

Noninnocent Behavior of PCP and PCN Pincer Ligands of Late Metal Complexes

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Abstract Pincer complexes are generally viewed as stable compounds in which the pincer ligand framework remains unchanged during stoichiometric and catalytic reactions. However, there are now several cases in which the pincer ligand itself undergoes transformations that result in extraordinary reactivity of the metal complex and formation of unusual species. In the current chapter, we review our work on “noninnocent” reactivity modes of various PCP and PCN-type pincer ligands of Rh, Ir, Ru, Os, Pd, and Pt. Participation of the arene ring in the reactivity of PCP type complexes has led to formation of unprecedented quinonoid complexes, including complexes in which the pincer ligand adopts structures of quinone methides, thioquinone methides, xylylenes, methylene arenium, and oxo-arenium compounds. In addition, pincer systems can collapse and be regenerated under redox conditions, and reduction can lead to a ring-localized radical anion complex. The generation of C–H agostic arene PCP complexes has led to new insights regarding the C–H bond activation process, and the effect of CO ligands on it.

Keywords Pincer ligands, xylylene complex, quinone methide complex, thioquinone methide complex, phenoxonium complex, methylene arenium complex, agnostic pincer complex, late transition metals, reactive intermediates

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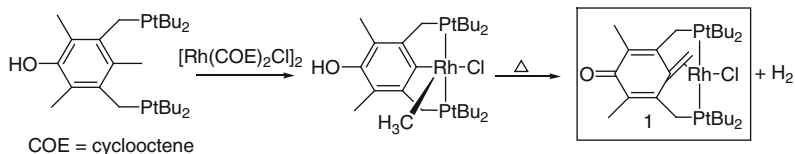
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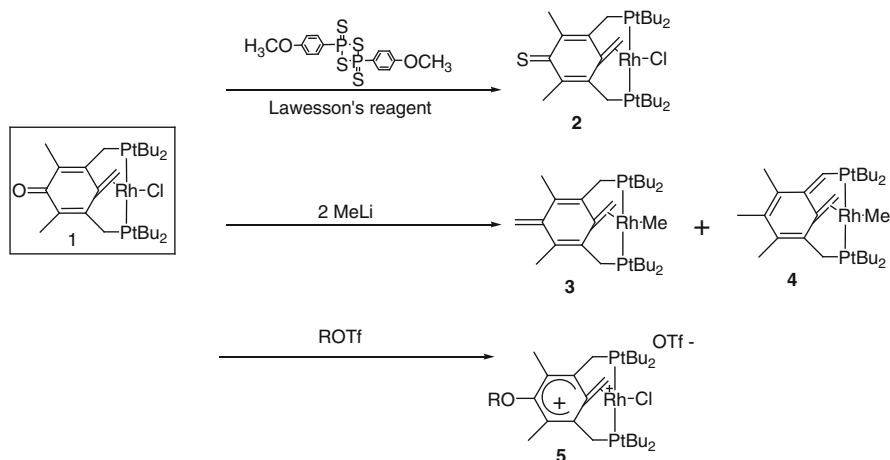
1 Introduction and Background

Pincer-type complexes constitute a large family of important compounds in organometallic chemistry [1–5]. Such complexes play key roles in chemical transformations relevant to organic synthesis, catalysis, bond activation, mechanistic studies, and the design of new materials [6, 7]. By systematic ligand modifications and/or by variation of the metal center it has been possible to readily control their reactivity and stability. The first pincer complexes, reported in the early 1970s, were PCP-type pincer complexes [8]. Since then, such pincer complexes have been utilized in various studies, including bond activation studies, such as carbon–carbon bond activation [9–11], formation of carbene species [12], trapping of elusive compounds [13], and in various catalytic applications [1, 2, 14]. For instance, PCP-type d^8 metal complexes have been utilized in alkane dehydrogenation [15–18] and C–C bond forming reactions such as Heck [19–22] and Suzuki [23–25] coupling.

While traditionally pincer complexes are viewed as stable compounds in which the pincer ligand framework remains unchanged during stoichiometric and catalytic reactions, in some cases the pincer ligand itself is capable of undergoing transformations that result in extraordinary reactivity of the metal complex and/or formation of unusual species. In the current chapter, we review the “noninnocent” reactivity modes of pincer-type complexes which were observed in our laboratory with PCP and PCN-type pincer ligands. Transformations of the aromatic part (to generate xylylene, methylene arenium, phenoxonium, radical anion type structures), C–H agostic coordination, N-arm hemilability, and collapse and regeneration of PCP and PCN pincer ligands are illustrated. Noninnocent behavior on PNP and PNN pyridine- and acridine-based complexes, which involve metal ligand cooperation by dearomatization of the pincer ligand [26, 27], and have led to the design of various catalytic reactions [28–32], are outside the scope of this chapter.



Scheme 1 Formation of the rhodium quinone methide complex **1** based on a PCP ligand



Scheme 2 Reactivity of the rhodium quinone methide complex **1**

2 Arene System Perturbation

2.1 Quinone Methides and Quinonoid Compounds

Quinone methides (QMs) are quinones in which one oxygen atom has been replaced by an alkylidene group. They are highly reactive compounds which participate in many chemical and biological processes ([33–35] and references therein), such as formation of substituted phenols [36], Diels–Alder reactions [37], biosynthesis of the natural polymers [38–40], and radical scavenge [41, 42]. Quinone methides are also able to react with functional groups of biopolymers, such as DNA and proteins, and several drugs are believed to generate QM moieties as an active form [43, 44].

Quinone methides, especially the simple ones (those not having substituents at the exocyclic methylene group) are very unstable compounds and their isolation is seriously obstructed or requires extremely diluted solutions and low temperatures [45]. Being a highly polarized molecule, QMs rapidly react with both nucleophiles and electrophiles and easily convert to their bi-radical triplet form, opening up several additional reactivity patterns.

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