

Novel Reactivity of Pincer-type Complexes

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Applications of pincer-type complexes are largely focused on catalysis,^{1,2} and activation of strong C-H, C-O, C-C and N-H bonds.^{1,3} Alternatively, pincer complexes are currently being investigated in the formation of functional multi-metal assemblies, selective detection of SO₂, and the development of gas-triggered switches.^{1,4} Past research in this area has generated highly efficient dehydrogenation and Heck type catalysts, the latter having turnover frequencies as high as 400000 (TON/h) using an iodobenzene substrate.⁵ Pincer complexes also catalyze asymmetric allylic substitution of electrophiles, enantioselective adol condensation of methyl isocyanoacetate and aldehydes, and hydroamination of olefins. The high catalytic activity of pincer complexes is attributed to a unique balance of reactivity vs. stability. The pincer ligand is amenable to modifications enhancing selectivity and reactivity. Recent research has led to pincers capable of hemilabile coordination, new catalysts for dehydrogenation of alcohols to esters, and more efficient alkane dehydrogenation catalysts.

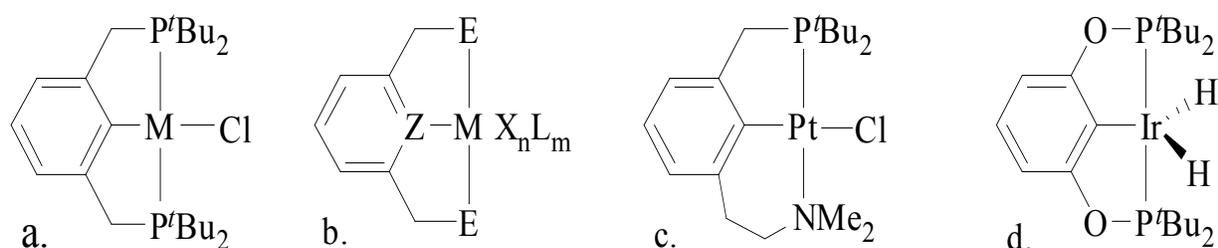


Figure 1: (a) Shaw's PCP complexes M = Pt, Pd, Ni (b) Generic EZE pincer-type complex E = PR₂, NR₂, OR, SR; Z = C, N; M = Platinum metals (c) "Long-arm" PCNPtCl complex. (d) POCOPtIrH₂, catalyst for alkane and ammonia borane dehydrogenation

Pincer complexes were first reported by Shaw in 1976 (Figure 1a).⁶ In general, pincer-type ligands are a 5 or 6 e⁻ donor which impose a *mer*-tridentate bonding mode (figure 1b) The formation of a metal-carbon or metal-nitrogen bond and two trans electron donors results in formation of two five-member metallacycles providing a rigid structure that is thermally robust (many complexes stable above 250 °C). Pincer complexes are usually classified according to the heteroatoms in the side arms of the pincer ligands E, and the central bonding atom in the backbone designated by Z (Figure 1b). Initial studies focused on PCP based systems, but the introduction of heteroatoms (N, O, P, and S) with alkyl or aryl substituents has resulted in fine-tuning of electronics and sterics.¹ Alternative central backbones other than benzene have been explored, including pyridine, propane, and carbene moieties.

While the PCP ligand complexes demonstrated almost exclusive *mer*-tridentate binding, NCN ligand complexes are capable of coordination in several alternative modes including *fac*-tridentate, bidentate, monodentate, and bidentate bridging two metal centers.^{1b} Combining the rigidity of PCP systems, and reactivity of NCN systems has led to the recent report of PCN systems.⁷ PCN systems have demonstrated hemilabile coordination of the amine arm in the presence of nucleophiles. Hemilability of the amine was improved by lengthening the normal methyl arm to an ethyl arm (Figure 1c). The "long arm" PCN complexes have shown increased reactivity relative to the short arm PCN complexes.^{7a} The long arm amine also enabled isolation of a rare anionic dihydride Pt^{II} complex with no stabilizing π -accepting ligands.^{7b}

A similar approach to increased hemilability has resulted in a new PNN ligand (2-(di-tert-butylphosphinomethyl)-6-diethylaminomethyl)pyridine.⁸ The coordinatively saturated complex *trans*-RuH₂(PNN)(CO) (**1**) and the symmetric PNP analogue were prepared for direct comparison of activity. **1** is an effective catalyst for the hydrogenation of non-activated esters to alcohols. The PNP analogue displayed limited reactivity, attributed to the lack of lability of the phosphine arm. TON's for the PNN complex were unprecedented for the mild conditions (no fluorinated solvents, 115 °C, 5.3 atm H₂).^{8a} Interestingly, **1** has also shown catalytic activity for the selective dehydrogenation of primary alcohols to esters.^{8b} This reverse process is driven by removal of H₂ with an Ar purge. Again, the reaction proceeds efficiently at 115 °C with no additives. Catalysis of both hydrogenation of esters, and dehydrogenation of alcohols with the PNN complex are more environmentally friendly than traditional processes with no generation of waste material. Current work has shown that **1** has great promise for industrially relevant catalysis, but more facile removal of catalyst from substrate precludes these applications.

Production of terminal alkenes as major organic feedstocks by selective dehydrogenation of aliphatic groups remains elusive despite large economical incentives.⁹ The first example of catalytic turnover for alkane dehydrogenation with a PCPIrH₂ pincer complex was achieved through hydrogen transfer from alkanes to hydrogen acceptors, such as *tert*-butylethene.¹⁰ Excess amounts of hydrogen acceptors result in slow turnover rates, and a more efficient catalytic process without sacrificial acceptors is necessary for large scale application. Mechanistic studies of hydrogen-transfer reactions have led to the development of pincer complexes capable of dehydrogenation of alkanes to alkenes with direct elimination of H₂.^{9,11} Homogenous catalytic dehydrogenations including conversion of cycloalkanes to arenes, ethylbenzene to styrene, and tetrahydrofuran to furan were all first accomplished by these improved pincer systems.

A highly active bis-phosphinite “POCOP” pincer-based catalyst (Figure 1d) for the dehydrogenation of alkanes has also recently been reported to effectively release H₂ from ammonia borane, a proposed hydrogen-storage material.¹² Experimental and computational studies of the selectivity, stability, and mechanisms of dehydrogenation with release of H₂ continue with alkanes and new hydrogen storage materials. Previous research has provided many advances toward commercially viable applications of pincer complexes in the near future.

References

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