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A Aloisi, J.-C Berthet, C Genre, Pierre Thuéry, T Cantat. Complexes of tripodal phosphine ligands: synthesis, structure and catalytic activities in the hydroboration of C0_2. GECOM ConCOORD, May 2017, Forges-les-Eaux, France. cea-02342083

HAL Id: cea-02342083

<https://cea.hal.science/cea-02342083>

Submitted on 31 Oct 2019

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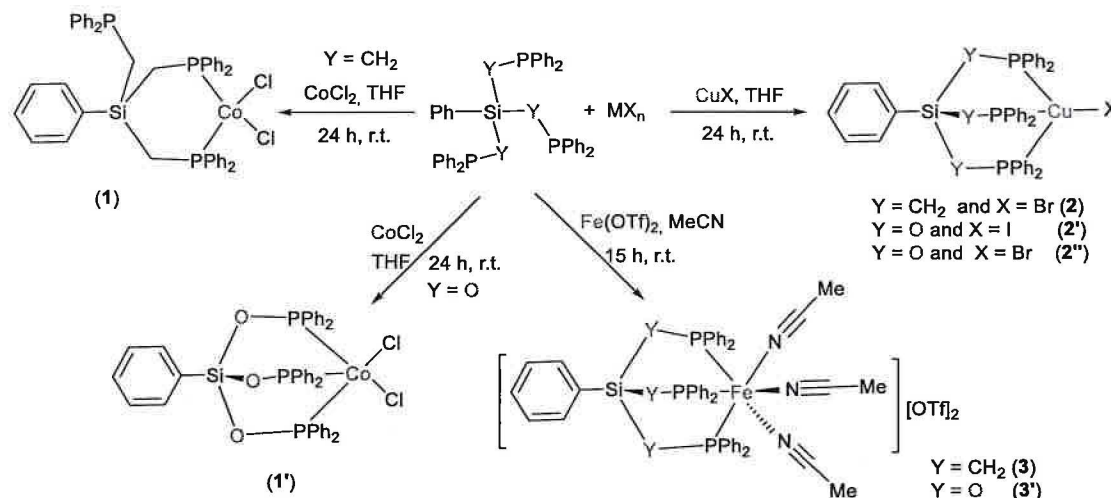
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Complexes of tripodal phosphine ligands: synthesis, structure and catalytic activities in the hydroboration of CO₂

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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 those ligands, triphos (MeC(CH₂PPh₂)₃) has attracted considerable attention these years as it was successfully used for several applications in catalysis, including CO₂ hydrogenation, disproportionation of formic acid and reduction of amides.¹ Because small changes within a ligand can induce different outcomes in a catalytic reaction, variations on the triphos backbone have been reported.² We report here the use of PhSi(CH₂PPh₂)₃ and its phosphinite derivative PhSi(OPPh₂)₃ in the coordination chemistry of first-row transition metals with iron(II), cobalt(II) and copper(I) (scheme 1).



Scheme 1: Synthesis of the Fe(II), Co(II) and Cu(I) complexes with the PhSi(YPPH₂)₃ (Y = O, CH₂) ligands

Because CO₂ is a stable chemical waste, its selective multi-electron reduction under mild conditions is challenging³ and an ideal platform to establish structure/activity relationships for analogous catalysts. The catalytic activity of each of the above complexes was evaluated in the hydroboration of CO₂ so as to determine the influence of the metal center and the electronic nature of the ligand in this model reaction. Among those complexes, copper catalysts (2 and 2') are the most reactive and display increasing selectivity enabling the formation of acetal.⁴

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