Coordination Chemistry

Heteroligated Rh^I Tweezer Complexes**

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The unique combination of the coordination geometry of transition-metal centers with the structural and geometric properties of organic ligands provides the basis for the synthesis and design of metallosupramolecular complexes[1] and metal–organic frameworks.[2] Indeed, the ability to incorporate multiple types of building blocks (namely, metal centers and ligands) into metallosupramolecular structures is a key requirement for the rational tailoring of their structural and electronic properties. Currently, the impetus for this research is shifting away from the synthesis of structurally complex and aesthetically pleasing structures towards the preparation of functional metallosupramolecular entities with preprogrammed catalytic and molecular-sensing properties.[3] We have previously demonstrated that tweezer-type salen-containing (salen = *N*,*N*′-bis(salicylidene)cyclohexyldiamine) complexes have improved catalytic rates and selectivities relative to the corresponding bimetallic macrocyclic analogues.[3b,c] These results motivated us to develop a general synthesis of "heteroligated" tweezer-type complexes.

Recently, we reported a novel halide-induced ligand-rearrangement process that was observed in multimetallic Rh^I metallomacrocycles and which results in the formation of two- and three-dimensional complexes that contain heteroligated coordination environments.[4] Herein, we report a general high-yielding methodology for the preparation and postsynthetic modification of heteroligated monometallic Rh^I tweezer-type complexes (Scheme 1). This methodology is based on a unique reaction that allows the preparation of condensed complexes **4b–f** which contain two distinct phosphine-substituted ligands or heteroligated systems that can undergo stepwise substitution reactions with Cl^- ions and/or CO to result in four unique geometries with respect to the orientation of each S- or O-appended aromatic group.

The neutral heteroligated "semiopen" tweezer complexes **3a–f** were synthesized in one step from stoichiometric amounts of the corresponding hemilabile ligands $Ph_2P(CH_2)_2SAr$ (Ar = aryl), $Ph_2P(CH_2)_2XC_6H_5$ (X = O, CH_2), and $[\{RhCl(nbd)\}_2]$ (nbd = norbornadiene) in CH_2Cl_2. Initially, the kinetic products **1a–f,** which have *cis*-thioether and *cis*-phosphine ligands around a Rh^I center, and **2a–f**, which have nbd and *cis*-phosphine ligands around a Rh^I center, are

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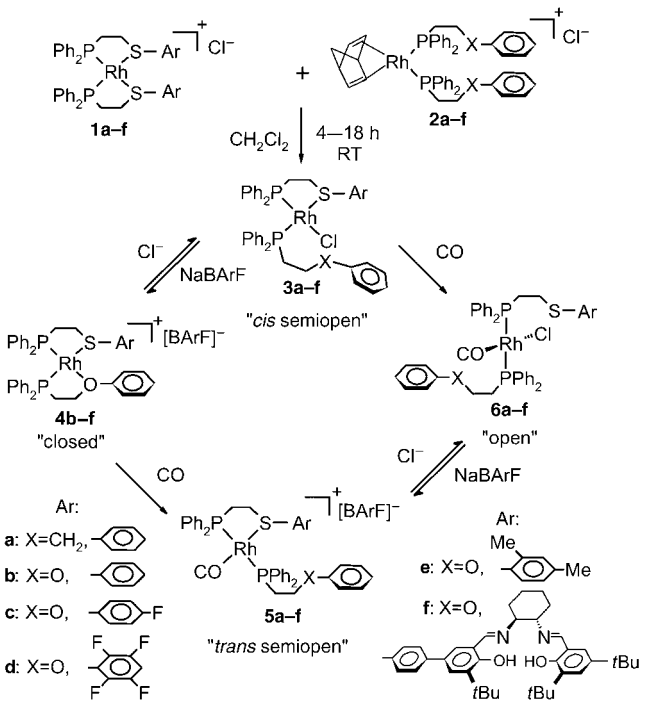

Scheme 1. Synthesis of the heteroligated Rh^{I} tweezer complexes **3a–f**, and the stepwise synthesis of closed complexes **4b–f**, neutral *cis* semiopen complexes **3a–f**, cationic *trans* semiopen complexes **5a–f**, and open tweezer complexes **6a–f**. BArF = $B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$

formed, but convert over 18 h into the semiopen neutral complexes **3a–f** (Scheme 1). Elemental analysis, ^{1}H, ^{19}F, and ^{31}P NMR spectroscopic, and ESIMS data are in full agreement with the proposed formulations. For example, complex **3b** exhibits highly diagnostic resonances in its $^{31}P\{^{1}H\}$ NMR spectrum at $\delta = 73.61$ ppm (dd, J(Rh-P) = 185 Hz, J(P-P) = 41 Hz), which corresponds to the P center of the η^2-P,S chelating ligand, and $\delta = 30.1$ ppm (dd, J(Rh-P) = 168 Hz, J(P-P) = 41 Hz), which corresponds to the P center of the η^1-P,O ligand.[4,5] Further evidence for the formation of these neutral complexes was obtained from a single-crystal X-ray study of complex **3e** (Figure 1).[6] The Rh^{I} center in **3e** exhibits a square-planar geometry with Cl1-Rh1-P2 and Cl1-Rh1-S1 angles of 87.8 and 86.8°, respectively.

The rate of these conversions was also studied by ^{31}P NMR spectroscopy at 25 °C in CD_2Cl_2, and the corresponding half-lives of the reactions were measured (**3a**: $t_{1/2}$ = 180 min, **3b**: 95 min, **3c**: 65 min, **3d**: 40 min, **3e**: 152 min, **3f**: 95 min; 20 mM [{RhCl(nbd)}$_2$]). These rates appear to be inversely proportional to the electron density of the aryl groups tethered to the S atom: As the electron density of the aryl subsitutent in the P,S ligand decreases, the Rh–S bonds in **1** weaken and the rate of the formation of **3** increases. This trend in the reaction rates reflects the increase in the strength of the Rh–S bond as a function of the increase in electron density of the aromatic group appended to the S atom.

The reversible abstraction of Cl^- ions from **3b–f** with one equivalent of NaBArF results in the clean formation of condensed cationic complexes **4b–f** in which the Rh^{I} center coordinates to the O atom. All the data obtained are

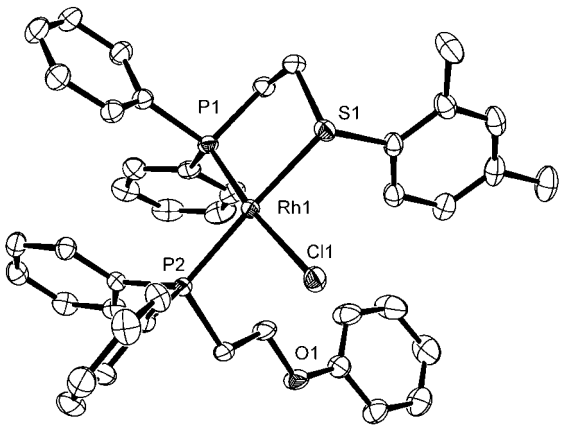

Figure 1. ORTEP diagram of **3e** ($C_{42}H_{42}ClOP_2RhS$) with thermal ellipsoids set at 50% probability. Hydrogen atoms and solvent molecules have been omitted for clarity.[6]

consistent with the proposed formulations. For example, complex **4b** exhibits highly diagnostic resonances in its $^{31}P\{^{1}H\}$ NMR spectrum at $\delta = 73.5$ ppm (dd, J(Rh-P) = 200 Hz, J(P-P) = 41 Hz) and $\delta = 51.8$ ppm (dd, J(Rh-P) = 168 Hz, J(P-P) = 41 Hz), which are characteristic of P centers in a coordination environment in which a Rh^{I} center has *cis*-phosphine, *cis*-thioether, and ether ligands. Furthermore, a signal at m/z 731.2 is observed in its ESIMS spectra that corresponds to a $[C_{40}H_{38}P_2S_2Rh]^+$ ion. Complexes **4b–f** react with stoichiometric quantities of benzyltriethyl ammonium chloride in CH_2Cl_2 to regenerate the corresponding chloride-ligated semiopen complexes **3b–f**. Abstraction of the Cl^- ion from **3a** results in a mixture of products because there is no O atom to which the Rh^{I} center can coordinate. However, the addition of one equivalent of benzyltriethylammonium chloride in solution or excess CO to **4a** in CH_2Cl_2 results in the formation of complexes **3a** or **5a**, respectively.

The addition of CO to complexes **4b–f** selectively cleaves the Rh–O bond and results in the formation of cationic semiopen tweezer-type complexes **5b–f**, in which the P atoms are *trans* to one another. Again, all the data collected are consistent with the proposed formulations. For example, semiopen complex **5b** exhibits resonances in its $^{31}P\{^{1}H\}$ NMR spectrum at $\delta = 63.1$ ppm (dd, J(Rh-P) = 116 Hz, J(P-P) = 268 Hz), which corresponds to a P center coordinated to a Rh^{I} center with phosphine and thioether ligands, and $\delta =$ 19.2 ppm (dd, J(Rh-P) = 121 Hz, J(P-P) = 268 Hz), which corresponds to a P center coordinated to a Rh^{I} center with phosphine and CO ligands. Alternatively, complexes **5a–f** may also be synthesized from complexes **6a–f** and stoichiometric quantities of NaBArF in diethyl ether. In this case, the lack of an O atom in **6a** does not affect the abstraction of the Cl^- ion and results in the clean formation of **5a**.

The neutral open complexes **6a–f** are synthesized from **5a–f** and stoichiometric quantities of benzyltriethylammonium chloride in CH_2Cl_2. Alternatively, the addition of CO to complexes **3a–f** cleaves the Rh–S bonds and results in the fully open tweezers **6a–f** in which the phosphines are *trans* to one another, thus resulting in further separation of the phosphine substituents. Each of these complexes exhibits

overlapping doublets of doublets in their $^{31}P\{^1H\}$ NMR spectra at approximately $\delta = 24$ ppm, which corresponds to two inequivalent phosphines.

The Cl^- ion is an integral component in these transformations. For example, the independently synthesized intermediate Rh^I complexes **1b** and **2b** were stirred together for 18 hours and the semiopen complex **3b** was formed. However, this reaction was repeated with the BF_4^- salt instead of the chloride salt and resulted in no ligand rearrangement, as determined by ^{31}P NMR spectroscopy.

The interconversion between complexes **3**–**6** allows the spatial separation between the aryl groups and the overall flexibility of these complexes to be systematically controlled (Scheme 1). The synthetic approach described herein is amenable to the inclusion of a variety of aromatic groups, including free-base salen functionalities, as demonstrated in **3f**–**6f**. With this approach, we now have the ability to synthesize designer catalytic intramolecular systems, which could be used to incorporate a catalytic functionality into one arm of a tweezer and add a separate cocatalyst, activator, or enantioselectivity-influencing agent on the other arm, with a precise control over spatial separation and flexibility. These types of structures are becoming important as allosteric catalysts[3b,c] and sensors,[3a] and the ability to modulate their properties through this type of chemistry will help researchers to finetune the reactivity of these complexes.

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[6] Crystal data for **3e**: $C_{42}H_{42}ClOP_2RhS$: Monoclinic space group $P21/c$, $a = 9.7234(9)$, $b = 18.5595(2)$, $c = 21.697(2)$ Å, $\alpha = 90.00$, $\beta = 102.686(2)$, $\gamma = 90°$, $V = 3819.9(6)$ Å^3, $Z = 4$, $T = 153$ K, $2\theta_{max} = 57.84°$, $Mo_{K\alpha}\lambda = 0.71073$ Å, $R1 = 0.0318$ (for 8061 reflections with $I > 2\sigma(I)$) $wR2 = 0.0787$ and $S = 1.070$ for 434 parameters and 9263 unique reflections. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-415095.

