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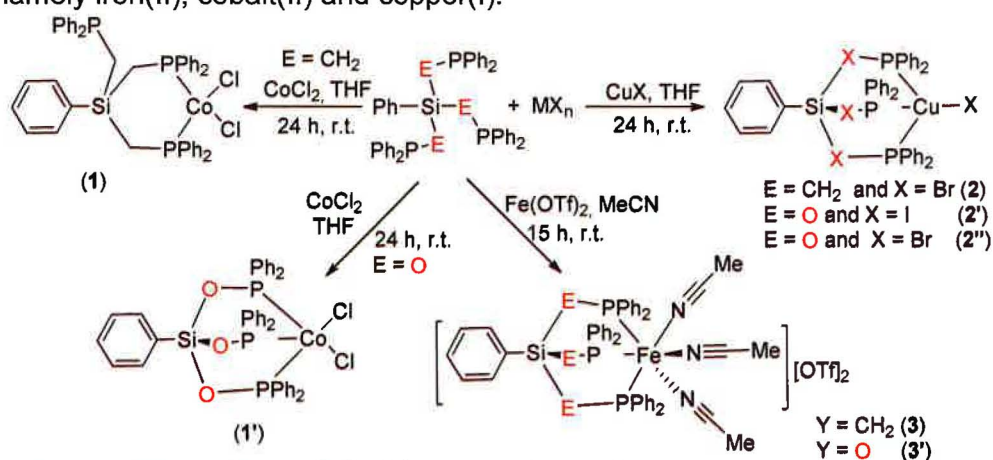
## COMPLEXES OF TRIPODAL PHOSPHINE LIGANDS: SYNTHESIS, STRUCTURE AND CATALYTIC ACTIVITIES IN THE HYDROBORATION OF CO<sub>2</sub><sup>1</sup>

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Tripodal ligands play a major role in transition metal chemistry by increasing the stability of their complexes and enabling a fine control of the reactivity at the metal center through their steric and electronic properties and their specific coordination geometry. Among these ligands, triphos (MeC(CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>) has attracted considerable attention over the last years as it was successfully used for several applications in catalysis, including CO<sub>2</sub> hydrogenation, disproportionation of formic acid and reduction of amides<sup>2</sup>. Because small changes within a ligand can induce different outcomes in a catalytic reaction, variations on the triphos backbone have been reported<sup>3</sup>. In this study we report the use of PhSi(CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub> and its phosphinite derivative PhSi(OPPh<sub>2</sub>)<sub>3</sub> in the coordination chemistry of first-row transition metals, namely iron(II), cobalt(II) and copper(I).



Scheme: Synthesis of iron, cobalt and copper complexes with PhSi(EPPH<sub>2</sub>)<sub>3</sub> ligands (E = O, CH<sub>2</sub>)

Because CO<sub>2</sub> is a stable chemical waste, its selective multi-electron reduction under mild conditions remains a challenge<sup>4</sup> and an ideal platform to establish structure/activity relationships for analogous catalysts. The catalytic activity of complexes (1, 1', 2, 2', 2'', 3, 3') was thus evaluated in the hydroboration of CO<sub>2</sub> so as to determine the influence of the metal center and the electronic nature of the ligand in this model reaction. Within this range of complexes (scheme), copper catalysts (2 and 2') are both more reactive and more selective, enabling the formation of an acetal product from CO<sub>2</sub>.

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