J|A|C|S COMMUNICATIONS

Published on Web 09/23/2005

Unprecedented Coordination Modes and Demetalation Pathways for Unbridged Polyenyl Ligands. Ruthenium η^1,η^4-Cycloheptadienyl Complexes from Allyl/Alkyne Cycloaddition

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Metal-mediated cycloaddition reactions provide a range of cyclic polyenyl ligands coordinated to transition metals. The coordination mode adopted by such ligands determines to a considerable extent the strategies available for subsequent elaboration and demetalation of the organic moiety. For the most part, cyclic polyenyl ligands unconstrained by bridged structures adopt fully conjugated coordination modes, typically as a direct consequence of thermodynamic preferences. New coordination modes and, in particular, *less* conjugated coordination modes raise new possibilities for post-cyclization functionalization and demetalation pathways, both essential to the development of synthetically valuable transformations.

All unbridged cycloheptadienyl complexes of the transition metals exhibit fully conjugated η^5-coordination.[1−5] Transient formation of η^1,η^4-coordinated intermediates has been proposed for cobalt- and iridium-mediated allyl/alkyne [3 + 2 + 2] cycloaddition reactions,[4−6] but no evidence to support this conjecture has been obtained. Here, however, we report the selective formation of unprecedented η^1,η^4-cycloheptadienyl complexes from ruthenium-mediated allyl/alkyne cycloaddition. The unique coordination mode promotes unique oxidative demetalation pathways, leading to the efficient construction of synthetically valuable seven-membered carbocycles.

To induce ruthenium to mediate seven-membered ring formation over cyclization to the kinetically favored six-membered ring, the ancillary η^6-benzene ligand used in previous investigations[7] was replaced with the sterically larger η^6-hexamethylbenzene ligand. In the event, treatment of allyl complex **1a**[8] with excess ethyne leads to the clean formation of two inseparable cycloaddition products, strongly favoring seven- over six-membered ring formation (Scheme 1).[9] The major product was identified as the unexpected *symmetric* η^1,η^4-cycloheptadienyl complex **2** by two-dimensional NMR spectroscopy.[10] The resonance for the unique σ-bonded methine appears characteristically shifted upfield in both ^{1}H NMR (δ −0.09) and ^{13}C NMR (δ −38.1) spectra.

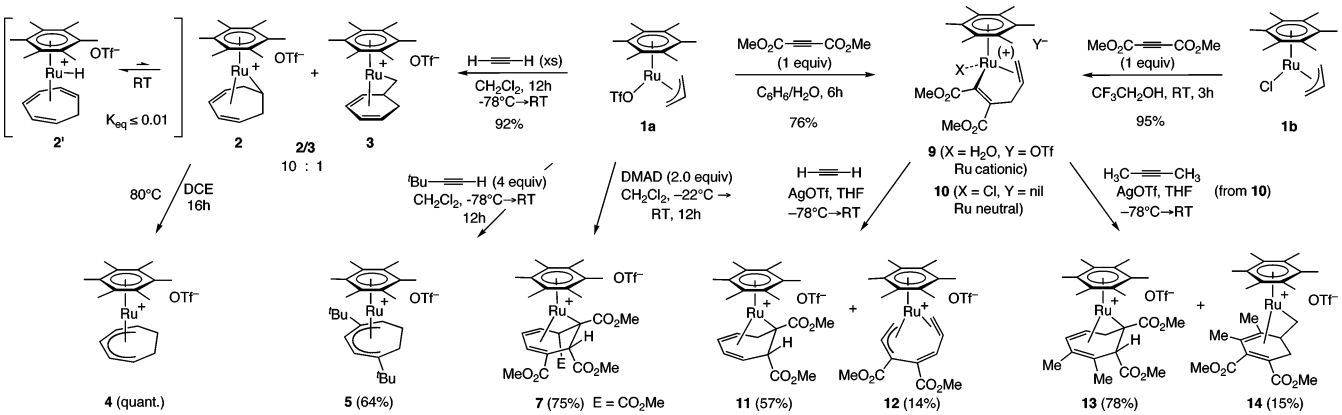
Surprisingly, complex **2** is both indefinitely stable *and* fluxional at room temperature, as established by double irradiation experiments,[9] rapidly equilibrating with the otherwise undetected cycloheptatriene hydride complex **2′**. At 80 °C, however, slow isomerization occurs to give the more thermodynamically stable η^5-coordinated isomer **4**.[9,11] The formation and subsequent isomerization of the η^1,η^4-complex **2** strongly supports prior mechanistic proposals rationalizing η^5-cycloheptadienyl ring formation in the cobalt and iridium series.[4a,b]

A lower activation barrier for η^1,η^4- to η^5-isomerization is apparent in the reaction of *tert*-butylacetylene, which proceeds directly to η^5-cycloheptadienyl complex **5**[9,12] even under mild reaction conditions. No η^1,η^4-coordinated isomer is detected in the crude reaction mixture. Among several minor products, the simple acyclic 1-*tert*-butyl-η^5-pentadienyl complex **6**[9] (∼4%, not shown) can be isolated by chromatography.

Although some reactions of complex **1a** with alkynes are complicated,[13] treatment with dimethylacetylene dicarboxylate (DMAD) provides η^1,η^4-cycloheptadienyl complex **7** free from significant byproducts.[9,14] The substituent array in complex **7** can arise only by extensive isomerization of the initial η^1,η^4-cycloheptadienyl intermediate, presumably via iterative β-hydride elimination and reinsertion (Scheme 2). Notably, the system reacts *with perfect fidelity for migration to η^1,η^4-coordination rather than fully conjugated η^5-hapticity*. No further reaction is induced upon heating, strongly suggesting that the η^1,η^4-coordination mode is thermodynamically favored.

The electron-deficient alkyne also allows for cycloaddition reactions incorporating two different alkynes. Unique among alkynes,[8] treatment of complex **1a** with 1 equiv of DMAD leads to exclusive formation of the *acyclic* adduct, [(C_6Me_6)Ru(1,2-*syn*-dicarbomethoxypentadienyl)]OTf **8** (90%, not shown).[9] In wet benzene, however, the reaction stops at the η^1,η^2-vinyl olefin intermediate, providing cationic aquo complex **9** (Scheme 1).[9] This

Scheme 1



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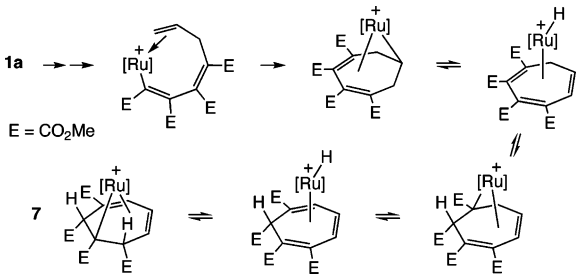
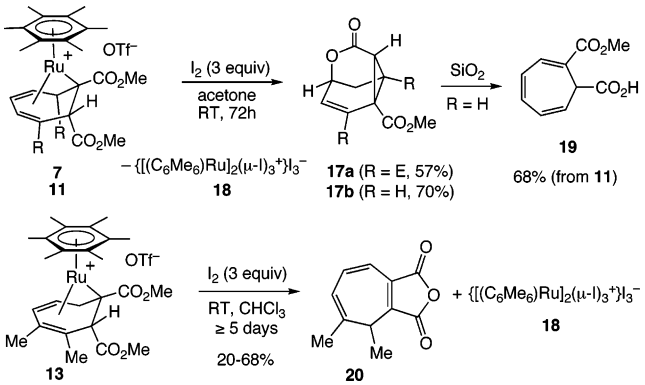
Scheme 2



Scheme 3



complex converts slowly and quantitatively at room temperature to η^5-pentadienyl complex **8**. Similarly, solvolysis of allyl chloride complex **1b**[15] in trifluoroethanol containing DMAD gives the analogous but neutral vinyl olefin complex **10** in near quantitative yield.[9]

Complexes **9** and **10** transform selectively to η^1,η^4-cycloadducts on treatment with a second alkyne. Optimal yields and selectivity are obtained from neutral complex **10** under conditions of assisted ionization, providing η^1,η^4-cycloheptadienyl complexes **11** and **13** from the reactions of ethyne and 2-butyne, respectively (Scheme 1).[9,16] Structurally distinct minor products are isolated from each reaction, including the unusual *acyclic* η^3,η^2-heptadienyl complex **12**, which presumably arises from allylic C−H bond activation following migratory insertion of ethyne. Structural assignments for complexes **12**, **13**, and **14** have been confirmed by X-ray crystallography.[9]

The unique coordination of the η^1,η^4-cycloheptadienyl ring suggested the use of oxidative bond heterolysis as a novel demetalation strategy, simultaneously effecting both scission of the metal−carbon σ-bond and minimization of metal−diene backbonding.[17] In the event, exhaustive iodinolysis indeed mediates the decomplexation of cycloadducts **7** and **11**, returning the unusual tricyclic lactones **17** in moderate to good yields (Scheme 3).[9,18] The Ru(III) coproduct was identified crystallographically as triiodide salt **18**,[9] accounting for the unexpected stoichiometry in iodine. Direct chromatography of the crude reaction mixture without thiosulfate workup unmasks the latent seven-membered ring, providing cycloheptatriene **19** exclusively.[9,19] Iodinolysis of complex **13** leads directly to cycloheptatriene anhydride **20** in as yet variable yields,[9] a bicyclic ring system of considerable synthetic interest.[20]

The use of stoichiometric (but recyclable) ruthenium obviously limits the potential use of this cycloaddition reaction in organic synthesis. Nonetheless, the strong preference for η^1,η^4-coordination of the seven-membered ring is unique in transition metal chemistry, offering mechanistic insight and raising new opportunities for developing synthetically valuable metal-mediated cycloaddition and demetalation reactions.

Acknowledgment. Financial support from NSERC and the University of Alberta is gratefully acknowledged. R.M. is affiliated with the Department of Chemistry X-ray Crystallography Laboratory.

Supporting Information Available: Experimental procedures and complete characterization data for all new compounds; details of the X-ray crystallography for complexes **12**−**14** and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) See, for example: (a) Salzer, A.; Werner, H. *J. Organomet. Chem.* **1975**, *87*, 101−108. (b) Bennett, M. A.; Matheson, T. W. *J. Organomet. Chem.* **1978**, *153*, C25−27. (c) Salzer, A.; Bigler, P. *Inorg. Chim. Acta* **1981**, *48*, 199−203. (d) Williams, G. M.; Fisher, R. A.; Heyn, R. H. *Organometallics* **1986**, *5*, 818−819. (e) Chen, W.; Sheridan, J. B.; Cote, M. L.; Lalancette, R. A. *Organometallics* **1996**, *15*, 2700−2706 and references therein.

(2) Nonconjugated pentahapticity (invariably as η^2,η^3-coordination) occurs more commonly in larger rings with greater coordination strain and/or conformational barriers: (a) Lewis, J.; Parkins, A. W. *J. Chem. Soc. (A)* **1969**, 953−957. (b) Bennett, M. A.; Matheson, T. W.; Robertson, G. B.; Smith, A. K.; Tucker, P. A. *Inorg. Chem.* **1981**, *20*, 2353−2365. (c) Itoh, K.; Nagashima, H.; Ohshima, T.; Oshima, N.; Nishiyama, H. *J. Organomet. Chem.* **1984**, *272*, 179−188 and references therein.

(3) An early claim[2a] that protonation of $(C_5H_5)Co(\eta^4$-cycloheptatriene) provides $(C_5H_5)Co(\eta^2,\eta^3$-cycloheptadienyl$)^+$ is not supported by spectroscopic data and remains unsubstantiated. The isolated product of this reaction was subsequently identified as the expected η^5-cycloheptadienyl complex.[1c]

(4) (a) Schwiebert, K. E.; Stryker, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 8275−8276. (b) Etkin, N.; Dzwiniel, T. L.; Schwiebert, K. E.; Stryker, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 9702−9703. (c) Dzwiniel, T. L.; Etkin, N.; Stryker, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 10640−10641. (d) From cyclopentenyl ring expansion: Dzwiniel, T. L.; Stryker, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 9184−9185.

(5) Mn/η^3-allyl/α,ω-diyne: (a) Tang, J.; Shinokubo, H.; Oshima, K. *Organometallics* **1998**, *17*, 290−292. (b) Nishikawa, T.; Kakiya, H.; Shinokubo, H.; Oshima, K. *J. Am. Chem. Soc.* **2001**, *123*, 4629−4630.

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(7) (a) Lutsenko, Z. L.; Aleksandrov, G. G.; Petrovskii, P. V.; Shubina, E. S.; Andrianov, V. G.; Struchkov, Y. T.; Rubezhov, A. Z. *J. Organomet. Chem.* **1985**, *281*, 349−364. (b) Lutsenko, Z. L.; Petrovskii, P.; Bezrukova, A.; Rubezhov, A. Z. *Bull. Acad. Sci. USSR* **1988**, 735−738.

(8) Older, C. M.; Stryker, J. M. *Organometallics* **1998**, *17*, 5596−5598.

(9) Complete experimental details are provided as Supporting Information.

(10) The minor product **3** is spectroscopically very similar to Rubezhov's $[(C_6H_6)Ru(2,3,4,5$-tetramethyl-1-methanocyclohexadiene$)]^+PF_6^-$ complex.[7b]

(11) Complex **4** is spectroscopically identical to the known PF_6^- salt.[2c]

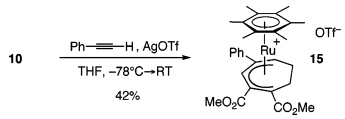
(12) The substitution pattern for η^5-cycloheptadienyl complex **5** is identical to that obtained from $(C_5Me_5)Co$(allyl)OTf and 3,3-dimethyl-1-butyne.[4b]

(13) Phenylacetylene undergoes oligomerization rather than cyclization. Disubstituted alkynes undergo exclusive [3 + 2] cycloaddition with concomitant demethylation of the hexamethylbenzene ligand.[8] Reactions involving 2-butyne (≥2 equiv) diverge substantially and will be discussed elsewhere.

(14) Neither the cobalt nor the iridium system reacts with DMAD. No tractable product was obtained from the reaction of DMAD with $(C_6H_6)Ru(allyl)^+$.[7]

(15) Bennett, M. A.; Huang, T.-N.; Turney, T. W. *J. Chem. Soc., Chem. Commun.* **1979**, 312−313.

(16) That η^1,η^4-complexes **7**, **11**, and **13** face no significant kinetic barrier to conjugation is strongly suggested by the isolation of η^5-cycloheptadienyl complex **15** in modest yield (42%) as the major among many products obtained from the reaction of complex **10** with phenylacetylene:[9]



(17) This demetalation strategy fails in the cobalt η^5-cycloheptadienyl series.

(18) This extensive transformation presumably involves intramolecular iodolactonization/iodide elimination, with concomitant iodide-mediated ester demethylation. Related, *completely* organic, transformations are known: Garratt, D. G.; Ryan, M. D.; Beaulieu, P. L. *J. Org. Chem.* **1980**, *45*, 839−845.

(19) This process nominally involves lactone elimination followed, presumably, by cycloreversion driven by norcaradiene/cycloheptatriene equilibration.

(20) See, for example: (a) Tanino, K.; Shimizu, T.; Miyama, M.; Kuwajima, I. *J. Am. Chem. Soc.* **2000**, *122*, 6116−6117. (b) Wockenfufl, B.; Wolff, C.; Tochtermann, W. *Tetrahedron* **1997**, *53*, 13703−13708. (c) Bowden, S. L.; Harris, S. A.; Heller, H. G.; Hewlins, M. J. E. *J. Chem. Soc., Perkin Trans. 1* **1992**, 725−728. (d) Rainer, H. Ugi, I. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 594−596.

JA0556023