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

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The self-assembly of supramolecular species is a major area of research interest.[1] 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.[2]

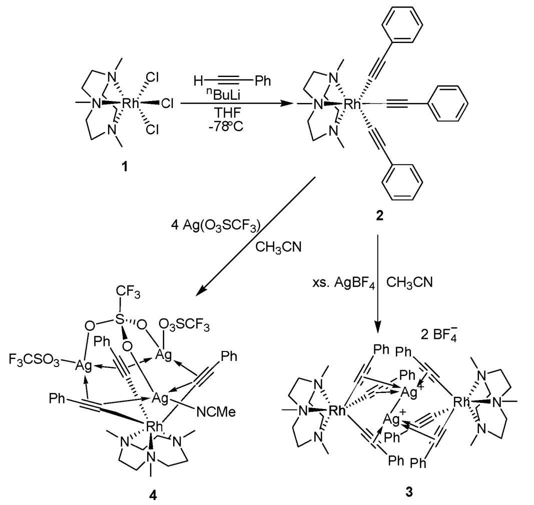
Our group has been interested in alkyne-containing cyclophanes (cyclynes),[2b,h,k] as well as heterocyclynes, such as platinum−alkyne-based molecular squares, for some time.[3] We have previously used silver coordination chemistry to self-assemble supramolecular complexes of cyclynes.[4] Anions have been shown to play a directing role in the coordination chemistry of silver alkynes.[5] Herein, we report the synthesis of the rhodium tripodal acetylide **2** (Scheme 1) and the study of the coordination chemistry of **2** with $AgBF_4$ and $Ag(O_3SCF_3)$. 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 ^{Me_3}tacnRhCl$_3$ (^{Me_3}tacn = *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane), **1**,[6] with an excess of PhCCLi results in the formation of the tripodal rhodium phenylacetylide, ^{Me_3}tacnRh(CCPh)$_3$, **2**, as a white solid (65%). Combining **2** with excess $AgBF_4$ in acetonitrile gives **3** (97%) as off-white crystals. Interestingly, the combination of excess $Ag(O_3SCF_3)$ 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 tripodal 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 ^{13}C NMR spectra of the cationic portions of **3** and **4** were indistinguishable.

Crystals of **2** and **3**, suitable for X-ray diffraction studies, were grown from a concentrated acetonitrile solution. The structures of **2** and **3** are depicted in Figures 1 and 2, respectively. Complex **2** is an octahedral complex with rhodium acetylide distances ranging from 1.977(5) to 2.010(5) Å. In the solid state, **3** exists as a dimer with two silver cations bridging two ^{Me_3}tacnRh(CCPh)$_3$ moieties. The tetrafluoroborate anions are noncoordinating. Each silver cation is coordinated to two alkynes of one tripodal ligand [C(18)−C(19) and C(26)−C(27)] and one alkyne of the other [C(10A)−C(11A)], as well as to the other silver cation. The Ag(1)−Ag(1A) distance is 2.9439(8) Å, which is slightly longer than silver−silver distances of 2.89 Å in metallic silver.[7] The shortest Ag−alkyne interaction is the acetylene C(10A)−C(11A) (2.363(4) and 2.377(5) Å, respectively). The remaining two alkynes, C(18)−C(19) and C(26)−C(27), have bonding distances to Ag(1) ranging from 2.387(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.

Scheme 1



Crystals of **4**, 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 to all three silver atoms with Ag(1)−O(1), Ag(2)−O(2), and Ag(3)−O(3) distances of 2.482(7), 2.397(5), and 2.424(5) Å, respec-

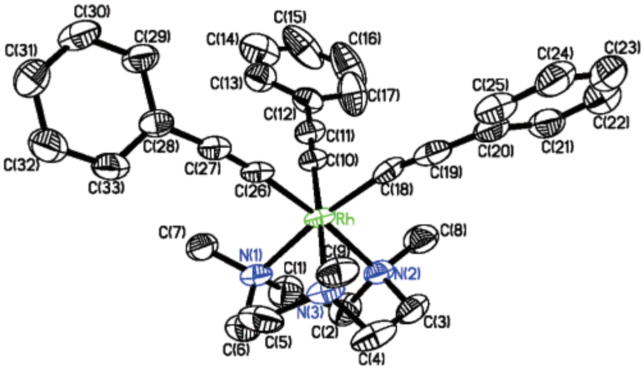


Figure 1. Molecular structure of **2**. Selected bond distances (Å) and angles (deg): Rh−C(10) = 1.995(4), Rh−C(18) = 2.010(5), Rh−C(26) = 1.977(5), C(10)−C(11) = 1.181(6), C(18)−C(19) = 1.135(7), C(26)−C(27) = 1.197(6), C(10)−Rh−C(18) = 91.16(18), C(18)−Rh−C(26) = 91.94(17), C(10)−Rh−C(26) = 90.00(17),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

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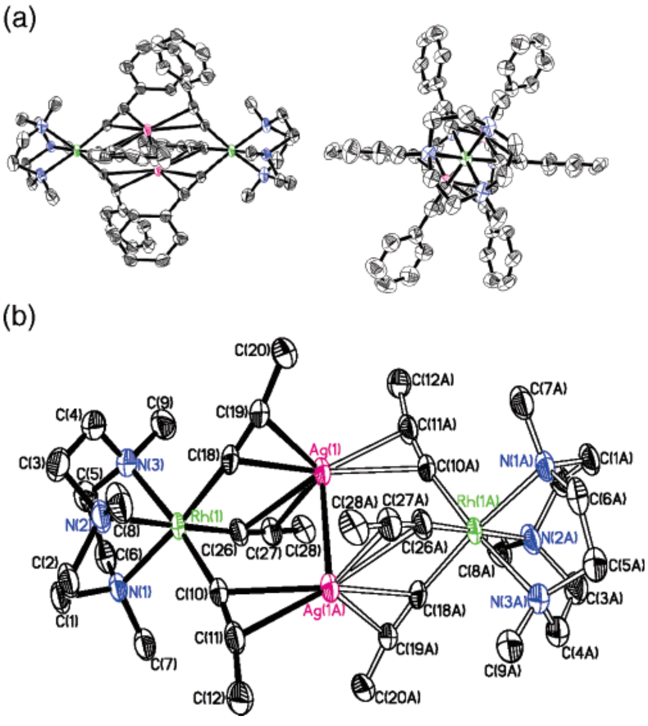

Figure 2. (a) Cationic portion of **3** showing the paddlane arrangements. (b) Emphasizing the coordination about the silver cations. All of the phenyl carbon atoms except the meso ones have been removed for clarity. Selected bond distances (Å) and angles (deg): Ag(1)−Ag(1A) = 2.9439(8), Ag(1)−C(10) = 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).

tively. 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 paddlane complex, as well as a unique trinuclear silver alkyne complex of **2**. The two complexes appear to be formed by the directing effects of the anions upon the silver alkyne 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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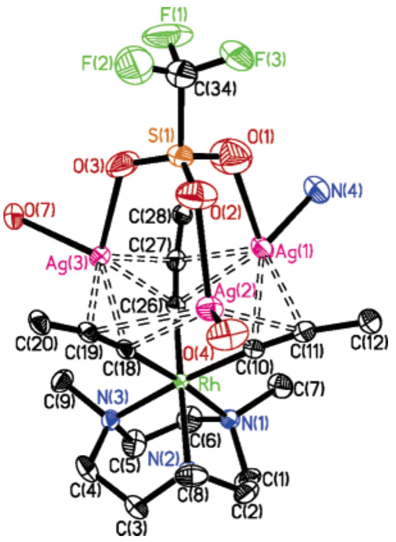

Figure 3. Detailed view of the acetylene coordination chemistry of **4**. All of the phenyl carbons except the meso ones have been removed for clarity. Exterior triflate anions and the acetonitrile molecule have been removed, except for the donor atoms. Selected bond distances (Å) and angles (deg): Ag(1)−C(10) = 2.443(5), Ag(1)−C(11) = 2.468(6), Ag(1)−C(26) = 2.551(5), Ag(1)−C(27) = 2.565(5), Ag(1)−O(1) = 2.482(7), Ag(1)−N(4) = 2.220(6), 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.

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