Carbon−Carbon Bond Activation by Electrophilic Complexes of Cobalt: Anomalous [3 + 2 + 2] Allyl/Alkyne Cycloaddition Reactions and [5 + 2] Cyclopentenyl/Alkyne Insertion−Ring Expansion Reactions

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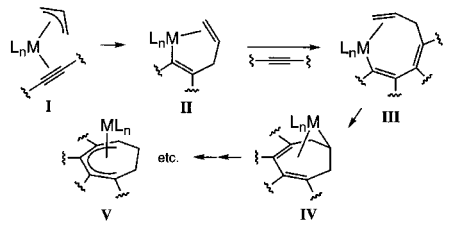
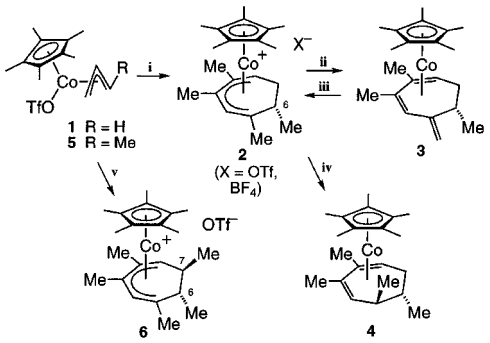
Carbon−carbon bond activation is mediated by transition metals in a range of contexts.[2,3] Many take advantage of an unsaturated electrophilic metal center, where the electron deficiency promotes β-alkyl elimination type reactions.[4,5] In this contribution, we report an unprecedented class of carbon−carbon bond activation reactions, using an electrophilic late transition metal to induce the ring-opening of coordinated cyclopentenyl rings, including some derived in situ from simple η^5-cyclopentadienyl ligands. The ring cleavage is integrated into "anomalous" [3 + 2 + 2] allyl/alkyne cycloaddition reactions, which lead to the formation of η^5-cycloheptadienyl complexes bearing substitution patterns different from those obtained from "normal" allyl/alkyne cycloaddition.[6] The net transformation of an unstrained five-membered ring into a seven-membered ring by selective alkyne insertion provides a conceptual model for the development of novel metal-mediated ring expansion reactions.

Allyl/alkyne [3 + 2 + 2] cycloadditions produce η^5-cycloheptadienyl complexes in both the pentamethylcyclopentadienyl iridium and cobalt series.[6] The substitution patterns obtained from these reactions are best rationalized on the basis of the mechanistic outline presented in Scheme 1. Thus, sequential alkyne insertions (**I** → **III**) occur prior to cyclization (**III** → **IV**), providing η^5-cycloheptadienyl derivatives in which the alkyne-derived substituents are located on contiguous positions.[7] It was, therefore, perplexing to obtain the *non-contiguously substituted* η^5-cycloheptadienyl complexes **2** and **6** from the reactions of η^3-allyl and η^3-crotyl complexes **1** and **5**, respectively, with 2-butyne (Scheme 2).[8] Compounds **2** and **6** were obtained in high yield[9] and unambiguously characterized by two-dimensional NMR spectroscopy and by the characterization of derivatives **3** and **4** prepared by deprotonation and hydride addition (Scheme 2).[8,10]

Scheme 1

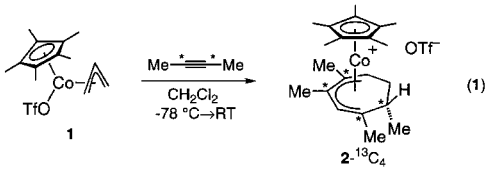


Scheme 2[a]



[a] Conditions: i. (R = H) 2-butyne (xs), CH_2Cl_2, −78 °C → RT, 12 h, 81%; ii. NaH, THF, RT, 10h, 77%; iii. $HBF_4{\cdot}Et_2O$, Et_2O, RT, 99%; iv. $LiEt_3BH$, THF, −78 °C → RT, 10 h, 53%; v. (R = Me) 2-butyne (xs), CF_3CH_2OH, 55 °C, 7 h, 78%.

Two rearrangement processes can be proposed to rationalize the observed products: (i) specific migration of methyl substituents along the ring periphery or (ii) skeletal reorganization of the carbon framework, either prior to or after cyclization. Neither of these proposals connotes any mechanistic detail and neither is readily accommodated by standard mechanistic arguments. The reaction using doubly ^{13}C-labeled 2-butyne,[8,11] however, yields quadruply labeled η^5-tetramethylcycloheptadienyl complex **2**-$^{13}C_4$ (eq 1),[8] demonstrating that the methyl substituents remain bonded to the alkyne carbon atoms throughout the reaction.



The skeletal rearrangement can be suppressed by subtle changes in alkyne reactivity: the reaction of complex **1** with cyclooctyne yields exclusively the "normal" 1,2,3,4-tetrasubstituted tricyclic η^5-cycloheptadienyl complex **7** in 84% yield.[8,12] The reactions of less-substituted cyclopentadienyl templates, in contrast, provide even more unusual products (Scheme 3). While η^3-crotyl complexes **8** and **9** both deliver straightforward [3 + 2 + 2] cycloadducts **10**[8] and **11**,[8] the η^3-allyl complexes **12** and **13**

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(2) Reviews: Herrmann, W. A.; Cornils, B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1048. Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

(3) Additional references are provided in the Supporting Information.

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(5) Electrophilic late metal examples: (a) Terheijden, J.; van Koten, G.; Vinke, I. C.; Spek, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 2891. (b) Nicholls, J. C.; Spencer, J. L. *Organometallics* **1994**, *13*, 1781. Cracknell, R. B.; Nicholls, J. C.; Spencer, J. L. *Organometallics* **1996**, *15*, 446.

(6) (a) Etkin, N.; Dzwiniel, T. L.; Schwiebert, K. E.; Stryker, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 9702. (b) Schwiebert, K. E.; Stryker, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 8275.

(7) The exact position of the substituents is dependent on the nature of the alkyne and the series of β-hydride elimination and reinsertion reactions that provide the final product.[6]

(8) Experimental details and complete spectroscopic and analytical data are provided as Supporting Information.

(9) Both complexes **2** and **6** are obtained from reactions conducted in either dichloromethane or trifluoroethanol; Scheme 2 reports optimal procedures.

(10) The 6-*exo* stereochemistry was established by spectroscopic comparison to the known 6-*endo*-methyl-η^5-cycloheptadienyl complexes,[6a] together with unambiguous assignments extracted from correlated spectroscopy.[8]

(11) Gaseous 2,3-$^{13}C_2$-2-butyne was prepared by alkylation of doubly ^{13}C-labeled Li_2C_2 using dimethylsulfate in HMPA. Complete experimental details are provided.[8]

(12) The reaction of complex **1** with excess diphenylacetylene or 4,4-dimethyl-2-pentyne leads to exclusive incorporation of a *single* alkyne, providing η^5-cyclopentadienyl products by [3 + 2] cycloaddition.[13]

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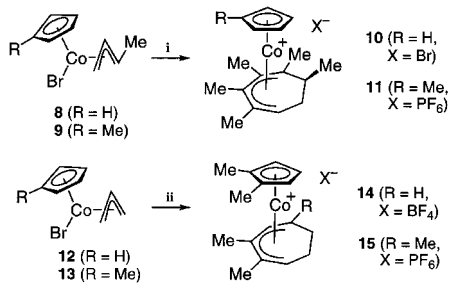
Scheme 3[a]

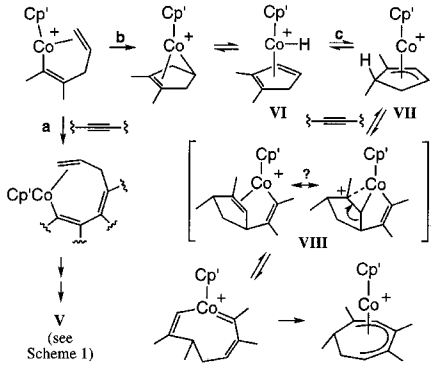


[a] Conditions: i. R = H: 2-butyne (xs), CF_3CH_2OH, 60 °C, 12 h, 54%; R = Me: same as for R = H, but followed by KPF_6, H_2O, 39%. ii. R = H: 2-butyne (xs), $AgBF_4$, acetone, −78 °C → RT, 12 h, 6%; R = Me: 2-butyne (xs), CF_3CH_2OH, 55 °C, 7h; then KPF_6, 43%.

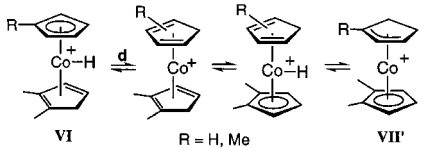
provide *η*^{5}*-dimethylcyclopentadienyl* complexes **14**[8] and **15**[8] containing *η*^{5}*-cycloheptadienyl ring systems derived from ring expansion of the original η*^{5}*-cyclopentadienyl and η*^{5}*-methylcyclopentadienyl ancillary ligands*![14] Two mechanistic features can be deduced from these unexpected but illuminating results: (i) cyclization of the vinyl olefin intermediate (cf., **II**) can be faster than incorporation of the second alkyne[12,15] *even in reactions that give cycloheptadienyl products*, and (ii) electrophilic cobalt(III) is capable of activating carbon−carbon bonds in coordinated five-membered rings under very mild conditions.[16] Thus, the allyl and one alkyne cyclize to form the dimethylcyclopentadienyl ligands in complexes **14** and **15**, transferring two hydrogen atoms to the original cyclopentadienyl ring, which then undergoes alkyne insertion and carbon−carbon bond cleavage.

An integrated mechanistic hypothesis consistent with these results can be constructed. At the vinyl olefin stage (Scheme 4), an initial kinetic partition selects between [3 + 2 + 2] cycloaddition (path **a**) and [3 + 2] cyclization to form a *η*^{1},*η*^{2}-cyclopentenyl ligand (path **b**). After *β*-hydride elimination along the latter pathway, a second kinetic partition determines whether the new cyclopentenyl ligand or the "ancillary" cyclopentadienyl ligand transforms into the *η*^{5}-cycloheptadienyl ring. Reinsertion of the hydride (path **c**) leads to *η*^{3}-cyclopentenyl intermediate **VII**.[17] Alternatively, migration of the hydride to the *η*^{5}-cyclopentadienyl ligand (path **d**, Scheme 5) provides a bis(*η*^{4}-diene) intermediate that equilibrates to the transposed *η*^{3}-cyclopentenyl complex **VII′**. Both *η*^{3}-cyclopentenyl intermediates react with alkyne to form *η*^{5}-cycloheptadienyl products, as illustrated for complex **VII** (Scheme 4). This transformation, we propose,

Scheme 4



Scheme 5



proceeds via alkyne insertion, providing a second vinyl olefin intermediate **VIII**, which undergoes activation of the carbon−carbon bond adjacent to the coordinated olefin. The *η*^{5}-cycloheptadienyl product then results from a 1,2-migration of the vinyl ligand.[18] The strongly electrophilic cobalt center and the constrained geometry of complex **VIII** may act in concert to promote carbon−carbon bond activation, perhaps by distorting the olefin coordination toward the illustrated carbocationic canonical. Scission of the proximal *β*-carbon bond then benefits from stabilization of the incipient carbocation by electron donation from the metal. The selective cleavage of the less substituted cyclopentenyl ring suggests that **VII** (Cp′ = C_5H_5, MeC_5H_4) and **VII′** equilibrate completely, with the cleavage controlled by the relative rates of alkyne insertion.

Consistent with this proposal, the sterically crowded pentamethylcyclopentadienyl vinyl olefin intermediates undergo cyclization faster than alkyne insertion; however, the permethylated ring resists disruption and the reaction proceeds along pathway **c**. In the sterically more accessible cyclopentadienyl and methylcyclopentadienyl series, the terminal methyl substituent present in the crotyl-derived vinyl olefin complex inhibits initial cyclization, leading to selective formation of normal [3 + 2 + 2] cycloadducts. The use of terminal[7b] or highly reactive alkynes also favors sequential double insertion. It is nonetheless remarkable that all three pathways lead to *η*^{5}-cycloheptadienyl products, via two mechanistically distinct processes: [3 + 2 + 2] cycloaddition and [5 + 2] ring expansion. The latter can perhaps be cast as a metal-induced Wagner−Meerwein rearrangement, in which the electron-deficient metal weakens the carbocyclic framework and directs subsequent transformations. Detailed mechanistic and synthetic investigations are in progress.

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Supporting Information Available: Experimental procedures and complete spectroscopic and analytical data for all new compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) The conversion of either complex **12** or the corresponding triflate complex[8] to **14** proceeds in low yield regardless of conditions.

(15) The selective formation of five-membered ring products even in the presence of excess alkyne has also been noted for ruthenium-mediated allyl/alkyne cycloadditions using sterically large alkynes[13d] and for cobalt-mediated reactions conducted in a coordinating solvent.[6a,13c]

(16) Spencer[5b] has established that a related agostic *η*^{3}-cyclopentenyl complex of cobalt undergoes ring-opening to an acyclic *η*^{5}-pentadienyl complex at elevated temperature. No trace of acyclic *η*^{5}-pentadienyl products are observed in the present system, even under conditions of alkyne deficiency.

(17) Unsaturated *η*^{3}-cyclopentenyl intermediates **VII** and **VII′** are almost certainly stabilized by agostic C−H interactions.[5b]

(18) Alkyl/alkylidene 1,2-migration: Casty, G. L.; Stryker, J. M. *Organometallics* **1997**, *16*, 3083 and references therein.