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Synthesis, structure and electrochemical behavior of new R^{PONOP} ($R = {}^t\text{Bu}$, ${}^i\text{Pr}$) pincer complexes of Fe^{2+} , Co^{2+} , Ni^{2+} , and Zn^{2+} ions

Synthèse, structure et comportement électrochimique de nouveaux complexes pinceurs des ions divalents Fe^{2+} , Co^{2+} , Ni^{2+} and Zn^{2+} avec les ligands R^{PONOP} ($R = {}^t\text{Bu}$, ${}^i\text{Pr}$)

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ABSTRACT

The coordination chemistry of the M^{2+} ions of the first-row elements iron, cobalt, nickel and zinc was explored with the ligands R^{PONOP} (2,6-($R_2\text{PO}$)($\text{C}_5\text{H}_3\text{N}$), $R = {}^i\text{Pr}$ and ${}^t\text{Bu}$). Syntheses and characterization of the complexes $\text{Fe}(R^{\text{PONOP}})\text{Br}_2$, $\text{Co}({}^t\text{BuPONOP})\text{Cl}_2$, $\text{Ni}({}^i\text{PrPONOP})\text{I}_2$ and $\text{Zn}({}^i\text{PrPONOP})\text{I}_2$ ($R = {}^t\text{Bu}$, ${}^i\text{Pr}$) are reported together with the crystal structures of $\text{Fe}(R^{\text{PONOP}})\text{Br}_2$ ($R = {}^i\text{Pr}$ and ${}^t\text{Bu}$), $\text{Co}({}^t\text{BuPONOP})\text{Cl}_2$, $\text{Co}({}^i\text{PrPONOP})\text{Cl}(\mu\text{-Cl})\text{CoCl}_2(\text{THF})$, $\text{Ni}({}^i\text{PrPONOP})\text{I}_2$, $\text{Zn}({}^i\text{PrPONOP})\text{I}_2$ and of the oxidation product $\text{Zn}({}^t\text{BuP}(=\text{O})\text{ONOP}(=\text{O}))\text{I}_2$ resulting from the reaction with oxygen. The electrochemical behavior of the $M({}^t\text{BuPONOP})\text{X}_2$ complexes has been investigated in acetonitrile. While the nickel compound is stable, all the complexes are sensitive to dissociation of the R^{PONOP} ligand or ligand scrambling in strongly coordinating media. Catalytic activity in formic acid dehydrogenation with TONs up to 1143 has been found for $\text{Ni}({}^t\text{BuPONOP})\text{I}_2$.

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R É S U M É

La chimie de coordination des ions divalents M^{2+} des éléments de la première ligne de la classification périodique a été explorée pour le fer, le cobalt, le nickel et le zinc avec les ligands R^{PONOP} (2,6-($R_2\text{PO}$)($\text{C}_5\text{H}_3\text{N}$), $R = {}^i\text{Pr}$ et ${}^t\text{Bu}$). Les synthèses et les caractérisations des complexes $\text{Fe}(R^{\text{PONOP}})\text{Br}_2$, $\text{Co}({}^t\text{BuPONOP})\text{Cl}_2$, $\text{Ni}({}^i\text{PrPONOP})\text{I}_2$ et $\text{Zn}({}^i\text{PrPONOP})\text{I}_2$ ($R = {}^t\text{Bu}$, ${}^i\text{Pr}$) sont présentées avec les structures cristallines des composés $\text{Fe}(R^{\text{PONOP}})\text{Br}_2$ ($R = {}^i\text{Pr}$ et ${}^t\text{Bu}$), $\text{Co}({}^t\text{BuPONOP})\text{Cl}_2$, $\text{Co}({}^i\text{PrPONOP})\text{Cl}(\mu\text{-Cl})\text{CoCl}_2(\text{THF})$, $\text{Ni}({}^i\text{PrPONOP})\text{I}_2$, $\text{Zn}({}^i\text{PrPONOP})\text{I}_2$ et celle du dérivé $\text{Zn}({}^t\text{BuP}(=\text{O})\text{ONOP}(=\text{O}))\text{I}_2$ résultant de l'oxydation de $\text{Zn}({}^i\text{PrPONOP})\text{I}_2$ par l'oxygène de l'air. Le comportement électrochimique des complexes $M({}^t\text{BuPONOP})\text{X}_2$ a été étudié dans l'acétonitrile. À l'exception du complexe du nickel, les complexes s'avèrent

Mots-clés:

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instables et tendent à perdre leur ligand R^i PONOP ou à se réarranger dans un milieu fortement coordonnant. $Ni(t^iBuPONOP)I_2$ montre une activité catalytique dans la déshydrogénation de l'acide formique, avec un TON atteignant 1143.

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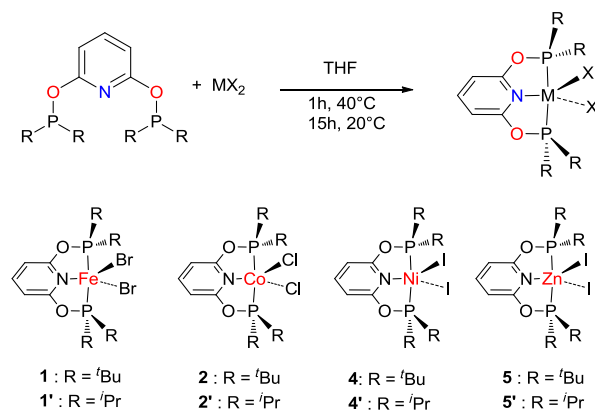
1. Introduction

Polydentate ligands play a crucial role in transition metal chemistry, as they increase the stability of their complexes and enable a fine control of the reactivity at the metal center through their steric and electronic properties. For these reasons, mixed hard/soft donor pincer ligands have been considerably studied for their ability to stabilize metal cations in a variety of oxidation states [1] and for their role in stoichiometric and catalytic reactions [2]. A plethora of pincer ligands, coordinated to a number of d and f transition metals, has now been reported in the literature. Recently, a series of neutral mixed hard/soft donor pincer ligands has attracted considerable attention, in particular the PNP-type 2,6-(R_2PX)(C_5H_3N) ($X=O, CH_2, NH$) ligands containing a central pyridine connected to two PR_2 fragments. Considerable work, by the groups of Milstein, Jones, Brookhart and others, has demonstrated the importance of such ligands and the non-innocent role of X in hydrogen transfer catalysis [2,3]. With the reactive $X=NH_2$ or CH_2 moiety replaced by an oxygen atom ($X=O$), the $R_2PO(py)OPR_2$ (PONOP) ligands offer the advantage of a convenient and facile synthesis, but the potential of the corresponding complexes remains quite unexplored. Indeed, only a handful of PONOP complexes have been reported and structurally characterized, mostly with noble metals of the second and third rows (Ru, Rh, Pd, Ir, and Pt) [4–9] and recently with Ni [6,9] and Co [10] for metals of the first row. Here we report the synthesis and structural characterization of a series of R^i PONOP complexes with late first row divalent metals (Fe, Co, Ni, and Zn) and their electrochemical behavior in organic solvents.

2. Results and discussion

2.1. Syntheses and crystal structures of the complexes

The R^i PONOP ligands were prepared following literature protocols by mixing the 1,6-dihydroxy pyridine hydrochloride salt in THF with di(*tert*-butyl)-chlorophosphine or di(*isopropyl*)-chlorophosphine in the presence of triethylamine and tetramethylethylenediamine [4,8,9]. The series of $M(t^iBuPONOP)X_2$ ($MX_2 = FeBr_2$ (**1**), $CoCl_2$ (**2**), NiI_2 (**4**), ZnI_2 (**5**)) and $M(iPrPONOP)X_2$ ($MX_2 = FeBr_2$ (**1'**), NiI_2 (**4'**), ZnI_2 (**5'**)) complexes was then readily synthesized by the addition of $t^iBuPONOP$ or $iPrPONOP$ to the anhydrous MX_2 halides (Scheme 1). Because of the poor solubilities of the metal halide starting materials, a polar solvent such as THF is preferred over toluene in order to avoid extended reaction time. The reaction procedure is similar for all the compounds with initial heating at 40 °C for 1 h and then stirring overnight at room temperature. All the compounds proved to be soluble in THF except $Ni(t^iBuPONOP)_2$ (**4**) which



Scheme 1. Synthesis of the $M(R^iPONOP)X_2$ complexes ($R = t^iBu$ and iPr).

deposited as a dark-red solid from the crude mixture. Removal of the solvent and washings with pentane of the solid residue afforded pure $M(R^iPONOP)X_2$ compounds with yields ranging from 77 to 83%.

All the compounds have been characterized by elemental analysis and 1H , ^{31}P and $^{13}C\{^1H\}$ NMR spectra except $Co(t^iBuPONOP)Cl_2$ (**2**), for which paramagnetism of the $3d^7 Co^{2+}$ ion impedes any NMR observation. While the 1H NMR signals of the $3d^8$ nickel complex **4** are relatively narrow and in the diamagnetic zone (δ 1.65 (t^iBu) and 7.12 and 8.22 for the pyridine moiety), the corresponding signals for the $3d^6$ paramagnetic iron analog **1** are large and strongly shifted at δ 16.89 (t^iBu) and -20.39 and 54.01 for the pyridine signals, respectively, with full width at half maximum in the range of 70–150 Hz.

In contrast to **1**, **2**, and **5**, the nickel complex **4** is almost insoluble in THF. While $[Ni(t^iBuPONOP)Cl][Cl]$ is cationic in THF [9], the insolubility of **4** would suggest the formation of a similar species, e.g. $[Ni(t^iBuPONOP)I][I]$. Formation of discrete ion pairs for **4** and **4'** would also be in agreement with the lesser coordinating properties of iodide compared to the chloride anion. Surprisingly, **4'** crystallized in the neutral form $[Ni(t^iBuPONOP)_2]$ (vide infra), suggesting that an equilibrium exists in solution between the cationic and neutral forms.

Crystallization of compounds **1**, **2**, **4**, and **5** was attempted by slow diffusion of pentane into a THF solution of the complex. With the $t^iBuPONOP$ ligand, only the iron complex **1** and the cobalt analog **2** crystallized as large yellow and blue crystals, respectively. Changing the solid $t^iBuPONOP$ with the liquid $iPrPONOP$ ligand clearly favored crystallization and the iron and nickel compounds **1'** and **4'** were obtained under conditions similar to those giving **1** and **2** whereas the zinc complex **5'** was obtained by cooling

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