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► **To cite this version:**

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 CO₂. Journées de Chimie de Coordination de la SCF, Jan 2017, Grenoble, France. cea-02342086

HAL Id: cea-02342086

<https://hal-cea.archives-ouvertes.fr/cea-02342086>

Submitted on 31 Oct 2019

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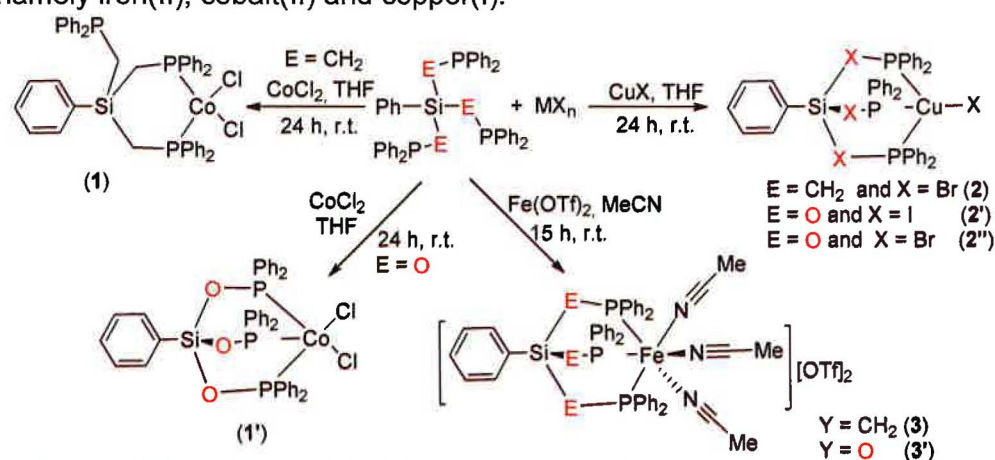
COMPLEXES OF TRIPODAL PHOSPHINE LIGANDS: SYNTHESIS, STRUCTURE AND CATALYTIC ACTIVITIES IN THE HYDROBORATION OF CO₂¹

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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(CH₂PPh₂)₃) has attracted considerable attention over the last years as it was successfully used for several applications in catalysis, including CO₂ hydrogenation, disproportionation of formic acid and reduction of amides². Because small changes within a ligand can induce different outcomes in a catalytic reaction, variations on the triphos backbone have been reported³. In this study we report the use of PhSi(CH₂PPh₂)₃ and its phosphinite derivative PhSi(OPPh₂)₃ 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(E)PPh₂ ligands (E = O, CH₂)

Because CO₂ is a stable chemical waste, its selective multi-electron reduction under mild conditions remains a challenge⁴ 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 CO₂ 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 CO₂.

Acknowledgments : This work was supported financially by the CEA, CNRS, CHARMMMAT Laboratory of Excellence, and the European Research Council (ERC starting grant agreement no. 336467). T.C. thanks the Foundation Louis D.-Institut de France for its support. The authors thank Dr. Emmanuel Nicolas for fruitful discussions regarding NMR spectroscopy.

Statut : Doctorant, 2^e année

N° adhérent SCF : (si applicable) 28363

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