Synthesis and Isolation of Highly Reactive η^3-Allyl Alkyne Complexes of Iridium via the Inner-Sphere η^3-Allyl Triflate Complex $(C_5Me_5)Ir(\eta^3-C_3H_5)OTf$. Facile Conversion to Alkyne Metallacyclobutane Complexes by Nucleophilic Addition

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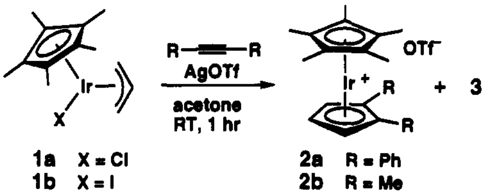
*Summary: The inner-sphere triflate complex $[(C_5Me_5)Ir(\eta^3-C_3H_5)OTf]$ (**5**), formed quantitatively on photolysis of $[(C_5Me_5)Ir(\eta^3-C_3H_5)(\eta^2-C_3H_6)]^+OTf^-$, reacts with disubstituted alkynes to form the highly reactive allyl alkyne complexes $[(C_5Me_5)Ir(\eta^3-C_3H_5)(RC{\equiv}CR)]^+OTf^-$ (**3**), inaccessible by conventional methodology. Although the allyl alkyne complexes undergo facile reductive ligand coupling to form the substituted bis(cyclopentadienyl) complexes **2**, these complexes can be isolated and converted selectively to the metallacyclobutane alkyne complexes **6** in high yield by reaction with nucleophiles.*

To expand our investigation of the factors governing the regioselectivity of nucleophilic attack on η^3-allyl ligands[2] and explore the reactivity of metallacyclobutane complexes resulting from central carbon addition, we sought to prepare metallacyclobutanes coordinating noninnocent ancillary ligands. On the basis of the potential for subsequent migratory insertion reactions,[3] alkyne metallacyclobutanes were targeted, requiring general access to cationic η^3-allyl alkyne complexes of the form $[(C_5R_5)Ir(\eta^3\text{-allyl})(\eta^2\text{-alkyne})]^+$ (R = H, Me). Isolable complexes incorporating an allyl and one or more alkyne ligands are rare;[4] in related systems, direct synthetic approaches are complicated by facile reductive cyclization of the allyl and alkyne ligands to form a new cyclopentadienyl ligand.[5] Once such preparative difficulties are overcome, nucleophilic addition to the allyl alkyne complexes is further complicated by the potential for competitive addition to the electrophilic alkyne.[6]

Our attempts to prepare complexes **3** by halide abstraction from $(C_5Me_5)Ir(\eta^3-C_3H_5)X$ (X = Cl,[3] I; **1**) using Ag(I) in the presence of alkyne gave mixtures of the allyl alkyne complexes **3** and cyclization products **2** in ratios dependent on the reaction conditions (eq 1). The ionization reaction is unusually slow and, as previously noted,[7] requires 2 equiv of Ag(I) and prolonged reaction times ($\geq$1 h at room temperature, much longer at lower temperature), during which the presumed allyl alkyne intermediates cyclize to complexes **2** at a rate commensurate with ionization.[8] Bis(cyclopentadienyl) complexes **2** are waxy solids (70–80% isolated) that could not be recrystallized to analytical purity. The structures were assigned on the basis of spectroscopic and mass spectral data.[9]



(1)

An alternative strategy for the synthesis of complexes **3** was developed using the allyl triflate complex **5**[9,10] (Scheme I), a versatile precursor to complexes of the form $[(C_5Me_5)Ir(\eta^3-C_3H_5)L]^+OTf^-$. Complex **5** is isolated in low yield (43%) from allyl chloride complex **1** by halide abstraction with AgOTf but is generated quantitatively by photolysis (450-W Hanovia, Pyrex) of $[(C_5Me_5)M(\eta^3-C_3H_5)(\eta^2-C_3H_6)]^+OTf^-$ (**4**)[11] in CH_2Cl_2 or acetone at 0 °C under a strong nitrogen purge. The triflate complex **5** is soluble in both ether and benzene, suggesting coordination of the triflate to form a neutral complex in these media.[12] Comparison of the IR spectra of **5** in solvents of varying polarity shows that the absorption at 1265 cm^{-1}, attributable to the asymmetric OSO stretch in ionic triflate,[12c] is strong in polar solvents (e.g., CH_2Cl_2, THF) but very weak in nonpolar solvents (e.g., C_6H_6). Conversely, the band at 1320 cm^{-1}, assigned to the asymmetric stretch of coordinated triflate,[12c] is weak in polar solvents and strong

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[1] Department of Chemistry, Indiana University, Bloomington, IN 47405.

[2] (a) Tjaden, E. B.; Stryker, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 6420. (b) Wakefield, J. B.; Stryker, J. M. *J. Am. Chem. Soc.* **1991**, *113*, 7057. (c) Tjaden, E. B.; Stryker, J. M. *Organometallics* **1992**, *11*, 16. (d) Tjaden, E. B.; Schwiebert, K. E.; Stryker, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 1100.

[3] Insertion of 2-butyne into an intermediate iridacyclopentene complex has been proposed: McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 4246.

[4] (a) Green, M.; Taylor, S. H. *J. Chem. Soc., Dalton Trans.* **1975**, 1142. (b) Fischer, R. A.; Herrmann, W. A. *J. Organomet. Chem.* **1989**, *377*, 275.

[5] Lutsenko, Z. L.; Aleksandrov, G. G.; Petrovskii, P. V.; Shubina, E. S.; Andrianov, V. G.; Struchkov, Yu. T.; Rubezhov, A. Z. *J. Organomet. Chem.* **1985**, *281*, 349.

[6] Review of nucleophilic attack on alkyne ligands: Reger, D. L. *Acc. Chem. Res.* **1988**, *21*, 229.

[7] Treatment of $(C_5R_5)M(\eta^3-C_3H_5)Cl$ (M = Rh, R = H, Me; M = Ir, R = H) with excess $AgBF_4$ and alkyne is reported[5] to lead only to the substituted bis(cyclopentadienyl) complexes, with no detection of intermediate allyl alkyne complexes.

[8] The influence of reaction conditions on the conversion of allyl alkyne complexes **3** to cyclized products **2** will be discussed in greater detail in a subsequent paper.

[9] Experimental and characterization data are included as supplementary material.

[10] Selected spectroscopic data for **5**: IR (C_6H_6, cm^{-1}) 1335 (s, ν_{OSO}), 1265 (w, ν_{OSO}); IR (CH_2Cl_2, cm^{-1}) 1315 (w, ν_{OSO}), 1265 (s, ν_{OSO}); ^1H NMR (400 MHz, $CDCl_3$) δ 4.71 (m, 1H, $H_{central}$), 3.80 (d, J = 6 Hz, 2H, H_{syn}), 2.58 (d, J = 10 Hz, 2H, H_{anti}), 1.81 (s, 15H, C_5Me_5); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 117.4 (J = 318 Hz, CF_3), 92.3 (C_5Me$_5$), 86.6 ($C_{central}$), 51.6 ($C_{terminal}$), 9.4 (C_5Me_5); HRMS calcd for $C_{14}H_{20}IrSO_3F_3$ 477.0326, found 477.0319 ($M^+ - C_3H_5$).

[11] White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 1305.

[12] A number of transition-metal complexes containing coordinated triflate groups have been reported: (a) Stang, P. J.; Huang, Y.; Arif, A. M. *Organometallics* **1992**, *11*, 231 and references therein. (b) Beck, W.; Sunkel, K. *Chem. Rev.* **1988**, *88*, 1405. (c) Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17 and references therein.

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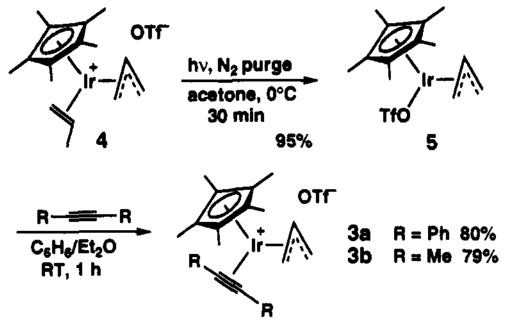
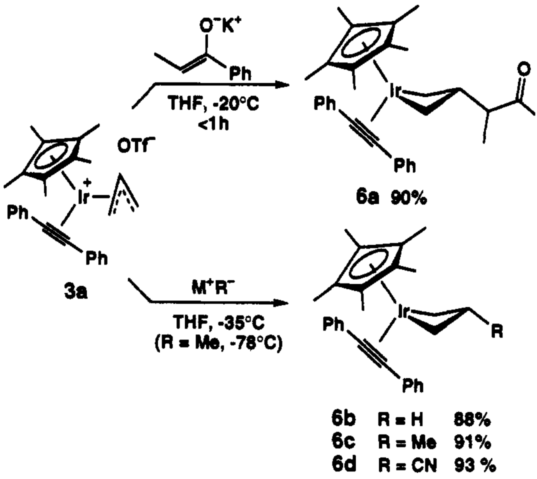
Scheme I



Scheme II



in nonpolar solvents. The triflate carbon in the ^{13}C NMR spectrum appears at δ 117 ($CDCl_3$), upfield from those in the ionic complexes $[(C_5Me_5)Ir(\eta^3\text{-}C_3H_5)L]^+OTf^-$,[13] which resonate consistently at δ 121.[14] Mass spectral analysis of complex **5** generates $[(C_5Me_5)Ir(OSO_2CF_3)]^+$ as the major fragmentation product, suggesting strong association of the triflate. Complex **5** is labile in solution, decomposing to unidentified materials at room temperature.

The solubility of triflate complex **5** in nonpolar solvents can be exploited to provide pure allyl alkyne complexes **3** in high isolated yield. Addition of diphenylacetylene or 2-butyne to complex **5** in C_6H_6/ether leads to the precipitation of alkyne complexes **3** as colorless solids in 70–80% yield (Scheme I). These products have been characterized spectroscopically, with the configuration of the allyl ligand in complex **3b** assigned as exo by difference NOE spectroscopy.[15] Complexes **3** are reactive even in the solid state, decomposing to unidentifiable products when stored under nitrogen at room temperature (ca. 2 days for **3a** and <12 h for **3b**). Both complexes persist indefinitely in the solid state below −20 °C, even under air. In solution, the lability and reactivity toward reductive cyclization precludes recrystallization; FAB mass spectrometric analysis of the less labile complex **3a** was consistent with the assigned structure.[15] The formation of allyl alkyne complexes **3** appears general for alkyl- or aryl-substituted alkynes.[16] Alkynes bearing highly electron withdrawing or donating substituents, however, do not coordinate readily: neither dimethyl acetylenedicarboxylate nor bis(trimethylsilyl)acetylene reacts cleanly with triflate complex **5** (by ^{1}H NMR spectroscopy), in each case giving a complex mixture of reaction and/or decomposition products over time.

The limitations in the range of accessible allyl alkyne complexes and the high reactivity of those that can be formed may be attributed to the balance of electronic properties required for metal–alkyne bonding. Both alkyne ligands in complexes **3** exhibit high-field ^{13}C chemical shifts, minimally perturbed from those of free alkyne, suggesting weak coordination.[17] Bonding of the alkyne to the fragment $[(C_5Me_5)Ir(\eta^3\text{-}C_3H_5)]^+$ results in close proximity of the orthogonal alkyne π orbital to a filled metal-based orbital. Such four-electron repulsive interactions have been invoked previously to rationalize both structure and reactivity of other two-electron alkyne complexes.[18] Consistent with this rationalization, complex **3b**, formed from the more electron rich butyne, is significantly more reactive than **3a**, formed from coordination of the π-acidic diphenylacetylene. While electron-withdrawing groups mitigate this four-electron repulsion, strongly electron deficient alkynes may lack sufficient donor character to coordinate effectively.

Addition of nucleophiles to allyl diphenylacetylene complex **3a** results in conversion to iridacyclobutanes without concomitant formation of products from either reductive cyclization or competitive addition to the alkyne moiety (Scheme II).[19] Thus, iridacyclobutane complexes **6a–d** are isolated in high yield on addition of propiophenone enolate, $LiAlH_4$, MeLi, and $Bu_4N^+CN^-$, respectively, as thermally stable, intensely yellow crystalline solids.[9] The spectroscopic data for complexes **6** are fully consistent with the metallacyclobutane formulation, including characteristic upfield signals for the α-hydrogen and α-carbon atoms in the ^{1}H and ^{13}C NMR spectra[2,20] and alkyne absorptions in the IR spectra. The stereochemistry of the

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

(14) ^{13}C NMR spectroscopy has not previously been used to characterize triflate coordination; however, a similar upfield ^{13}C NMR shift of the triflate resonance upon coordination to a "$(C_5Me_5)Ir$" fragment has been noted.[12a]

(15) Selected spectroscopic data for **3a**: IR (KBr, cm^{-1}) 2040 (w), 1905 (m, $\nu_{C\equiv C}$), 1265 (s, ν_{OSO}), 1220 (sh, ν_{C-F}), 1145 (s, ν_{C-F}), 1030 (s, ν_{C-F}), 635 (s, ν_{OSO}); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7 Hz, 4H, H_{Ph}), 7.52 (t, J = 8 Hz, 4H, H_{Ph}), 7.44 (t, J = 8 Hz, 2H, H_{Ph}), 4.70 (m, 1H, $H_{central}$), 4.26 (d, J = 6 Hz, 2H, H_{syn}), 1.95 (s, 15H, C_5Me_5), 1.89 (d, J = 10 Hz, 2H, H_{anti}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.7 (dt, J = 162 Hz, 8 Hz, $C_{p\text{-}Ph}$), 131.9 (dt, J = 160 Hz, 7 Hz, $C_{m\text{-}Ph}$), 129.4 (dd, J = 162 Hz, 8 Hz, $C_{o\text{-}Ph}$), 120.3 (s, C_5Me_5), 122.2 (t, J = 8 Hz, $C_{i\text{-}Ph}$), 87.1 (d, J = 169 Hz, $C_{central}$), 79.6 (s, C_2Ph_2), 49.6 (t, J = 164 Hz, $C_{terminal}$), 9.4 (q, J = 129 Hz, $C_5\mathit{Me}_5$), triflate carbon not located; MS (FAB, glycerol standard) molecular ion envelope 547.9 (7%, $M^+ + 1$), 546.8 (19%, M^+), 544.7 (41%, $M^+ - 2$), 542.7 (26%, $M^+ - 4$), $[(C_5Me_5)Ir(C_3H_5)]^+$ 368.8 (100%). Selected spectroscopic data for **3b**: IR (KBr, cm^{-1}) 2040 (w), 2010 (m, $\nu_{C\equiv C}$), 1270 (s, ν_{OSO}), 1225 (sh, ν_{C-F}), 1035 (s, ν_{C-F}), 660 (s, ν_{OSO}); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.41 (m, 1H, $H_{central}$), 3.78 (d, J = 6 Hz, 2H, H_{syn}), 2.30 (s, 6H, C_2Me_2), 1.92 (s, 15H, C_5Me_5), 1.52 (d, J = 10 Hz, 2H, H_{anti}); difference NOE, irradiation of δ 1.92 (C_5Me_5) δ 1.52 (3%, H_{syn}), 2.30 (2%, C_2Me_2), 3.78 (−1%, H_{anti}), 4.41 (11%, $H_{central}$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 120.8 (J = 319 Hz, CF_3), 100.2 (C_5Me_5), 84.4 (C_2Me_2), 65.0 (allyl $C_{central}$), 47.5 (allyl $C_{terminal}$), 9.7 ($C_2\mathit{Me}_2$), 8.7 ($C_5\mathit{Me}_5$). Additional data for complexes **3** are included as supplementary material.

(16) Addition of 4-octyne and 1-phenylpropyne to triflate complex **2** lead to products tentatively formulated as the corresponding allyl alkyne complexes on the basis of ^{1}H NMR data.

(17) Discussions of ^{13}C chemical shifts for coordinated alkynes: Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1. See also: Kowalczyk, J. J.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1991**, *10*, 1079. Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288.

(18) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585. Templeton, J. L.; Winston, P. B.; Ward, B. C. *J. Am. Chem. Soc.* **1981**, *103*, 7713. Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. Lomprey, J. R.; Selegue, J. P. *J. Am. Chem. Soc.* **1992**, *114*, 5518.

(19) Preliminary spectroscopic analysis reveals that 2-butyne complex **3b** also forms iridacyclobutanes on addition of nucleophiles; however, the metallacycles are quite reactive, complicating detailed analysis. Characterization of both reaction products and downstream reactivity will be presented in a full account.

(20) McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3388.

metallacycle β-substituents is tentatively assigned on the basis of the expected nucleophilic addition to the *exo*-allyl ligand from the face opposite the metal.[2]

The use of the inner-sphere triflate complex 5 thus enables the preparation and isolation of allyl alkyne complexes too reactive to be isolated using standard methodology. These complexes are readily diverted to iridacyclobutanes on treatment with a broad range of nucleophiles, confirming the overriding kinetic selectivity for central carbon alkylation in this series and providing a general synthesis of otherwise inaccessible alkyne iridacyclobutanes. The potential for alkyne migratory insertion in this system is currently under investigation, as is incorporating other unsaturated organic molecules into more advanced intermediates in the reductive cyclization.

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Supplementary Material Available: Text giving experimental, spectroscopic, and analytical data for complexes **2**, **3a**,**b**, **5**, and **6a–d** (7 pages). Ordering information is given on any current masthead page.

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