Communication

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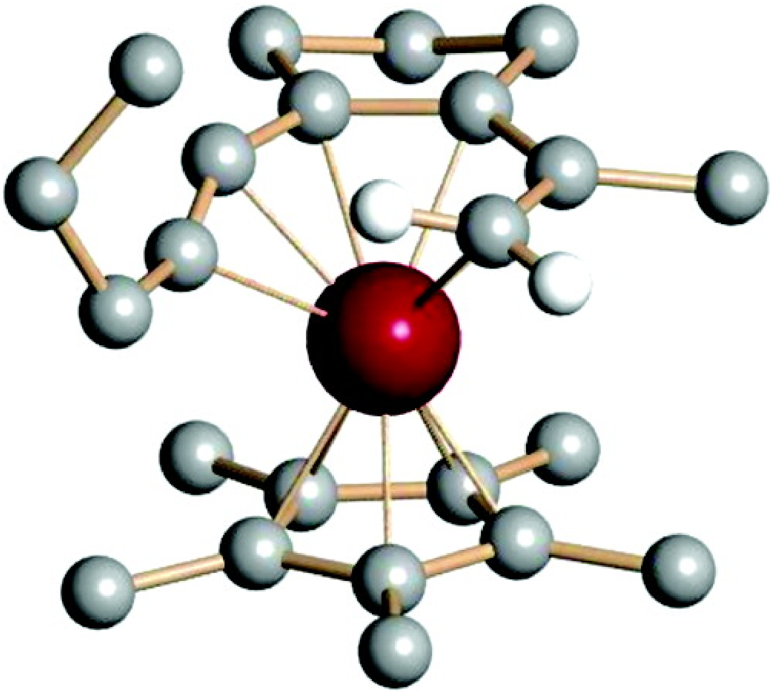

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An η^6-Dienyne Transition-Metal Complex

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Transition-metal η^4-diene and η^6-triene complexes play an important role in the chemistry of unsaturated hydrocarbons.[1] In contrast, only one η^4-1,3-enyne complex (**I**) has been claimed,[2] and there have been no examples of η^6-coordination to conjugated dienynes (**II**; Chart 1).

We previously reported that [(η^5-C_5Me_5)Ru(CH_3CN)$_3$]X (**1**-*Cp**, X = OTf, PF_6) triggers the room temperature cycloaromatization of enediynes (**2**) in THF-d_8 to give ruthenium−arenes **3**-d_2 (Scheme 1).[3] In addition, a single example was described in which **1**-*Cp** mediated the cycloisomerization of dienyne **4**-*H* to arene complex **5**.[3b] Mechanistic considerations for these cycloaromatization reactions raise a fundamental question as to the feasibility of η^6-coordination to conjugated enediynes and dienynes. Investigations into the scope and mechanism of the latter process have now led to the spectroscopic observation and structural characterization of the first η^6-dienyne complexes.

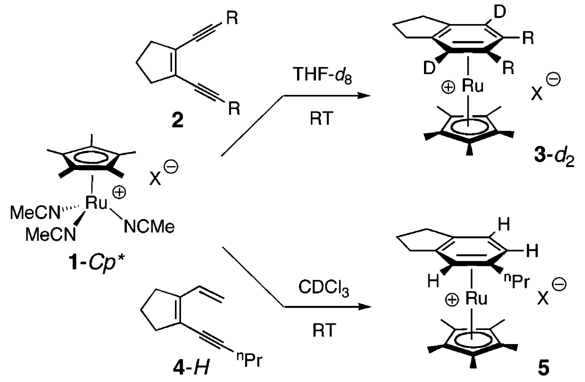
The well-established synthetic utility of CpRu(η^6-chloroarene)$^+$ complexes for the preparation of diaryl ethers[4] led us to examine the reactions of **1** with electron-deficient dienynes **6** (Scheme 2). When a $CDCl_3$ solution containing **6**-*E* (0.013 mmol) and **1**-*Cp* (0.019 mmol)[5] was monitored by ^1H NMR spectroscopy, the η^6-chloroarene complex **7**-*Cp* was cleanly formed in 95% yield over the course of 5 h.[6] There was no direct evidence for the formation of intermediates. A pronounced stereochemical preference for cycloisomerization was observed when a similar reaction was carried out with **6**-*Z* as the dienyne substrate. Addition of **1**-*Cp* (0.016 mmol) to a $CDCl_3$ solution of **6**-*Z* (0.016 mmol) rapidly (15 min) led to a mixture of **6**-*E* (~15%), **7**-*Cp* (25%), and unidentified decomposition products.[7] After 2 h, reaction was complete and **7**-*Cp* had formed in 50% yield.

In an effort to stabilize and observe reactive intermediates, the reaction of **6** with the more electron-rich ruthenium cation, **1**-*Cp**, was also examined by ^1H NMR spectroscopy. Once again, the reaction proved to be sensitive to dienyne stereochemistry. In the case of **6**-*E*, within 20 min, a new species (**III**-*Cp**) was observed to form in 95% yield, followed by a slow conversion to **7**-*Cp**. Complex **III**-*Cp** exhibited informative resonances in the ^1H NMR spectrum ($CDCl_3$) at δ 1.75 (s, 15H, CH_3 of Cp*) and 2.17 (s, 1H, $=CHCl$). The δ 2.17 resonance is shifted 4.1 ppm upfield of the $=CHCl$ hydrogen resonance for **6**-*E* (δ 6.29). In a similar fashion, **6**-*Z* and **1**-*Cp** were observed to rapidly form **IV**-*Cp** (30%), followed by a slow conversion to **7**-*Cp** (45% yield), with no observable formation of **6**-*E*. Complex **IV**-*Cp** exhibited a vinyl hydrogen singlet at δ 4.89 (1H, $=CHCl$), which is shifted 1.0 ppm upfield from the corresponding signal for **6**-*Z*. The chemical shift values for the vinyl−hydrogen resonances of **III**-*Cp** (δ 2.2) and **IV**-*Cp** (4.9) are consistent with *anti*- and *syn*-hydrogen environments in an η^4-diene complex. However, the observation of a singlet at δ 2.0 (~9H, $NCCH_3$) in the ^1H NMR spectrum of the **1**-*Cp**/**6**-*E* reaction mixture coincided with the formation of **III**-*Cp** and, thus, suggested that **III**-*Cp** may indeed be an unprecedented η^6-dienyne complex.

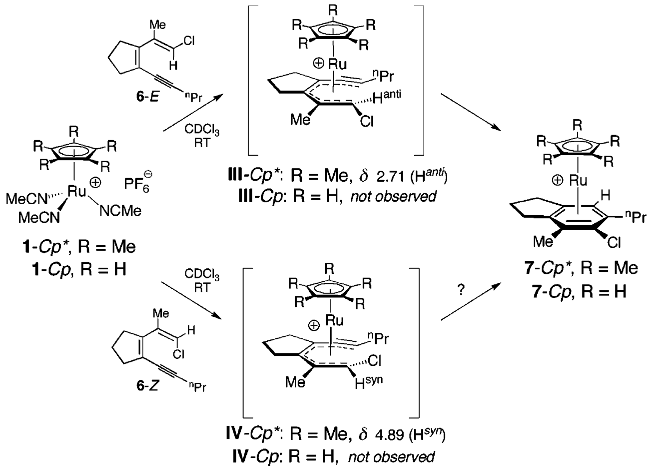
Chart 1

I **II**

Scheme 1



Scheme 2



The nature of these unusual transient species was further clarified by examining the reactions of dienyne **8** with **1**-*Cp* and **1**-*Cp** (Scheme 3). At −70 °C, a $CDCl_3$ solution of **1**-*Cp* and **8** gave rise to a new species, **V**, which exhibited resonances in the ^1H NMR spectrum at δ 5.32 (s, 5H, Cp), 3.98 (s, 1H, $=CH^{syn}$), and 0.05 (s, 1H, $=CH^{anti}$). In addition, acetonitrile hydrogen resonances were observed at δ 2.41 (from **1**-*Cp*) and 2.08 (free NCMe). The initially established 1:1 ratio of **8** (and **1**) to **V** remained constant for 3 h at −70 °C. Subsequent warming of the sample to −10 °C led to the clean formation of **9**-*Cp* within 2 h. In a similar fashion, a −60 °C $CDCl_3$ solution of **8** and **1**-*Cp** resulted in nearly quantitative formation of a new species, **10**, which was converted cleanly to **9**-*Cp** upon warming the sample to −10 °C. Complex **10** exhibited diagnostic ^1H NMR resonances at δ 1.75 (s, 15H, Cp*), 3.27 (s,

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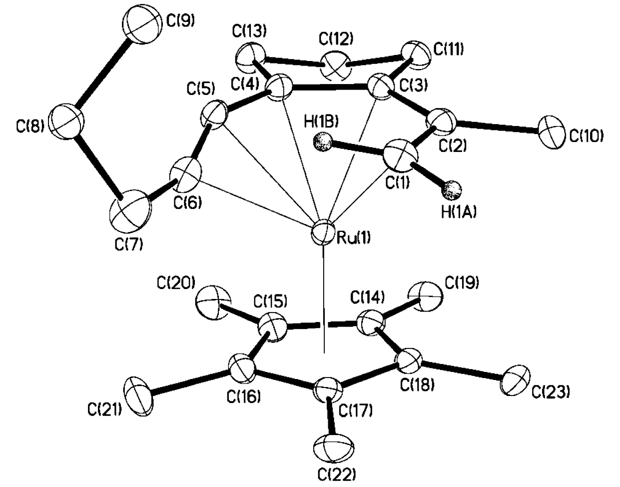
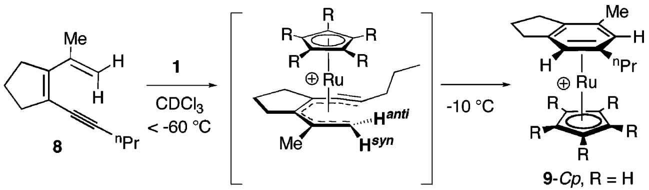


Figure 1. Solid-state molecular structure of the cation of **10**. Ellipsoids at the 30% probability level. Selected bond lengths (Å) and bond angles (deg): C(1)−C(2) 1.399(5), C(2)−C(3) 1.431(4), C(3)−C(4) 1.431(4), C(4)−C(5) 1.416(4), C(5)−C(6) 1.237(5), C(6)−C(7) 1.477(5), C(7)−C(8) 1.504(6), C(1)−C(2)−C(3) 122.2(3), C(2)−C(3)−C(4) 126.0(3), C(3)−C(4)−C(5) 122.5(3), C(1)−Ru−C(6) 100.55(13), C(1)−Ru−C(5) 79.50(13).

Scheme 3



V, R = H: δ 0.05 (H^{anti}), 2.41 (H^{syn})
10, R = Me: δ 0.11 (H^{anti}), 3.27 (H^{syn})

1H, =CH^{syn}), and 0.11 (s, 1H, =CH^{anti}). In addition, an acetonitrile hydrogen resonance was observed at δ 2.07. The significantly upfield *anti*-hydrogen chemical shifts observed for **V** (δ 0.05) and **10** (0.11) are similar to those observed for Cp*Ru(η^5-pentadienyl) complexes, such as [Cp*Ru(η^5-CH_2CHCMeCHCH_2)] (**11**),[8a] for which H^{anti} and H^{syn} resonate at 0.38 and 3.88 in C_6D_6, respectively.[8]

Ultimately, a crystal of **10** was obtained by layering diethyl ether on a −78 °C $CDCl_3$ solution containing **10** and cooling the two-phase mixture at −60 °C for 5 days. The crystal was kept cold during handling and was subjected to X-ray crystallographic analysis at −173 °C. The structural data confirm the η^6-coordination of ruthenium to all six unsaturated carbon atoms of the dienyne (Figure 1). The alkyne carbons C(5) and C(6) deviate +0.153(3) and −0.143 Å, respectively, from the mean plane defined by C(1)−C(6). Ruthenium is located 1.835 Å from the centroid of the Cp* ligand and 1.559 Å from the dienyne centroid defined by C(1)−C(6). These values are nearly identical to those observed for Cp*Ru(η^5-pentadienyl) complex **11** (1.834 and 1.567 Å).[8]

The Ru−C(6) distance of 2.326(4) Å is significantly elongated compared to the ruthenium−carbon distances for C(1)−C(5), which average 2.222 Å. The alkyne is bent substantially at both sp-carbons, with a C(4)−C(5)−C(6) angle of 151.8(3)° and a C(5)−C(6)−C(7) angle of 156.8(4)°.[9] The bending of the alkyne at C(5) results in a C(6)−C(1) nonbonded distance of 2.80 Å. H(1A) and H(1B) deviate from the C(1)−C(6) plane by −0.05 and +0.37 Å, respectively.[10] The Ru−H(1B) distance of 2.20 Å is short enough to be well within the range of crystallographically characterized ruthenium agostic C−H complexes,[11,12] and this short nonbonded distance is consistent with the chemical shift of H(1B) observed in the low-temperature ^{1}H NMR spectrum of **10**. For comparison, the Ru−H^{anti} nonbonded distances in a room temperature crystallographic analysis of **11** were 2.67 and 2.86 Å,[8a] and an unsymmetrically substituted pentadienyl complex has been reported with a Ru−H^{anti} nonbonded distance of 2.124 Å.[8b]

Finally, it should be stressed that although **10** is observed to convert cleanly to cycloaromatized product **9**-*Cp** at low temperature, the mechanism for this isomerization has yet to be established, and **10** may not lie on the direct pathway between **8** and **9**.[13]

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Supporting Information Available: Experimental and spectroscopic details of new compounds, ORTEPs, and complete listings of structural parameters for **7**-*Cp* and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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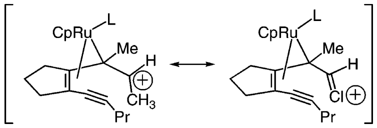

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(13) Metal−vinylidene intermediates have been proposed for cycloaromatization of substrates that incorporate a terminal alkyne,[13a,b] and activation by η^2-alkyne complexation has been proposed for cycloaromatization of aromatic enynes and dienynes that incorporate an internal alkyne.[13c,d] (a) Merlic, C. A.; Pauly, M. E. *J. Am. Chem. Soc.* **1996**, *118*, 11319−11320. (b) See ref 6a. (c) Herndon, J. W.; Zhang, Y.; Wang, K. *J. Organomet. Chem.* **2001**, *634*, 1−4. (d) Martin-Matute, B.; Nevado, C.; Cardenas, D. J.; Echavarren, A. M. *J. Am. Chem. Soc.* **2003**, *125*, 5757−5766.

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