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### **Basicity of Phosphaguanidine, and its Ru(II) Complex for CO<sub>2</sub> Hydrogenation**

Guanidines [(R<sub>2</sub>N)<sub>2</sub>C=NR] are superbases; their nucleophilic and basic properties have been widely used in organic reactions. When coordinated with metals, the basic N<sub>imine</sub> loses basicity. Replacing one of the less basic N<sub>amine</sub> with P encourages coordination to take place there, rather than or in addition to at the N<sub>imine</sub>, potentially preserving the nucleophilicity and basicity. If the ligand coordinates by both the P and the N<sub>imine</sub>, then the binding at the N<sub>imine</sub> is anticipated to be weak, making the ligand hemilabile when coordinated to soft metals.

Hemilabile ligands are useful because the activity at the metal centre can be manipulated and controlled by the labile groups. P,N donors are widely used hemilabile ligands in coordination and organometallic chemistry. Phosphorus is generally considered a soft donor and inert. Alternatively, nitrogen is considered a harder donor and is labile. Late transition metals can complex with either the P or the N as a monodentate ligand or through both the P and the N as a bidentate ligand depending on the hardness of the metal centre and the ligand sterics.

Phosphaguanidines [R<sub>2</sub>NC(PR<sub>2</sub>)=NR] are one of the most promising hemilabile ligands that can coordinate to a metal centre. Having the basic sites near the metal centre should promote hydrogen bond dissociation and assist in catalytic reactions like CO<sub>2</sub> hydrogenation by transfer of proton. We have developed an easy route to prepare acyclic and aprotic phosphaguanidine hemilabile ligands that coordinate to the metal centre through the P atom and maintain the Brønsted basicity at the N<sub>imine</sub>. Furthermore, phosphaguanidine Ru(II) complex and an *in situ* mixture of Rh(I) and the phosphaguanidine are shown to act as precatalysts for CO<sub>2</sub> hydrogenation to formic acid.

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