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PNNL-31900

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August 2021

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U.S. DEPARTMENT OF ENERGY

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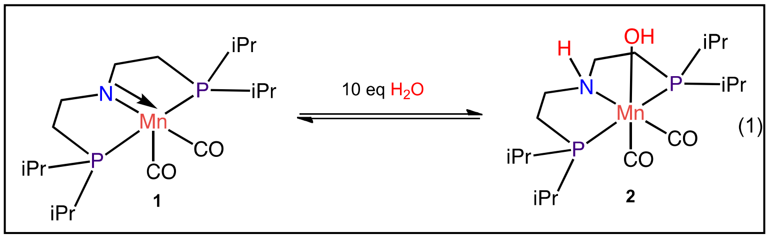
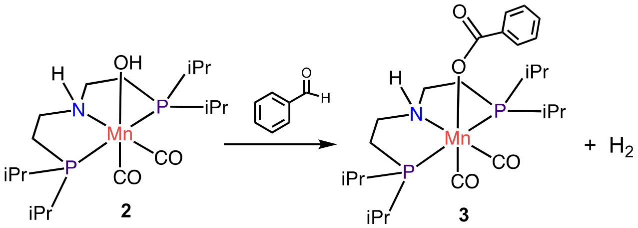
1.0 Introduction

In recent years, we have been involved in a project that is directed toward the catalytic decomposition of formic acid to generate gas pressure to do PV type work. During the search for viable formic acid decomposition catalysts, we have synthesized dozens of novel transition metal complexes of many different metals including complexes of Mn, [1,2] Fe,[3] Co, Ni, Cu, Ru,[4] Rh, Ir and Re. While some of these compounds have been useful for formic acid decomposition catalysis, many of them also possess other unusual properties and reactivity and can serve as catalysts for other interesting transformations. We propose to investigate and develop the chemistry of these compounds to develop capabilities in the synthesis and characterization of air sensitive materials. This portion of the project will serve as a gateway to more experimentally challenging actinide organometallic chemistry.

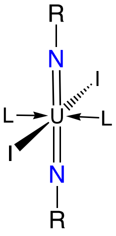
The Mn complex, **1**, shown in eq (1), reacts reversibly with water to give the hydroxide complex, **2**. While this reaction may seem trivial, the resultant metal complex has a very nucleophilic hydroxide ligand because its d^6 electronic structure prevents p donation to the metal center from the hydroxide lone pair p orbital. The complex is very soluble in hydrocarbons (>0.1M) and can be a source of nucleophilc hydroxide under “neutral” anhydrous pH conditions with a very high effective concentration of hydroxide. Under these conditions, there can be no modulation of hydroxide reactivity through hydrogen bonding to water molecules. The reactivity of the hydroxide complex, **2**, is fascinating. Compounds **1** and **2** are catalysts for the hydration of nitriles to form the corresponding amides. Interestingly, these catalysts do not display further reactivity for the hydration of the product amide to the carboxylic acid. The manganese hydroxide complex also reacts with water and aldehydes to give hydrogen and the carboxylate/amine complex as shown in eq (2). The transformation in eq (2) is similar to the Cannizzaro reaction except that water is the oxidant rather than a second equivalent of aldehyde. Making this transformation catalytic in the metal complex would be of great practical value since water is a readily available and “green” reagent and hydrogen is a valuable coproduct.





(2)

Compound **1** is inherently reactive because of the steric and electronic properties of the tridentate pincer ligand. Complex **1** is coordinatively unsaturated (5 coordinate), and possesses an 18 electron count only as a result of p donation from the ligand backbone amide N atom. In the reactions in eq (1) and eq (2), a lone pair of electrons on the ligand is intimately involved in the reaction chemistry, facilitating substrate activation by providing a “home” for the proton during H-X activation. This type of reactivity has been demonstrated to be important in the activation of hydrogen during metal catalyzed hydrogenation reactions. As a result, the use of pincer complexes related to compounds **1** and **2** as hydrogenation catalysts has dominated the chemistry of metal complexes of the and related ligands in the literature.



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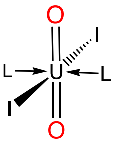

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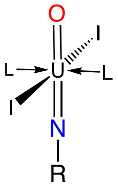

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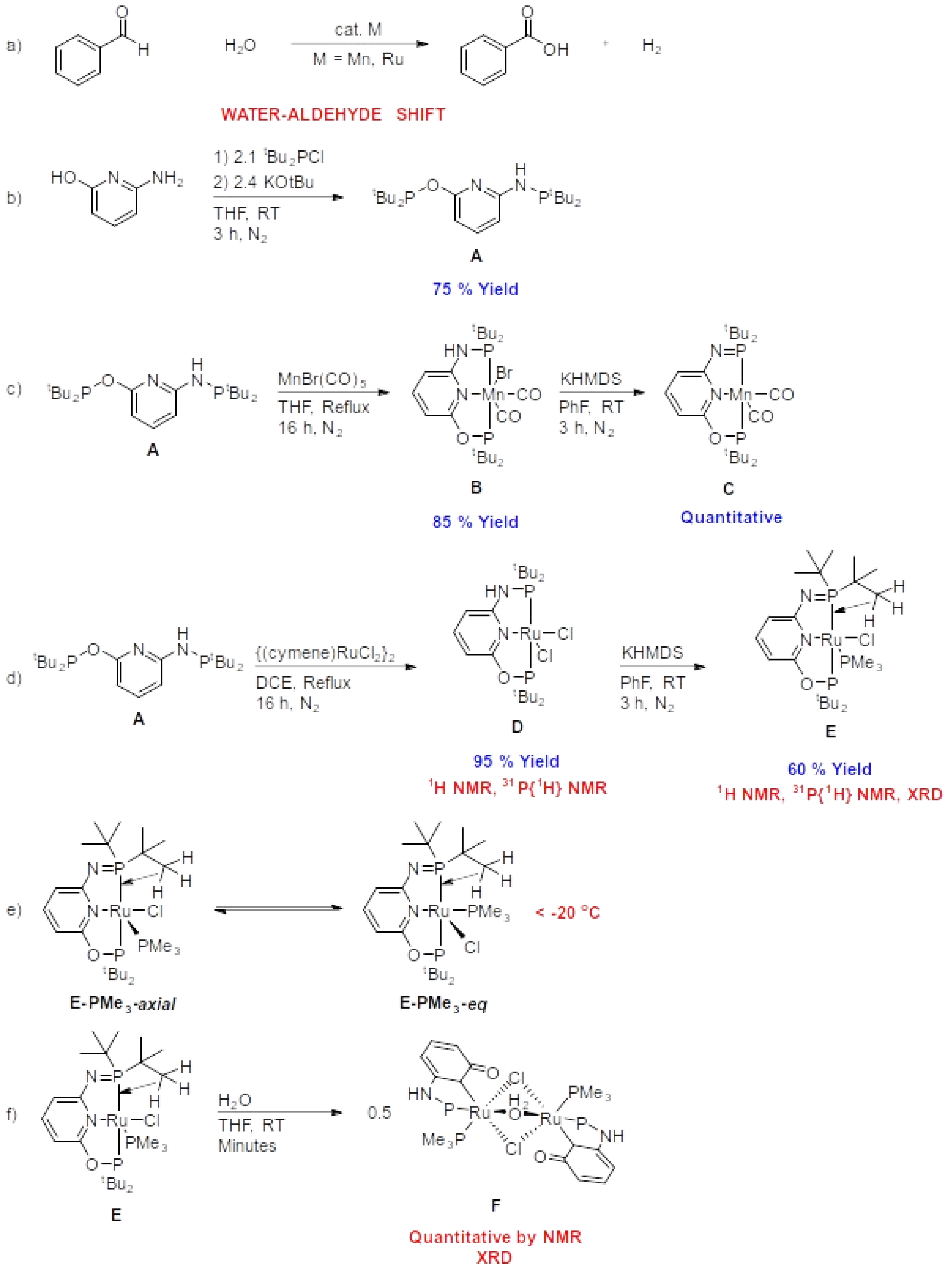
In the Mn portion of this project, we will investigate the non-hydrogenation reactivity of this family of metal complexes.

During the exploration of the chemistry of uranium nitrogen compounds, we discovered a simple procedure for the preparation of the first imido analogue, **4**, of the ubiquitous uranyl group, **5**.[5] This much sought after family of compounds has provided a unique opportunity to explore and consequently develop a deeper understanding of the role of covalency in the metal-ligand bonding of the actinide elements. The results of these studies have demonstrated that the uranium center in these molecules is a significantly softer Lewis acid than in the analogous uranyl complexes and that there is a greater degree of covalency in the U=N vs U=O interaction.[6] We have also been able to synthesize the mixed oxo-imido complexes, **6**.[7] This suite of compounds has given us the opportunity to explore and understand how ligand substituent effects are transmitted through the U=E (E = N, O) multiple bond to the metal center. The chemistry of the oxo-imido complexes an area of research that has not been explored to any significant extent. The compounds are readily synthesized and their chemistry is completely unexplored. We have also discovered that differences in the bonding in the U=N manifold leads to chemistry of the imido group that is unprecedented for the analogous uranium oxo groups.[8] Having both functionalities in the same molecule will allow us to discover whether there internal synergistic effects are possible.

2.0 Organomanganese and organoruthenium hydration catalysis

There is a great deal of interest in using transition-metal catalysts, for the water-aldehyde shift reaction, where an organic aldehyde is effectively oxidized by H_2O with the concomitant release of H_2 (Scheme 1a). These reactions do not require stoichiometric quantities of metal, use significantly less toxic reagents and solvents, and do not require O_2 as the terminal oxidant: in these cases the use of a stoichiometric reductant to turnover the catalyst sites is typically required. A variety of Mn and Ru complexes supported by a $PNNOP^{tBu}$ ligand (**A**) have been synthesized. The synthesis of **A** is achieved by reacting 2-amino-6-hydroxypyridine with $^tBu_2PCl$ followed by the addition of suspended or solid KO^tBu in THF. Washing the crude oil with H_2O and drying at 70 °C under vacuum overnight yields a white crystalline solid in 75 % yield. The metalation of **A** with $MnBr(CO)_5$ requires refluxing in THF overnight to yield $(PNNOP^tBu)MnBr(CO)_2$ (**B**, Scheme 1c) as a crystalline purple solid. Interestingly, the ^1H NMR behavior of **B** varies greatly depending the H_2O content of the NMR solvent. Using rigorously dried CD_2Cl_2 results in an exceedingly broad ^1H NMR spectrum, potentially indicative of oxidation to paramagnetic Mn(II). Using benchtop CD_2Cl_2 that contains even trace H_2O results in a sharp ^1H NMR spectrum. We hypothesize that the coordination of Br ligand to Mn is reversible and the free Br is potentially interacting with the -NH moiety, and we suspect that small amounts of H_2O in the solvent slows down this exchange process. Additionally, attempted metalation in THF or DCE at 50 °C yields ~10% of the tricarbonyl species $(PNNOP^tBu)MnBr(CO)_3$ (not shown). Dehydrohalogenation of **B** with KHMDS in PhF quantitatively yields $(PNNOP^tBu - H)Mn(CO)_2$ (**C**) as a purple powder (Scheme 1c). Metalation of **A** with $\{(cyeme)RuCl_2\}_2$ in refluxing DCE overnight yields $(PNNOP^tBu)RuCl_2$ (**D**) as a crystalline green solid in 95 % yield (Scheme 1d). The ^1H and $^{31}P\{^1H\}$ NMR spectra of **D** is broad due to isomerization between square-pyramidal and trigonal bipyramidal geometries. Rection of **D** with PMe_3 following by dehydrohalogenation with KHMDS in PhF yields $(PNNOP^tBu - H)Ru(PMe_3)Cl$ (**E**) as a brown powder in 60 % isolated yield due to high solubility; the reaction is quantitative by $^{31}P\{^1H\}$ NMR (Scheme 1d). Crystals of **E** were grown in DCM/Hex at -35 °C over a week and analyzed by single-crystal X-ray diffraction. The Ru center of **E** in the solid-state is six-coordinate with one of the Me groups of the ^tBu substituents on the N=P arm binding *via* a γ-agostic interaction. The γ-agostic interaction is seemingly present in solution as well: in CD_2Cl_2 there are 4 ^tBu resonances observed with one being significantly shielded relative to the other three. The $^{31}P\{^1H\}$ NMR is unexpectedly broad at room temperature however, and by VT NMR this broadness is not due any dynamic process involving the γ-agostic hydrogen. Below -20 °C, two species are observed in a 4/1 ratio and based on the chemical shift difference between the two species' PMe_3 resonances of ~ 30 ppm, we suspect that the broadness at RT is due to the isomerization of **E** between its **E-PMe$_3$-axial** and **E-PMe$_3$-eq** forms (Scheme 1e).

The catalytic water-aldehyde shift reaction using benzaldehyde and complex **C** was attempted, which unfortunately results in no conversion of the reactants and decomposition of **C** into a white, insoluble Mn(II) salt. Reaction of **E** with H_2O instantaneously cleaves the P-O bond of the ligand, releasing $^tBu_2P(=O)H$, resulting in the formation aqua-bridged dimer **F** (Scheme 1f). While the reactivity of the P-O bond of the $PNNOP^{tBu}$ ligand may preclude its use in the water-aldehyde shift reaction with Ru out right, we suspect that the bulky ^tBu groups prevents binding of the organic substrates to the metal center. The next step is to synthesize the $PNNOP^{iPr}$ ligand, which has less bulky ^iPr groups, and synthesize the analogous Mn and Ru compounds and test their catalytic potential in the water-aldehyde shift reaction.



Scheme 1: Reaction schemes for hydration catalysts

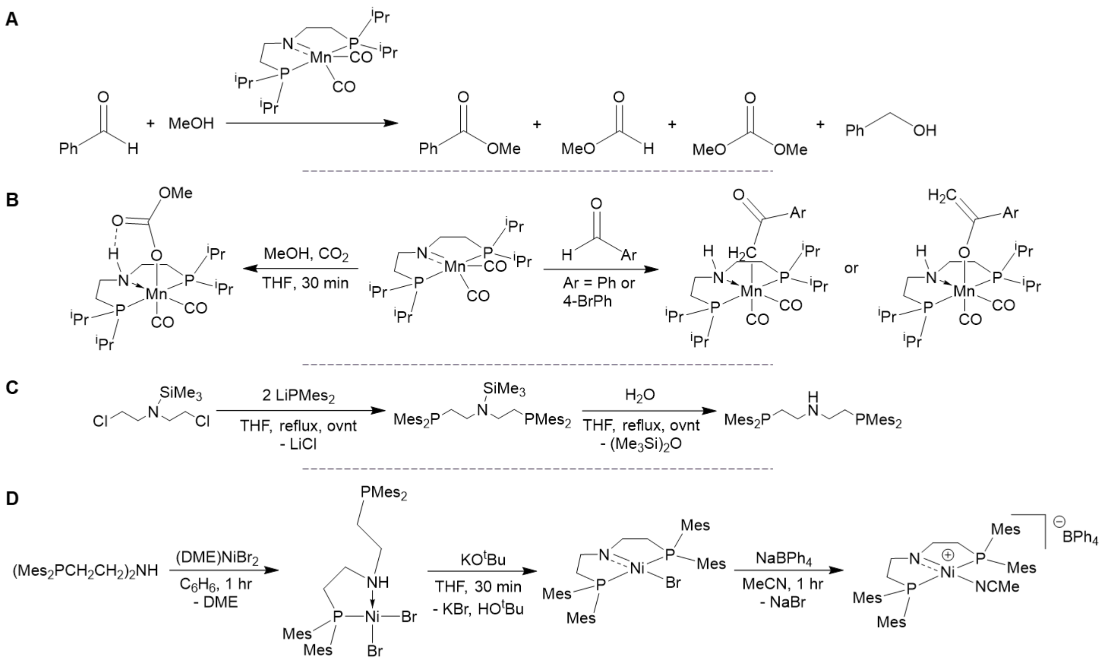
3.0 New reactivity of ^{i}PrPNPMn(CO)$_2$ and a bulky PNP pincer ligand

3.1 ^{i}PrPNPMn(CO)$_2$ new reactivity

^{i}PrPNPMn(CO)$_2$ has been shown to hydrate aldehydes (R-C=O) to yield carboxylic acids (R-C(O)OH). Analogously, it was hypothesized that ^{i}PrPNPMn(CO)$_2$ may be able to produce methyl esters (R-C(O)OMe) via coupling methanol (MeOH) and aldehydes (R-C=O). ^{i}PrPNPMn(CO)$_2$ does indeed couple benzaldehyde and methanol, however a significant amount of homocoupled methanol and benzyl alcohol is also produced as a result of methanol transfer hydrogenation forming formaldehyde (scheme 2A). Attempts to obtain the desired compound PhCOOMe cleanly were unsuccessful. ^{i}PrPNPMn(CO)$_2$ reacts with methanol and carbon dioxide to form ^{i}PrPNHPMn(CO)$_2$OC(O)OMe (scheme 2B). ^{i}PrPNPMn(CO)$_2$ reacts with a variety of element-H bonds such as mineral acids, organic acids, inorganic acids, alcohols, hydrogen, phenyl acetylenes, phenylsilane, and pinacol borane. This activation chemistry has been extended to the addition of acetophenones to ^{i}PrPNPMn(CO)$_2$ (scheme 2B).

3.2 MesPNHP and transition metal complexes

Bis((di(2,4,6-trimethylphenyl))phosphinoethyl)amine (MesPNHP, Mes = 2,4,6 – trimethylphenyl) was synthesized by refluxing two equivalents of lithium dimesitylphosphide with bis(chloroethyl)trimethylsilylamine in THF overnight, followed by deprotection with degassed water (scheme 2C). MesPNHP has been characterized by solution NMR spectroscopy. MesPNHP coordinates to several transition metals. MesPNHP reacts with dimethoxyethane nickel(II) bromide to form MesPNHPNiBr$_2$ (scheme 2D). By solution NMR, MesPNHPNiBr$_2$ appears to have one PMes2 arm coordinated to Ni whereas the other is dangling off in space. However, the arms are exchanging on the NMR time scale as evidenced by variable temperature ^{31}P NMR. MesPNHPNiBr$_2$ reacts with one equivalent of KO^{t}Bu to produce MesPNPNiBr. The bromide can be extracted with NaBPH$_4$ to form the salt [MesPNPNiNCMe][BPh$_4$]. [MesPNPNiNCMe][BPh$_4$] adds water across the Ni-N bond reversibly to form a Ni-OH which may have interesting reactivity. Preliminary evidence shows that MesPNHP also reacts cleanly with [(cymene)RuCl$_2$]$_2$ and FeCl$_2$ to yield [MesPNHPRuCl$_2$]$_2$ and MesPNHPFeCl$_2$ complexes, respectively. MesPNHP reacts with Mn(CO)$_5$Br forming Mn(II) decomposition products rather than the desired MesPNHPMn(CO)$_2$Br complex.



Scheme 2: Main reaction schemes for ^{i}PrPNPMn(CO)$_2$ and a new pincer ligand

4.0 Conclusion

This project has demonstrated the development, synthesis and isolation of new transition metal catalysts as candidates for the water-aldehyde shift reaction. A number of catalysis based on manganese and ruthenium were synthesized and their structures determined by X-ray diffraction and NMR spectroscopy. They showed no catalytic activity with aldehydes due to the steric bulk of the PNNOP ligand. Future work will explore replacing the butyl substituents on the ligand with propyl group to allow more facile approach of the reactants to the catalytic center. The manganese catalyst, ^{i}PrPNPMn(CO)$_2$, has been found promote reaction of acetophenones to the metal center. The new pincer ligand, MesPNHP, has been successfully synthesized and found to coordinate to several transition metals including Ni(II), Mn(II) and Fe(II) with interesting dynamical behavior as measured by NMR spectroscopy for the former complex.

5.0 Acknowledgements

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