

Dehydrogenation of Alcohols by Iridium Pincer Complexes. Synthesis of New Type Chelating Ligands

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Catalytic dehydrogenation of alcohols by three iridium pincer complexes, $\text{IrH}(\text{Cl})[2,6\text{-}(\text{tBu}_2\text{PO})_2\text{C}_6\text{H}_3]$ (**1**), $\{\text{IrH}(\text{acetone})[2,6\text{-}(\text{tBu}_2\text{PO})_2\text{C}_6\text{H}_3]\} \{\text{BF}_4\}$ (**2**) and $\text{IrH}(\text{Cl})[\{2,5\text{-}(\text{tBu}_2\text{PCH}_2)_2\text{C}_5\text{H}_5\}\text{-Ru}(\text{C}_5\text{H}_5)]$ (**3**), was studied, both in the presence and the absence of a sacrificial hydrogen acceptor. Dehydrogenation of secondary alcohols proceeds catalytically; for acceptorless dehydrogenation of 1-phenylethanol, the turnover number (TON) achieves 3420. Primary alcohols are readily decarbonylated even at room temperature to give catalytically inactive 16e Ir-CO adducts. The mechanism of this transformation was studied in details, especially in the case of EtOH; new intermediates were isolated and characterized. (*Organometallics* **2012**, accepted).

Rhodium and iridium complexes of a new ferrocene-derived bis(*N*-heterocyclic carbene) ligand, $[\text{M}(\text{cod})\{1,2\text{-(MeNCHCHNCCH}_2)_2\text{C}_5\text{H}_5\}\text{Fe}(\text{C}_5\text{H}_5)]\text{BF}_4$ (M=Rh, **8a**; M=Ir, **8b**; cod=1,5-cyclooctadiene), were synthesized from the corresponding bis(imidazolium) salt **6**. The molecular structure of **8a** was determined by X-ray diffraction. Complexes **8a** and **8b** smoothly react with CO with displacement of the chelating cod ligand to give the corresponding dicarbonyl derivatives **9a** and **9b** (*Dalton Trans.*, **2012**, 41, 9667-9671).

Precursors of the new type pincer ligands were prepared. Reaction of $[\text{CpRu}(\text{CH}_3\text{CN})_3][\text{PF}_6]$, $[\text{Cp}^*\text{RuCl}]_n$, and $[\text{Cp}^{\text{F}}\text{RuCl}]_n$ with 1,3-diformylindene give novel type zwitter-ionic complexes $[\eta^6\text{-}1,3\text{-(CHO)}_2\text{C}_9\text{H}_5]\text{RuL}$ (L=C₅H₅, C₅Me₅, C₅Me₄CF₃), whereas in the reaction of the same complexes with carbanion $\text{K}[1,3\text{-(CHO)}_2\text{C}_9\text{H}_5]$, the corresponding ruthenocenes are formed. *Russ. Chem. Bull., Int. Ed.* **2012**, №11).