Ethylene-assisted allylic carbon-hydrogen bond activation of substituted alkenes using dicationic iridium complexes. Synthesis, structure, and configurational isomerism of cationic iridium .eta.3-allyl ethylene complexes

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Ethylene-Assisted Allylic Carbon–Hydrogen Bond Activation of Substituted Alkenes with Use of Dicationic Iridium Complexes. Synthesis, Structure, and Configurational Isomerism of Cationic Iridium η^3-Allyl Ethylene Complexes

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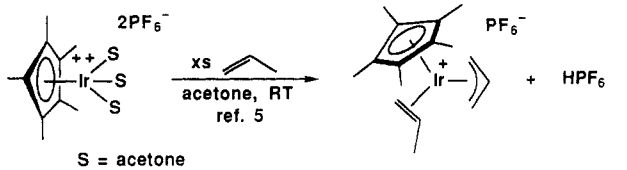
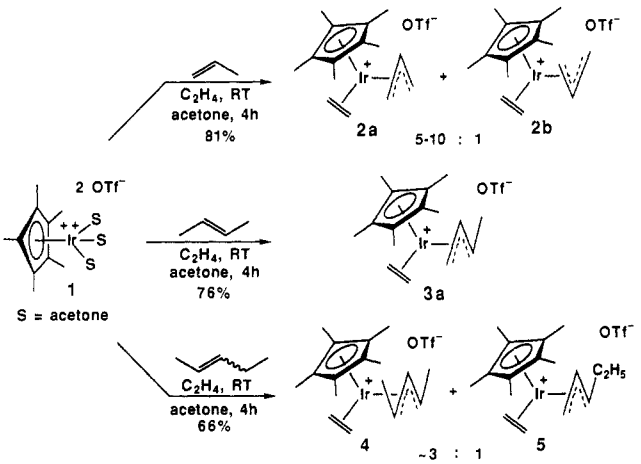
Summary: The use of ethylene as a sterically small, chemically inert "enabling" ligand allows the dicationic complex $[Cp^*Ir(S)_3]^{2+}(OTf^-)_2$ (S = acetone) to mediate the allylic carbon–hydrogen bond activation of substituted olefins, a reaction that fails in the absence of ethylene. This reaction produces the thermodynamically less stable exo isomers; the more stable endo isomers are obtained via isomerization reactions. X-ray crystal structures of one exo and one endo allyl complex are reported.

For a detailed investigation into regioselective nucleophilic addition to the central carbon of electron-rich η^3-allyl transition-metal complexes,[1] we required an efficient, high-yield synthesis of cationic iridium η^3-allyl complexes of the form $[Cp^*(L)Ir(allyl)]^+$ ($Cp^* = \eta^5$-C_5Me_5), in which both the ancillary ligand L and the extent of substitution on the allyl ligand could be easily and broadly varied. The most direct method for the formation of transition-metal η^3-allyl complexes is allylic carbon–hydrogen bond activation, requiring only the simple, unfunctionalized, olefin as the organic component and a single organometallic precursor. Discrete, controllable allylic activation of olefins is known, particularly for electrophilic palladium(II) complexes,[2,3] but is encountered infrequently compared to the use of functionalized olefin precursors incorporating an allylic leaving group.[4] Pertinent to our requirements, the allylic activation of propene by dicationic iridium tris(solvate) complexes has been reported, via spontaneous proton loss from one of two coordinated propene ligands (eq 1).[5] Except for some chelating diolefins, however, this



(1)

Scheme I



reaction fails for olefins more highly substituted than propene, giving dication decomposition products even in the case of 2-butene. In addition, from the synthetic perspective, the necessity of consuming 2 equiv of alkene to activate 1 equiv inherently limits this methodology to readily available olefins.

The failure of internal olefins to yield η^3-allyl complexes in this system can be reasonably attributed to unfavorable steric requirements necessary for coordination of two highly substituted olefins to the iridium center. To reduce the steric demands at the metal center without significantly perturbing the electronic environment favoring allylic activation, we have investigated the Maitlis reaction using ethylene as a small, inert, "enabling" ligand, in combination with the desired substituted olefins. Here we report the successful application of this strategy to the synthesis of the parent η^3-allyl ethylene complex and substituted η^3-allyl complexes. Characterization of configurational isomerism in η^3-allyl complexes within this series and interconversion of the η^3-allyl isomers are also described.

The dicationic tris(acetone) complex 1 used throughout this investigation was prepared according to the method of Maitlis,[5] except that AgOTf was used in the ionization procedure. Due either to the ionization kinetics or to the stability of the resulting dicationic complexes, the triflate counterion consistently results in cleaner conversions and higher yields than either the corresponding BF_4^- or PF_6^- salts.[6] Initial investigation into the effects of ethylene on allylic activation focused on propene activation, permitting an assessment of competitive ethylene coordination in a

(1) (a) Mo, W.: Ephretikhine, M.; Francis, B. R.; Green, M. L. H.; Mackenzie, R.; Smith, M. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1131. (b) Rh, Ir: Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7347. McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3388. (c) See also: Hegedus, L. S.; Darlington, W. H.; Russell, C. E. *J. Org. Chem.* **1980**, *45*, 5193. Theoretical discussions: (d) Davies, S., G.; Green, M. L. H.; Mingos, M. P. *Tetrahedron* **1978**, *34*, 3047. (e) Curtis, M. D.; Eisenstein, O. *Organometallics* **1984**, *3*, 887.

(2) See: Hüttel, R. *Synthesis* **1970**, 228. Trost, B. M. *Tetrahedron* **1977**, *33*, 2615. Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385 and references therein.

(3) (a) Base-induced deprotonation (Fp^+): Cutler, A.; Ehntholt, D.; Lennon, P.; Nicholas, K.; Marten, D. F.; Madhavarao, M.; Raghu, S.; Rosan, A.; Rosenblum, M. *J. Am. Chem. Soc.* **1975**, *97*, 3149 and references therein. (b) Photochemical activation (Re): Batchelor, R. J.; Einstein, F. W. B.; Jones, R. H.; Zuang, J.-M.; Sutton, D. *J. Am. Chem. Soc.* **1989**, *111*, 3468. (c) Thermal activation (Ir): Tanke, R. S.; Crabtree, R. H. *Inorg. Chem.* **1989**, *28*, 3444.

(4) Review: 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; Chapters 3 and 19, and references therein.

(5) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 1305. The mechanism of this allylic activation, particularly the role of the metal, has not been determined.

(6) Facile solvolytic decomposition of the PF_6^- counterion in tris(solvate)iridium dicationic complexes in acetone has been reported: Thompson, S. J.; Bailey, P. M.; White, C.; Maitlis, P. M. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 490.

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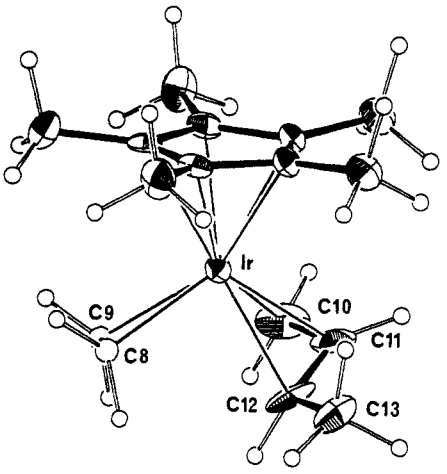


Figure 1. ORTEP diagram of complex **3a**. Final residuals: $R(F) = 0.033$, $R_w(F) = 0.036$.

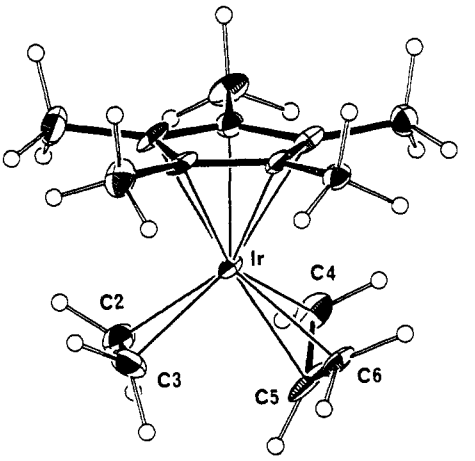
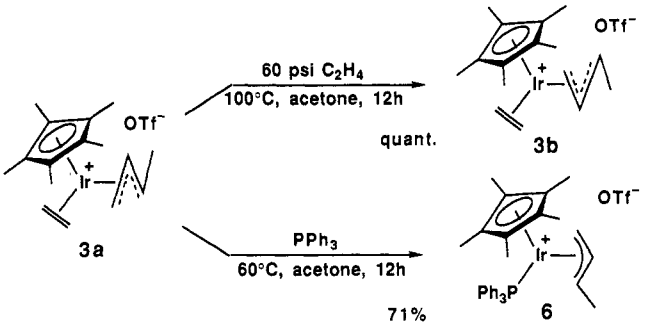


Figure 2. ORTEP diagram of complex **2b**. Final residuals: $R(F) = 0.068$, $R_w(F) = 0.067$.

system known to undergo clean allylic activation. Treatment of $[Cp^*IrCl_2]_2$ with 4 equiv of AgOTf in acetone at room temperature, followed immediately by placing the reaction mixture under an approximately equimolar mixture of ethylene and propene at atmospheric pressure, resulted in the formation of isomeric allyl ethylene complexes **2a** and **2b** in a somewhat variable ratio, up to about 10:1 (Scheme I). The major product from this reaction was isolated by fractional recrystallization from acetone/ether in 81% yield and identified as the exo isomer **2a** (vide infra),[7,8] an allyl orientation opposite that reported for the related $(C_5Me_5)(Me_3P)Rh(\eta^3\text{-allyl})^+$ complex,[1b] but apparently favored for the parent cyclopentadienyl complexes of Co, Rh, and Ir.[9] We note that, despite the stability of the allyl propene complex,[5] the selectivity for coordinating ethylene was very high; only a trace of the allyl propene complex was observed spectroscopically.

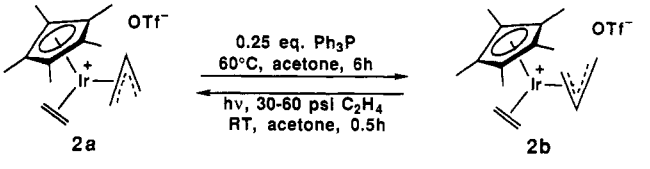
To investigate the use of ethylene to enable the allylic activation of disubstituted olefins, the tris(acetone) dication **1** was treated with excess ethylene and *trans*-2-butene, giving the exo,syn crotyl ethylene complex **3a** in 76% yield after recrystallization from acetone/ether (Scheme I). This material was spectroscopically closely analogous to the kinetic exo allyl complex **2a**,[10] and the configurational ambiguities in this system were resolved by X-ray crystallography (Figure 1).[11] Allylic activation of the unsymmetrical 2-pentene (ca. 2:1 mixture of trans and cis isomers) gave both internal and terminal exo,syn allyl isomers

Scheme II



4 and **5**, with approximately 3–4:1 selectivity for activation at the internal methylene.[12] The major product was isolated by a single fractional crystallization;[10] the minor isomer **5** was prepared independently from the dicationic complex **1** by activation of 1-pentene under ethylene (73% isolated yield).[10]

In an attempt to define the substitutional lability of the ancillary ethylene ligand in these complexes, the exo allyl ethylene complex **2a** was treated with triphenylphosphine. Warming to 60 °C in acetone did not result in ligand substitution, giving instead essentially quantitative isomerization of the allyl ligand to the thermodynamically more stable endo isomer **2b** (eq 2).[13] This reaction requires only



(2)

a catalytic quantity of phosphine but does not proceed at

(7) With use of the conventional nomenclature for allyl complexes of this type, exo refers to the allyl orientation "point up" toward the cyclopentadienyl ligand and endo to the corresponding "point down" orientation. On the allyl ligand the central proton is designated H_c, the methylene protons (or substituent) syn (cis) to the central proton or substituent are designated H_s, and those anti (trans) are designated H_a.

(8) Data for complex **2a**: IR (KBr) 3080 (w), 2980 (w), 2920 (m), 1470 (s), 1380 (m), 1260 (s), 1220 (s), 1140 (s), 1080 (w), 1020 (s), 750 (w), 630 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.11 (tt, J = 10.7, 6.9 Hz, 1 H, H_c), 3.79 (dd, J = 6.9, 2.6 Hz, 2 H, H_s), 3.11 (br s, 2 H, C_2H_4), 2.60 (br s, 2 H, C_2H_4), 2.04 (dd, J = 10.7, 2.6 Hz, 2 H, H_a), 1.91 (s, 15 H, C_5Me_5); ^{13}C NMR (gated decoupling, $CDCl_3$) δ 100.6 (q, J = 4.3 Hz, C_5Me_5), 86.3 (d, J = 164 Hz, allyl CH), 47.6 (t, J = 162 Hz, C_2H_4), 47.0 (br t, J = 161 Hz, allyl CH_2), 8.5 (q, J = 128 Hz, C_5Me_5), triflate carbon not observed above base line noise. Anal. Calcd for $C_{16}H_{24}IrF_3O_3S$: C, 35.22; H, 4.43. Found: C, 35.64; H, 4.41.

(9) See: Wolf, J.; Werner, H. *Organometallics* **1987**, *6*, 1164. Krivykh, V. V.; Gusev, O. V.; Petrovskii, P. V.; Rybinskaya, M. I. *J. Organomet. Chem.* **1989**, *366*, 129 and references therein. (b) Theoretical consideration of η^3-allyl configurational isomers: reference 1e.

(10) Complete spectroscopic and analytical data are provided as supplementary material.

(11) Details of the crystallography are included as supplementary material.

(12) (a) A trace amount of the syn,anti 1,3-dimethylallyl complex is also formed in this reaction. (b) A similar preference for internal allyl formation is observed in palladium-mediated allylic activation; see ref 2 and: Trost, B. M.; Dietsche, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 8200.

(13) Data for complex **2b**: IR (KBr) 3060 (w), 3020 (w), 2980 (w), 2950 (w), 2900 (w), 1480 (m), 1460 (m), 1450 (m), 1420 (w), 1370 (w), 1260 (s), 1210 (m), 1180 (w), 1140 (s), 1070 (w), 1020 (s), 770 (w), 740 (w), 630 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.06 (d, J = 6.6 Hz, 2 H, H_s), 2.98 (tt, J = 6.6, 10.9 Hz, 1 H, H_c), 2.43 (d, J = 10.9 Hz, 2 H, H_a), 2.13 (complex m, AA' of AA'BB', 2 H, C_2H_4), 2.04 (complex m, BB' of AA'BB', 2 H, C_2H_4), 1.96 (s, 15 H, C_5Me_5); ^{13}C NMR (gated decoupling, $CDCl_3$) δ 120.9 (q, J = 319 Hz, CF_3), 101.6 (q, J = 5.0 Hz, C_5Me_5), 97.7 (d, J = 166 Hz, allyl CH), 46.1 (br t, J = 162 Hz, allyl CH_2), 39.7 (t, J = 161 Hz, CH_2CH_2), 9.2 (q, J = 129 Hz, C_5Me_5). Anal. Calcd for $C_{16}H_{24}IrF_3O_3S$: C, 35.22; H, 4.43. Found: C, 35.26; H, 4.52.

all in its absence, even at higher temperature.[14] The ^1H NMR spectrum of this complex revealed an unusually shielded resonance for the central proton, greater than 1.1 ppm upfield from that in the kinetic isomer, and significantly deshielded resonances for the terminal protons.[13] In addition, the thermodynamic product **2b** showed well-resolved second-order multiplets for the ethylene ligand, contrasting the fluxionally broadened resonances seen at room temperature in kinetic product **2a**. Diffractable single crystals of complex **2b** were obtained from acetone/ether, and the configurational assignment was confirmed by X-ray crystallography, rigorously establishing the endo allyl orientation in the thermodynamic product (Figure 2).[11] Perhaps most interestingly, photolysis of the endo isomer **2b** in acetone under 30–60 psi of ethylene established a photostationary equilibrium favoring the less stable exo isomer in a ratio of ca. 10:1 (eq 2).[15]

In marked contrast to the unsubstituted allyl complex **2a**, the reaction of exo crotyl complex **3a** with Ph_3P resulted in clean substitution of the ethylene, giving the crotyl phosphine complex **6** in 71% isolated yield after purification (Scheme II).[10,16] Also in contrast to the reactivity of complex **2a**, thermal isomerization to the endo complex **3b**[14] is obtained between 60 and 100 °C in the absence of catalyst. Although not required, this isomerization is best conducted under ethylene, inhibiting decomposition from competitive ligand dissociation. The substitutional lability and facile thermal isomerization observed for the crotyl complex may indicate that ligand substitution in this complex follows an associative pathway, preceded by η^3 to η^1 isomerization of the allyl ligand to open a coordination site at the metal. Such dissociation is expected to be more facile for the substituted allyl ligand, with its weaker secondary carbon–metal interaction, than for the unsubstituted allyl ligand. This suggests that a fundamentally different mechanism is operative in the phosphine-catalyzed isomerization of unsubstituted complex **2a**. This process is under investigation.

While the kinetic selectivity for the less stable exo allyl isomers is difficult to rationalize, the use of ethylene indeed enables allylic activation to proceed for more highly substituted olefins, consuming only 1 equiv of the substrate olefin. Importantly, this methodology provides ready access to "polyfunctional" organometallic electrophiles (both the ethylene and two sites of the allyl ligand are potentially subject to nucleophilic attack[1d]) and both geometries of the allyl ligand, allowing a detailed investigation of nucleophilic addition in this system. Development of other potentially "enabling" ligands and extension of this methodology to complexes of other metals and to more highly substituted, cyclic, and functionalized olefins is also under investigation.

Acknowledgment. We thank Dr. John C. Huffman and Kirsten Folting of the Indiana University Molecular Structure Center for the X-ray crystal structure determinations and the Union Carbide Innovation Recognition Program for financial assistance.

Supplementary Material Available: Spectroscopic and analytical data for compounds **3a**, **3b**, and **4–6**, details of the data collection and structure solution for complexes **2b** and **3a**, and tables of atomic positional and thermal parameters and complete bond distance and angle data for **2b** and **3a** (30 pages); listings of F_o vs F_c for **2b** and **3a** (14 pages). Ordering information is given on any current masthead page.

(14) (a) Exo–endo allyl isomerization catalyzed by nucleophiles has been described: Faller, J. W.; Chao, K. H.; Murray, H. H. *Organometallics* **1984**, *3*, 1231 and references therein. VanArsdale, W. E.; Winter, R. E. K.; Kochi, J. K. Organometallics 1986, 5, 645. (b) Exo and endo allyl isomers are known in several systems; see: Hsu, L.-Y.; Nordman, C. E.; Gibson, D. H.; Hsu, W.-L. *Organometallics* **1989**, *8*, 241. Krivykh, V. V.; Gusev, O. V.; Petrovskii, P. V.; Rybinskaya, M. I. *J. Organomet. Chem.* **1989**, *366*, 129. See also ref 3b, and references therein.

(15) (a) Erker, G.; Berg, K.; Krüger, C.; Müller, G.; Angermund, K.; Benn, R.; Schroth, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 455. (b) Irradiation for 0.5 h, 450-W Hanovia lamp, Pyrex filter. In the absence of ethylene some photolytic decomposition of these complexes is observed.

(16) The ^1H NMR spectrum of the allyl ligand in complex **6** is closely analogous to that reported for $Cp^*(PMe_3)Ir(allyl)^+BF_4^-$,[1b] but because the allyl configuration in that complex has not been unambiguously assigned, the configuration in complex **6** also remains ambiguous.

Articles

π-Complexes of Alkenes to Trivalent Aluminum

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The structures of simple π-complexes of aluminum alkyls and aluminum alkyl halides were explored with use of ab initio molecular orbital theory. Such structures have been proposed as either intermediates or transition structures in mechanisms for oligomerization of ethylene, carbalumination, and hydroalumination. Complexes of $AlR_{3-n}Cl_n$ (R = H, CH_3) with ethylene and propene were found to be stable intermediates, not transition structures. The energies of binding have been estimated by using post-Hartree–Fock techniques.

The Lewis acidity of trivalent aluminum complexes has been both a blessing and a curse. The ability of the empty aluminum p orbital to accept an electron pair is the root of much of the rich chemistry of aluminum. On the other hand, a great deal of the early work in organometallic chemistry, e.g. the development of the Grignard reagent,

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