VIII-D Development of New Transformations Based on a Chelation-Assistance

We have developed a series of catalytic reactions, which involve the facile cleavage of unreactive bonds, such as C–H, C–C, C–F, and C–O bonds by taking advantage of the coordination of the directing group on the transition metals. Heteroatoms, such as carbonyl oxygen or sp^2 nitrogen, function as the directing group, and the coordination of the directing group to transition metals is a key step in those catalytic reactions. Various combination of directing group and catalysts would be expected to be available.

VIII-D-1 Ruthenium-Catalyzed C-H/CO/Olefin Coupling Reaction of *N*-Arylpyrazoles. Extraordinary Reactivity of *N*-Arylpyrazoles toward Carbonylation at C–H Bonds

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The reaction of 1-arylpyrazoles with CO and ethylene in the presence of $Ru_3(CO)_{12}$ resulted in regioselective carbonylation at the ortho C–H bonds. While it is found that the pyrazole ring also functions as the directing group for C–H bond cleavage, the efficiency of the reaction depends on position of the pyrazole ring.

VIII-D-2 A Chelation- Assisted Hydroesterification of Alkenes Catalyzed by Rhodium Complex

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[*Org. Lett.* **5**, 4329–4331 (2003)]

The hydroesterification of alkenes with 2-pyridylmethanol catalyzed by $Rh_4(CO)_{12}$ is described. The reaction is accelerated by the presence of a pyridine ring in the alcohol. The reaction is applicable to various alkenes, both terminal and internal alkenes.

VIII-D-3 Ruthenium- and Rhodium-Catalyzed Direct Carbonylation of the *Ortho* C–H Bonds in the Benzene Ring of *N*-Arylpyrazoles

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The direct carbonylation of C–H bonds in the benzene ring of *N*-phenylpyrazoles *via* catalysis by ruthenium or rhodium complexes is described. The reaction of *N*-phenylpyrazoles with carbon monoxide and ethylene in the presence of $Ru_3(CO)_{12}$ or $Rh_4(CO)_{12}$ resulted in the siteselective carbonylation of the *ortho* C–H bonds in the benzene ring to give the corresponding ethyl ketones. A variety of functional groups on the benzene ring can be tolerated. *N*-Phenylpyrazoles have higher reactivities than would be expected, based on the pK_a values of the conjugate acid of pyrazole. The choice of solvent for this reaction is significant, and *N*, *N*-dimethylacetamide (DMA) gives the best result.

VIII-D-4 Catalytic Cross-Coupling Reaction of Esters with Organoboron Compounds and Decarbonylative Reduction of Esters with HCOONH$_4$: A New Route to Acyl Transition Metal Complexes through the Cleavage of Acyl-Oxygen Bonds in Esters

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The $Ru_3(CO)_{12}$-catalyed cross-coupling reaction of esters with organoboron compounds leading to ketones is described. A wide variety of functional groups can be tolerated under the reaction conditions. Aromatic boronates function as a coupling partner to give aryl ketones. Acyl-alkyl coupling to dialkyl ketones is also achieved by the use of 9-alkyl-9-BBN in place of boronates. The $Ru_3(CO)_{12}$-catalyzed decarbonylative reduction of esters with ammonium formate ($HCOONH_4$) leading to hydrocarbons is also described. No expected aldehydes are produced, and controlled experiments indicate that aldehydes are not intermediate for the transformation. A hydrosilane can also be used as a reducing reagent in place of $HCOONH_4$. A wide variety of functional groups are compatible for both reactions. The key step for both catalytic reactions is the directing group-promoted cleavage of an acyl carbon-oxygen bond in esters, leading to the generation of acyl transition metal alkoxo complexes.