Anion Directed Synthesis of Paddlane and Trisilver Tweezer Complexes Based upon Silver Coordination Chemistry

Paul D. Custer, Jered C. Garrison, Claire A. Tessier,* and Wiley J. Youngs*

Department of Chemistry, The University of Akron, Akron, Ohio 44325

Received January 10, 2005; E-mail: youngs@uakron.edu

The self-assembly of supramolecular species is a major area of research interest. Many self-assembly motifs have been based upon metal coordination chemistry and labile σ donors. The advantages of these metal−labile donor systems are that the metals provide a fixed geometry, making it easier to design complex architectures. The coordination of transition metals to alkyne-containing moieties is well-known.

Our group has been interested in alkyne-containing cyclophanes (cyclynes), as well as heterocyclynes, such as platinum−alkyne-based molecular squares, for some time. We have previously used silver coordination chemistry to self-assemble supramolecular complexes of cyclynes. Anions have been shown to play a directing role in the coordination chemistry of silver alkynes. Herein, we report the synthesis of the rhodium triadpal acetylide 2 (Scheme 1) and the study of the coordination chemistry of 2 with AgBF₄ and Ag(O₃SCF₃). The silver tetrafluoroborate complex of 2 self-assembles to form a novel paddlane 3 based upon silver alkyne coordination chemistry. With silver triflate, 2 forms a unique trinuclear silver alkyne tweezer complex 4.

The combination of H₂tacnRhCl₃ (H₂tacn = N,N′,N″-trimethyl-1,4,7-triazacyclononane), with an excess of PhCCLi results in the formation of the triadpal rhodium phenylacetylide, H₂tacnRh(CPh₃)₂, 2, as a white solid (65%). Combining 2 with excess AgBF₄ in acetonitrile gives 3 (97%) as off-white crystals. Interestingly, the combination of excess Ag(O₃SCF₃) and 2 in acetonitrile does not produce the triflate salt of 3, but instead yields the trinuclear silver tweezer complex 4 as light-brown crystals (88%).

IR spectra of the triadpal alkyne ligand 2 show an alkyne stretching frequency of 2103 cm⁻¹. The alkyne stretching frequency of 3 is 2047 cm⁻¹; the frequency shift is consistent with coordination of a metal to the alkyne. ES-MS of crystalline 3, in acetone, reveals that the silver complex exists as the monomer and dimer in the gas phase. The ¹H and ¹³C NMR spectra of the cationic portions of 3 and 4 were indistinguishable.

Scheme 1

Crystals of 3, suitable for X-ray diffraction, were grown from a concentrated acetonitrile solution. The molecular structure of complex 4 is depicted in Figure 3. Complex 4 is a novel trinuclear silver alkyne complex with a silver cation bonding to each alkyne−rhodium−alkyne tweezer. The Ag−alkyne bond distances range from 2.378(5) to 2.662(5) Å, with an overall average of 2.517(5) Å. The silver cations are also stabilized by three triflate anions, as well as a coordinating acetonitrile. The axial triflate is coordinated from 2.378(5) to 2.627(6) Å. The alkyne bonds lengthen, compared to 2, by an average of 0.048(7) Å upon coordination to the silver cations.

Figure 1. Molecular structure of 2. Selected bond distances (Å) and angles (deg): Rh−C(10) = 1.995(4), Rh−C(18) = 2.010(5), Rh−C(26) = 1.977(5), C(10)−C(11) = 1.181(6), C(18)−C(19) = 1.135(7), C(26)−C(27) = 1.197(6), C(10)−Rh−C(18) = 91.16(18), C(18)−Rh−C(26) = 91.94(17), C(10)−Rh−C(26) = 90.00(17), Rh−C(10)−C(11) = 174.4(4), Rh−C(18)−C(19) = 167.1(4), Rh−C(26)−C(27) = 174.1(4).

Figure 2. Molecular structure of 4. Selected bond distances (Å) and angles (deg): C(10)−C(11) = 1.135(7), C(26)−C(27) = 1.197(6), C(10)−Rh−C(18) = 91.16(18), C(18)−Rh−C(26) = 91.94(17), C(10)−Rh−C(26) = 90.00(17), Rh−C(10)−C(11) = 174.4(4), Rh−C(18)−C(19) = 167.1(4), Rh−C(26)−C(27) = 174.1(4).

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of a novel silver–alkyne coordination chemistry. Our future work will explore the dynamic behavior of alkynes except the donors. The remaining triflate anions are coordinated to only one silver each, but with shorter silver–oxygen bond distances [Ag(2)–O(4) = 2.279(4) Å and Ag(3)–O(7) = 2.337(4) Å]. The acetonitrile is coordinated to Ag(1) with a Ag(1)–N(4) bond distance of 2.220(6) Å.

In conclusion, we have synthesized a rhodium tripodal acetylide complex 2. We reported the synthesis and structural characterization of a novel silver–alkyne paddle complex, as well as a unique trinuclear silver alkyn complex of 2. The two complexes appear to be formed by the directing effects of the anions upon the silver alkyn coordination chemistry. Our future work will explore the dynamic behavior of 3 and 4, as well as explore the coordination chemistry of these novel rhodium tripodal acetylide ligands with other metals.

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Figure 2. (a) Cationic portion of 3 showing the paddle arrangements. (b) Emphasizing the coordination about the silver cations. All of the phenyl carbon atoms except the meso ones have been removed for clarity. Selected bond distances (Å) and angles (deg): Ag(1)–Ag(1A) = 2.9439(8), Ag(1)–C(10) = 2.363(4), Ag(1)–C(11) = 2.377(5), Ag(1)–C(18) = 2.387(5), Ag(1)–C(19) = 2.466(5), Ag(1)–C(26) = 2.515(5), Ag(1)–C(27) = 2.627(6), C(10)–C(11) = 1.218(8), C(18)–C(19) = 1.221(7), C(26)–C(27) = 1.219(8), Rh(1)–C(10)–C(11) = 168.9(4), Rh(1)–C(18)–C(19) = 174.0(5), Rh(1)–C(26)–C(27) = 175.0(5).

Figure 3. Detailed view of the acetylene coordination chemistry of 4. All of the phenyl carbons except the meso ones have been removed for clarity. Exterior triflate anions and the acetonitrile molecule have been removed, except for the donor atoms. Selected bond distances (Å) and angles (deg): Ag(1)–C(10) = 2.443(5), Ag(1)–C(11) = 2.468(6), Ag(1)–C(26) = 2.551(5), Ag(1)–C(27) = 2.56(5), Ag(1)–O(1) = 2.482(7), Ag(1)–N(4) = 2.409(5), Ag(2)–C(10) = 2.378(5), Ag(2)–C(11) = 2.619(6), Ag(2)–C(18) = 2.467(5), Ag(2)–C(19) = 2.662(5), Ag(2)–O(2) = 2.397(5), Ag(2)–O(4) = 2.279(4), Ag(3)–C(18) = 2.418(5), Ag(3)–C(19) = 2.617(5), Ag(3)–C(26) = 2.409(5), Ag(3)–C(27) = 2.605(5), Ag(3)–O(3) = 2.424(5), Ag(3)–O(7) = 2.337(4), C(10)–C(11) = 1.233(8), C(18)–C(19) = 1.234(7), C(26)–C(27) = 1.227(8), Rh(1)–C(10)–C(11) = 172.7(5), Rh(1)–C(18)–C(19) = 176.0(4), Rh(1)–C(26)–C(27) = 176.0(5).

Supporting Information Available: Crystallographic data and detailed experimental preparations of 2, 3, and 4. ES-MS and IR spectra of 2 and 3. This material is available free of charge via the Internet at http://pubs.acs.org.

References

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