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Heteroligated Metallomacrocycles Generated via the Weak-Link Approach

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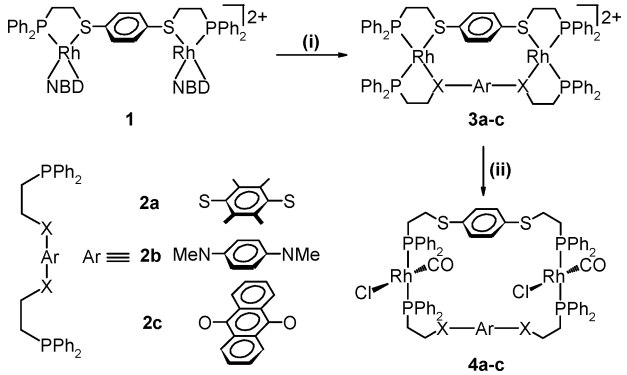
Sequential reaction of two different hemilabile ligands ($Ph_2PCH_2CH_2X)_2Ar$ (X = S, Ar = C_6H_4 or $C_6(CH_3)_4$; X = NCH_3, Ar = C_6H_4; X = O, Ar = 9,10-$C_{14}H_8$) with a Rh(I) metal center resulted in the formation of heteroligated metallomacrocycles in high yield. The specific reaction conditions for each pair of hemilabile ligands are discussed. The solid-state structure of [{1,4-$(Ph_2PCH_2CH_2S)_2C_6H_4$}-{1,4-$(Ph_2PCH_2CH_2S)_2C_6(CH_3)_4$}$Rh_2$]$(BF_4)_2$, as determined by X-ray crystallography, is presented.

Over the past two decades, several effective synthetic strategies for forming multimetallic macrocyclic functional architectures have been developed in the field of metallosupramolecular chemistry.[1−6] Our group has introduced and developed one of these synthetic strategies, termed the Weak-Link Approach (WLA), which allows one to prepare multimetallic macrocycles from flexible hemilabile ligands and transition metal precursors. This method typically allows one to assemble symmetric 2:2 metal-to-ligand structures with control over many architectural parameters including macrocycle size, shape, hydrophobicity, and chirality, and it has recently led to the development of a variety of allosteric catalysts.[7−10] Thus far, no methods have been developed for preparing macrocyclic structures with two distinct hemilabile ligands within one structure, or so-called dissymmetric systems. Herein, we report the first examples of such structures prepared via the WLA in a stepwise process (Scheme 1).

Scheme 1 [a]



[a] Key: (i) H_2 (1 atm) for **3b**,**c**, 1,4-$(Ph_2PCH_2CH_2X)_2Ar$ (**2**; 1 equiv), CH_2Cl_2, room temperature for **3a** and −78 °C → room temperature for **3b**,**c**; (ii) CO (1 atm), $[(CH_3)_4N]Cl$ (2 equiv), CH_2Cl_2, room temperature.

Complex **1** was prepared by treating $[Rh(NBD)Cl]_2$ (NBD = norbornadiene) with $AgBF_4$ in the presence of the hemilabile ligand 1,4-$(Ph_2PCH_2CH_2S)_2C_6H_4$.[11] Complex **1** was isolated as a yellow, air-sensitive solid in 93% yield and characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy and ES-MS. All data are consistent with the proposed formulation. The $^{31}P\{H\}$ NMR spectrum of **1** exhibits a doublet at δ 57 (J_{Rh-P} = 160 Hz) indicative of the phosphine ligand within the five-membered chelate around Rh(I).[12] Moreover,

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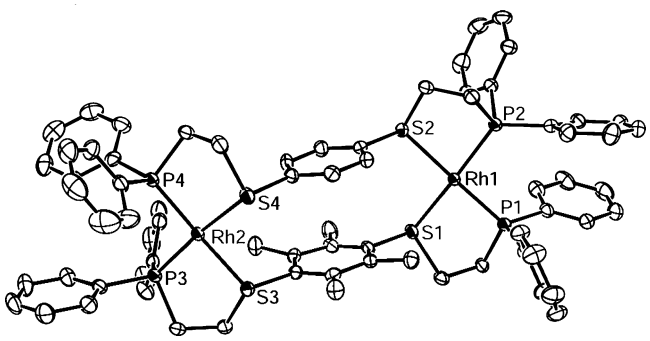
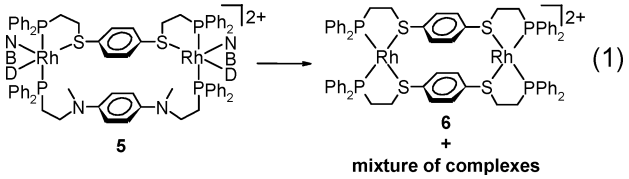


Figure 1. Thermal ellipsoid drawing of $[\{1,4\text{-}(Ph_2PCH_2CH_2S)_2C_6H_4\}\{1,4\text{-}(Ph_2PCH_2CH_2S)_2C_6(CH_3)_4\}Rh_2]^{2+}$, with 50% probability ellipsoids, in **3a** showing the labeling scheme. Selected distances (Å): Rh(1)−S(2) 2.364(1), Rh(2)−S(4) 2.359(1), Rh(1)−S(1) 2.326(1), Rh(2)−S(3) 2.344(1), Rh(1)--Rh(2) 8.758, $(C_6H_4)_{cent}-(C_6Me_4)_{cent}$ 3.591. Selected torsion angles (deg): ∠S(2)−$(C_6H_4)_{cent}$−$(C_6Me_4)_{cent}$−S(1) 5.3, ∠S(4)−$(C_6H_4)_{cent}$−$(C_6Me_4)_{cent}$−S(3) 6.6.

the ^{1}H NMR spectrum of **1** in CD_2Cl_2 indicates the presence of the η^4-NBD ligands.

The reaction between complex **1** and the hemilabile ligand $1,4\text{-}(Ph_2PCH_2CH_2S)_2C_6(CH_3)_4$ (**2a**) at room temperature in CH_2Cl_2 results in the clean formation of the corresponding dissymmetric binuclear complex, $[\{1,4\text{-}(Ph_2PCH_2CH_2S)_2\text{-}C_6H_4\}\{1,4\text{-}(Ph_2PCH_2CH_2S)_2C_6(CH_3)_4\}Rh_2]^{2+}$ (**3a**, Scheme 1), which was isolated in 94% yield and fully characterized. Complex **3a** exhibits a ^{31}P NMR spectrum that is diagnostic of the proposed structure. It shows two doublets of doublets at δ 63 ($J_{Rh-P,P-P}$ = 164, 36 Hz) and 65 ($J_{Rh-P,P-P}$ = 162, 36 Hz) due to the presence of two magnetically inequivalent P atoms. The ES-MS spectrum exhibited a single peak at *m*/*z* 697.2 [M − $2BF_4^-$] corresponding to the loss of two BF_4^- counterions. The solid-state structure of **3a** (Figure 1), as determined by X-ray crystallography, is consistent with its proposed solution structure.[13] Each Rh(I) metal center is coordinated to the PCH_2CH_2S fragments in a slightly distorted square-planar geometry. The metal−metal separation is 8.758 Å, and the interplanar distance between the nearly parallel central aryl rings of the ligands is 3.591 Å. The Rh−S(1,3) distances are approximately 0.025 Å shorter than Rh−S(2,4), presumably because of the stronger bonds between the Rh(I) and S(1,3) atoms of the more electron-rich $1,4\text{-}(Ph_2PCH_2CH_2S)_2C_6(CH_3)_4$ hemilabile ligand.

The reactions between complex **1** and the hemilabile ligands **2b**[14] or **2c**[15] under similar conditions (room temperature, CH_2Cl_2) failed to yield complexes analogous to **3**. For instance, complex **5** was formed as the initial product when a solution of **2b** (1 equiv) was added to a solution of **1**, as evidenced by ^{31}P{^{1}H} NMR spectroscopy (eq 1).[16] This intermediate undergoes fast ($t_{1/2}$ = 1.5 h, 20 mM concentration, room temperature) rearrangement to give complex **6**[11] and a complex mixture of products containing Rh(I), ligand **2b**, and NBD. However, complexes **3b** and **3c** were synthesized in excellent yields under optimized reaction conditions when a solution of **1** in CH_2Cl_2 was treated with H_2 (bubbling for ∼2 min at 1 atm) and a solution of the corresponding hemilabile ligand in CH_2Cl_2 was then added rapidly at −78 °C. The complete hydrogenation of NBD, which was evident from the ^{1}H NMR data of the crude reaction mixture, is crucial in obtaining high yields of complexes **3b** and **3c**. Presumably, Rh(I) has a stronger affinity toward the double bonds of the NBD ligand than the σ-donating N and O atoms. The NMR data of **3b** and **3c** are consistent with their proposed structures. For instance, the ^{31}P{^{1}H} NMR spectrum of **3c** exhibits two characteristic doublets of doublets at δ 73 ($J_{Rh-P,P-P}$ = 200, 41 Hz) and 65 ($J_{Rh-P,P-P}$ = 170, 41 Hz) due to the presence of two inequivalent P atoms in the η^2-PCH_2CH_2S and η^2-PCH_2CH_2O chelates. Notably, complex **3b** forms as a mixture of syn and anti isomers in a 1:1 ratio with respect to the orientation of the Me groups in the η^2-PCH_2CH_2NMe chelate. Therefore, the ^{31}P{^{1}H} NMR spectrum of **3b** exhibits four characteristic doublets of doublets, two for each isomer.[17] The ES-MS spectrum of **3b**, which shows a single isotopically resolved peak at *m*/*z* 666.2 [M − $2BF_4^-$], also confirms the proposed bimetallic formulation for complex **3b**.



(1)

Condensed macrocyclic complexes **3a**−**c** undergo clean expansion by selectively cleaving their Rh−heteroatom bonds with $[(CH_3)_4N]Cl$ under CO (1 atm), which results in the quantitative formation of the neutral open macrocycles **4a**,**b** (Scheme 1). Complexes **4a**−**c** were characterized by ^{1}H and ^{31}P{^{1}H} NMR and FTIR spectroscopies, giving results that are consistent with their proposed structural assignments. For example, the ^{31}P{^{1}H} NMR spectrum of each complex exhibit a single resonance [δ 24 (br d, J_{Rh-P} = 128 Hz) for **4a**, δ 24 (br d, J_{Rh-P} = 128 Hz) for **4b**, and δ 20 (br d, J_{Rh-P} = 133 Hz) for **4c**]. The broad nature of these resonances is presumably due to the presence of two types of magnetically inequivalent P atoms in each complex. FTIR spectra of **4a**−**c** exhibit characteristic ν_{CO} bands for their terminal CO ligands at 1968 cm^{-1}. The positions of these bands correlate well with homoligated binuclear Rh(I) complexes with similar coordination environments.[11] Complexes **4a**−**c** are stable in CH_2Cl_2 solution under CO (1 atm)

(13) Crystallographic details for **3a** (CH_2Cl_2): $C_{75}H_{78}B_2Cl_6F_8P_4Rh_2S_4$, *M* = 1823.63, yellow block, Bruker Smart Apex CCD (Mo Kα radiation), *T* = 173(2) K, triclinic, space group *P*1, *a* = 10.5464(7) Å, *b* = 14.9351(9) Å, *c* = 25.1498(16) Å, α = 86.123(1)°, *β* = 78.705(1)°, *γ* = 86.780(1)°, *V* = 3872.0(4) Å^3, *Z* = 2, D_{calc} = 1.564 g·cm^{-3}, *μ*(Mo Kα) = 0.886 mm^{-1}, 25 022 measured reflections, 17 447 independent reflections [R_{int} = 0.0201], θ_{max} = 28°, R1 = 0.0454, wR2 = 10.52, GOF = 1.024 [$I > 2\sigma(I)$].

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(16) ^{31}P{^{1}H} NMR (121.53 MHz, CD_2Cl_2, δ): 53 (dd, $J_{Rh-P,P-P}$ = 138, 27 Hz), 9 (br dd, $J_{Rh-P,P-P}$ = 128, 27 Hz). Complex **5** was not characterized further because of its fast rearrangement as shown in eq 1.

(17) Complex **3b**: ^{31}P{^{1}H} NMR (121.53 MHz, CD_2Cl_2, δ): 72 (dd, $J_{Rh-P,P-P}$ = 167, 42 Hz), 70 (dd, $J_{Rh-P,\ P-P}$ = 166, 43 Hz), 54 (dd, $J_{Rh-P,\ P-P}$ = 178, 43 Hz), 53 (dd, $J_{Rh-P,P-P}$ = 176, 43 Hz).

at room temperature for several days. However, exposure of complex **4a** to high vacuum or prolonged storage in the solid state under nitrogen resulted in its conversion to the Cl^- salt, analogous to **3a**.

The synthetic approach described herein demonstrates a new way of controlling chemical and physical properties of metallomacrocyclic structures via judicious choice of ligand building blocks. This strategy paves the way for the synthesis of functional metallomacrocyclic entities, in which one can incorporate functional groups capable of interaction via energy transfer processes or can alter the overall properties, e.g., catalytic activity and selectivity, of the macrocyclic structures in a different yet cooperative manner. Efforts to fully evaluate the potential of the presented synthetic strategy are underway.

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Supporting Information Available: X-ray structural data for **3a** in CIF format and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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