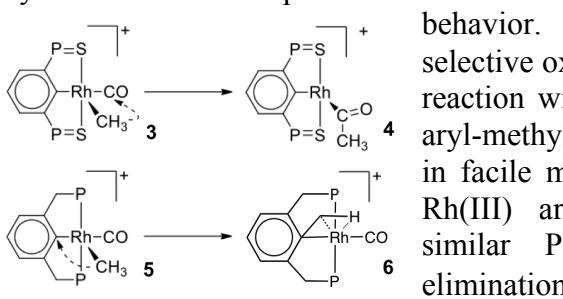
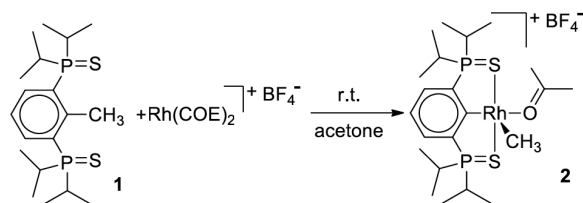


Ligand effect on the electronic structure and reactivity of rhodium pincer complexes

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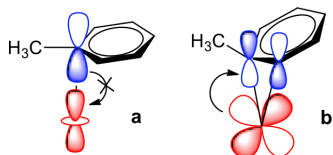
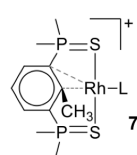
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Selective activation of strong C-H and C-C bonds is one of the fundamental challenges of modern organometallic chemistry. Stable pincer frameworks provide the opportunity for mechanistic insights on such reactions. Recently synthesized Rh complexes based on SCS pincer ligands exhibited unique chemical

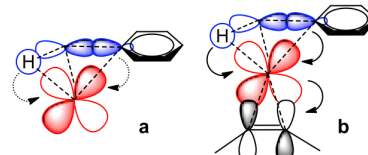
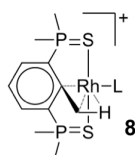


behavior. The SCS-type ligand **1** undergoes highly selective oxidative addition of an sp^2 - sp^3 C-C bond upon reaction with the Rh(I) precursor, affording the Rh(III) aryl-methyl complex **2**. Treatment of **2** with CO resulted in facile migratory insertion of CO, affording the new Rh(III) aryl-acetyl complex **4** whereas structurally similar PCP complex undergoes C-C reductive elimination to afford an η^3 -arene Rh(I) species **6**.

High-level DFT study of the SCS and PCP complexes vis-à-vis their reactions in solutions demonstrated that enhanced electron density on S atom rises its electrophilicity, so that in the SCS and PCP ligands Rh-bound S and P atoms have large opposite charges. This results in different oxidation state of the Rh atom, Rh(III) in the PCP aryl-methyl complexes and Rh(V) in their SCS analogs. Excessive electron density in the SCS system determines the thermodynamic selectivity for C-C over C-H cleavage, as it is attributed to the higher electronegativity of a methyl vs. hydride ligand. It also gives rise to formation of two pre-cleaved intermediates: an η^2 arene complex **7** with no bonding between the metal and the methyl moiety and a novel η^3 -C-C-H agostic complex **8**, the immediate precursor for both observed C-C and unobserved C-H bond cleavage.



Key interaction in an η^1 -arene structure (a) and its stabilization by electron transfer to the arene ring, leading to an η^2 -arene structure (b) in intermediate **7**.



Key electronic interaction in the η^3 -C-C-H agostic intermediate **8** (a) and its stabilization by *cis*-2-butene through metal-to-olefin electron transfer (b).

Higher Rh oxidation state decreases Rh→CO π backdonation and weakens Rh-CO bonding in the SCS system. In contrast, stronger Rh-CO bonding in the PCP system causes enhanced CO→Rh→phenyl σ donation that weakens the Rh-C_{ipso} bond. These effects determine different direction for migration of the methyl group in the carbonyl complexes **3** and **5**.