

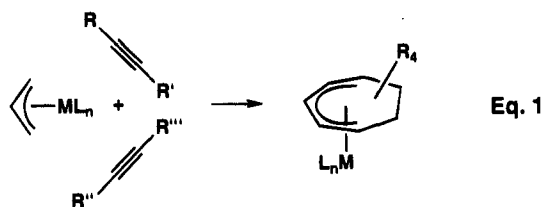
Transition Metal-Mediated [3 + 2 + 2] Allyl/Alkyne Cycloaddition Reactions. A New Reactivity Pattern for the Synthesis of Seven-Membered Carbocycles

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The investigation of transition metal-mediated allyl/alkyne coupling reactions has revealed a range of synthetically valuable¹ or potentially exploitable^{2,3} reactivity patterns. Particularly interesting are the η^3 -allyl/alkyne cyclization reactions reported by Rubeshov, assembling the η^5 -cyclopentadienyl^{3a} and η^1, η^4 -methanocyclohexadiene^{3b} ring systems by incorporation of one or two alkyne equivalents, respectively. In this communication, we report a new reactivity pattern on this energy surface: seven-membered-ring synthesis via metal-mediated [3 + 2 + 2] cycloaddition, coupling an η^3 -allyl ligand with two alkynes to yield the η^5 -cycloheptadienyl ring system (eq 1).



Treatment of η^3 -allyl 2-butyne complex **2a**, prepared as previously described or generated *in situ* from triflate complex **1**,⁴ with diphenylacetylene leads to the formation of the tetrasubstituted η^5 -cycloheptadienyl complex **3**⁵ in 56% yield,

(1) Cyclization or linear coupling of allyl and alkyne ligands. (a) Chiusoli reaction and related Ni "metalla-ene" processes: Chiusoli, G. P. *Acc. Chem. Res.* **1973**, *6*, 422. Recent references: Oppolzer, W.; Bedoya, M. Z.; Switzer, C. Y. *Tetrahedron Lett.* **1988**, *29*, 6433. Camps, F.; Coll, J.; Moreto, J. M.; Torras, J. J. *Org. Chem.* **1989**, *54*, 1969. Jenny, T. A.; Ma, L. *Tetrahedron Lett.* **1991**, *32*, 6101. Camps, F.; Llebaria, A.; Moreto, J. M.; Pages, L. *Tetrahedron Lett.* **1992**, *33*, 109, 113. Ikeda, S.; Cui, D.; Sato, Y. *J. Org. Chem.* **1994**, *59*, 6877. (b) Ni-diene/alkyne processes: Semmelhack, M. F. *Org. React. (N.Y.)* **1972**, *19*, 115. Heimback, P.; Jolly, P. W.; Wilke, G. *Adv. Organomet. Chem.* **1970**, *8*, 29. Bussemeier, B.; Jolly, P. W.; Wilke, G. *J. Am. Chem. Soc.* **1974**, *96*, 4726. (c) Pd-mediated processes: Oppolzer, W.; Bienayme, H.; Genevois-Borella, A. *J. Am. Chem. Soc.* **1991**, *113*, 9660 and references therein. Inoue, Y.; Ohuchi, K.; Kawamata, T.; Ishiyama, J.-I.; Imaizumi, S. *Chem. Lett.* **1991**, 835. Benn, R.; Jolly, P. W.; Mynott, R.; Raspel, B.; Schencker, G.; Schick, K.-P.; Schroth, G. *Organometallics* **1985**, *4*, 1945. (d) Dipolar additions of alkynes with η^1 -allyl complexes: Welker, M. E. *Chem. Rev.* **1992**, *92*, 97. See also: Williams, J. P.; Wojcicki, A. *Inorg. Chem.* **1977**, *16*, 3116. Abram, T. S.; Baker, R.; Exon, C. M.; Rao, V. B. *J. Chem. Soc., Perkin Trans. 1* **1982**, 285. Baker, R.; Exon, C. M.; Rao, V. B.; Turner, R. W. *J. Chem. Soc., Perkin Trans. 1* **1982**, 295. (e) Ru-mediated alkyne/olefin coupling: Trost, B. M.; Indolese, A. *J. Am. Chem. Soc.* **1993**, *115*, 4361.

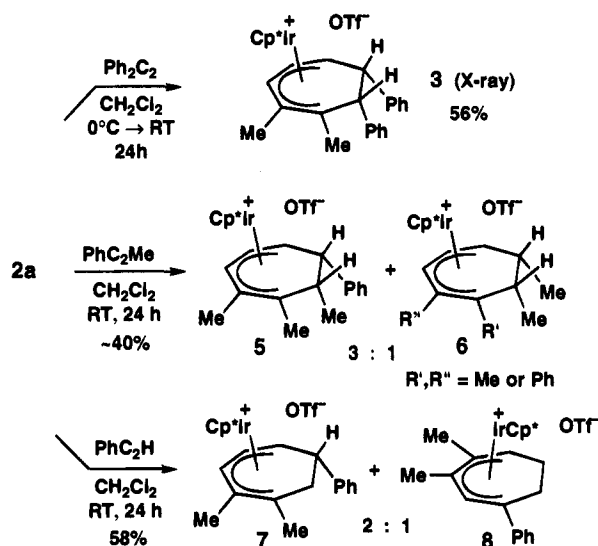
(2) Fundamental studies. (a) Pd: Appleton, T. G.; Clark, H. C.; Poller, R. C.; Puddephatt, R. J. *J. Organomet. Chem.* **1972**, *39*, C13. (b) Co: Greco, A.; Green, M.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 3476. Bottrill, M.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 292. (c) Ir: Green, M.; Taylor, S. H. *J. Chem. Soc., Dalton Trans.* **1975**, 1142. (d) Ru: Sbrana, G.; Brac, G.; Benedetti, E. *J. Chem. Soc., Dalton Trans.* **1975**, 754. (e) Mo: Davidson, J. L.; Green, M.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2044. (f) Re: Fischer, R. A.; Herrmann, W. A. *J. Organomet. Chem.* **1989**, *377*, 275. (g) Cr: Betz, P.; Jolly, P. W.; Kruger, C.; Zakrzewski, U. *Organometallics* **1991**, *10*, 3525.

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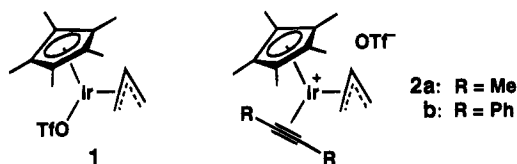
(4) Schwiebert, K. E.; Stryker, J. M. *Organometallics* **1993**, *12*, 600.

(5) Complete experimental, spectroscopic, and analytical data, including tables of comparative ¹H and ¹³C NMR spectroscopic data (Table 1, complexes **3**, **5**, **7**; Table 2, complexes **8**, **9**, **11**), are provided as supporting information.

Scheme 1



as determined by ¹H NMR integration against an internal standard (Scheme 1). Complex **3** was isolated by crystallization



from THF/Et₂O and the structure deduced from extensive one- and two-dimensional ¹H-NMR and ¹³C-NMR spectroscopy.⁵ Confirmation of this structural assignment was obtained by X-ray crystallography,⁶ providing an unambiguous basis for comparative analysis of other adducts in this series. Optimal reaction conditions require the use of excess alkyne (~3 equiv), although byproduct formation appears to arise largely from competitive dissociation of the labile 2-butyne.⁴ Lower reaction temperature leads to the formation of Cp*Ir(η^5 -C₃H₃Me₂)⁺OTf⁻ (**4**)⁴ (Cp* = η^5 -C₅Me₅) as a minor byproduct, from incorporation of only one alkyne unit.⁷ The η^5 -cycloheptadienyl complex **3** is also formed on treatment of allyl diphenylacetylene complex **2b** with excess 2-butyne, although the yield is lower and the crude product less clean.

The reaction of complex **2a** with an unsymmetrical or terminal alkyne⁸ similarly produces the η^5 -cycloheptadienyl ring system, isolated as an isomeric mixture in modest yield (Scheme 1). The major product **5** from the reaction with 1-phenylpropyne was recrystallized to analytical purity, revealing spectroscopic data closely analogous to those obtained for complex **3**; the minor isomer **6** could not be obtained in pure form and is assigned only tentatively.⁵ Treatment with phenylacetylene affords a 2:1 mixture of η^5 -cycloheptadienyl isomers **7** and **8**, which cocrystallize in analytical purity as a 1:1 mixture. The marginally less soluble isomer **8** was obtained in pure form by repeated fractional recrystallization; structural assignment of the major product **7**⁵ was based on close spectroscopic analogy to

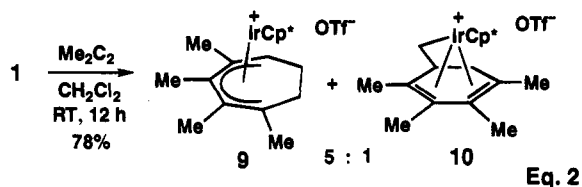
(6) The crystal structure determination was performed by Drs. K. Folting and J. D. Martin of the Indiana University Molecular Structure Center, Department of Chemistry, Bloomington, IN 47405. A description of the structure solution, along with an ORTEP diagram and selected bond lengths and angles, are provided as supporting information. Full details are available directly from the structure center: request report No. 92039.

(7) This complex is the only product isolated when complex **2** is allowed to stand in CH₂Cl₂ at room temperature in the absence of added alkyne.⁴

(8) Terminal alkynes can be incorporated only as the second alkyne component: no tractable product is isolated from treatment of triflate complex **1** with phenylacetylene (1–5 equiv).

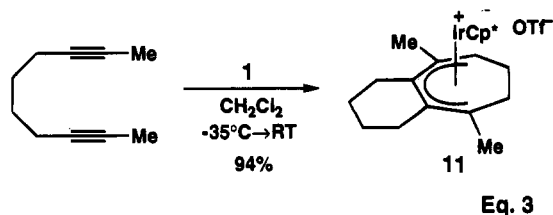
complexes **3** and **5**.⁵ The common substitution pattern defined for complexes **7** and **8** reveals that the alkyne insertion is highly regioselective, but the subsequent hydrogen redistribution is less so. No interconversion of isomers is observed at temperatures up to 110 °C, suggesting that the product distribution results from a kinetic partitioning.

Higher yielding [3 + 2 + 2] cycloadditions are obtained directly from triflate complex **1**, minimizing the complications associated with alkyne lability. The reaction with 2-butyne (~10 equiv) leads to an inseparable 5:1 mixture of two products, isolated as a colorless solid in 78% yield (eq 2).⁹ The structure



of the major product, η^5 -cycloheptadienyl complex **9**,⁵ was assigned on the basis of NMR spectroscopic analysis, yielding data analogous to those obtained for phenylacetylene adduct **8**. The minor product is tentatively assigned as the η^1, η^4 -methanocyclohexadiene complex **10**⁵ on the basis of spectroscopic data and comparison to previously reported complexes of this structural class.^{3b} Minor amounts of η^5 -cyclopentadienyl complex **4**⁴ are observed upon significant reduction in alkyne concentration (3 equiv). Treatment of triflate complex **1** with excess diphenylacetylene, however, leads exclusively to incorporation of a single alkyne, giving the known η^5 -cyclopentadienyl complex, $\text{Cp}^*\text{Ir}(\eta^5\text{-C}_5\text{H}_3\text{Ph}_2)^+\text{OTf}^-$.⁴

The reaction of triflate complex **1** with 2,8-decadiyne also yields the η^5 -cycloheptadienyl ring system, demonstrating the potential for polycyclization reactions based on this reactivity pattern. Despite concern over the regioselectivity of the initial



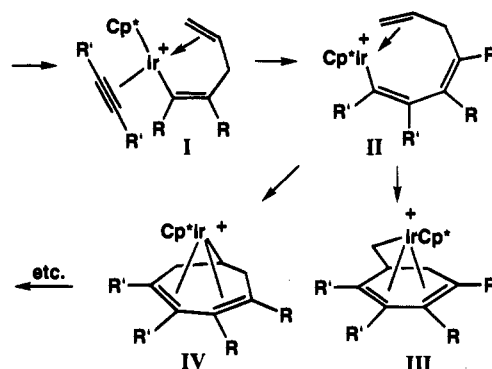
alkyne insertion, fused-bicyclic complex **11**⁵ is obtained as a spectroscopically homogeneous white solid in high yield using only a slight excess (1.3 equiv) of the diyne (eq 3). Although this material could not be recrystallized to analytical purity, the structural assignment, by extensive NMR spectroscopic analysis, is nonetheless unambiguous.⁵

This unique three-component cycloaddition reaction proceeds via initial coupling of the allyl and alkyne ligands, producing an unsaturated σ, π -vinyl olefin complex,¹⁰ as previously proposed.³ Coordination and insertion of the second alkyne (Scheme 2, **I** \rightarrow **II**) sets the stage for the regioselective migratory insertion that partitions the reaction between η^1, η^4 -methano-

(9) Recrystallizations from various solvent systems retain both complexes in an invariant ratio.

(10) This intermediate, analogous to **I** (Scheme 2) but lacking the alkyne, can be trapped and isolated upon addition of phosphine or CO. Details will be presented in a full account.

Scheme 2



cyclohexadiene and η^1, η^4 -cycloheptadienyl ring systems **III** and **IV**, respectively. Subsequent rearrangement of **IV** to the conjugated η^5 -cycloheptadienyl product(s) then occurs via a series of β -hydride elimination/reinsertion reactions, presumably directed by the steric and/or electronic profile of the peripheral substituents. *The regioselectivity of the critical vinyl migration thus appears to be controlled by the character of the ancillary ligand:* the sterically large, electron-rich $\eta^5\text{-C}_5\text{Me}_5$ used in this work compared to the small, less electron-donating $\eta^5\text{-C}_5\text{H}_5$ or $\eta^6\text{-benzene}$ ligands used by Rubezhov.³

The origin and extent of this ancillary ligand directing effect is currently under investigation, as is the development of alternative metal templates holding greater potential for applications to organic synthesis, where metal-mediated methodology for seven-membered-ring synthesis remains comparatively rare.^{11,12}

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Supporting Information Available: Experimental procedures and complete spectroscopic data for all new compounds and details of the crystal structure determination, diagrams, and selected bond lengths and angles for complex **3** (33 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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