreases

(1) (a) Rappoport, Z. *Adv. Phys. Org. Chem.* **1969**, *7*, 1. (b) Modena, G. *Acc. Chem. Res.* **1971**, *4*, 73. (c) Rappoport, Z. *Acc. Chem. Res.* **1981**, *14*, 7. (d) Rappoport, Z. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 309. (e) Shainyan, B. A. *Usp. Khim.* **1986**, *55*, 942.

(2) (a) Miller, S. I. *Tetrahedron* **1977**, *33*, 1211. (b) Rappoport, Z. *Tetrahedron Lett.* **1978**, 1073.

(3) Stang, P. J.; Datta, A. K. *J. Am. Chem. Soc.* **1989**, *111*, 1358.

(4) For synthesis and reactions of the alkenyliodonium salts, see: (a) Ochiai, M.; Sumi, K.; Nagao, Y.; Fujita, E. *Tetrahedron Lett.* **1985**, *26*, 2351. (b) Ochiai, M.; Sumi, K.; Takaoka, Y.; Kunishima, M.; Nagao, Y.; Shiro, M.; Fujita, E. *Tetrahedron* **1988**, *44*, 4095. (c) Nesmeyanov, A. N.; Tolstaya, T. P.; Petrakov, A. V.; Goltsev, A. N. *Dokl. Akad. Nauk SSSR*, **1977**, *235*, 591.

(5) Nesmeyanov and his co-workers reported that thermolysis of bis-[(*E*)-1-propenyl(phenyl)iodonium] hexachlorostannate at 85 °C without solvent gave (*Z*)-1-propenyl chloride: Nesmeyanov, A. N.; Tolstaya, T. P.; Petrakov, A. V.; Leshcheva, I. F. *Dokl. Akad. Nauk SSSR* **1978**, *238*, 1109.

(6) Zweifel, G.; Miller, J. A. *Org. React.* **1984**, *32*, 375.

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