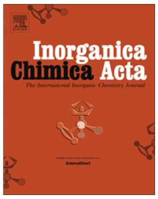
ARTICLE IN PRESS

Inorganica Chimica Acta xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica



Synthesis, characterization and reactivity of vanadium, chromium, and manganese PNP pincer complexes

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ARTICLE INFO

Article history:
Received 28 January 2016
Accepted 29 February 2016
Available online xxxx

Keywords:
Vanadium
Chromium
Manganese
Pincer ligands
Homo coupling

ABSTRACT

The synthesis of a series of vanadium, chromium, and manganese PNP complexes of the types [M(PNP)Cl_3] (M = V, Cr) and [M(PNP)Cl_2] (M = Cr, Mn) is reported. Vanadium and manganese PNP pincer complexes are described for the first time. All complexes are characterized by their magnetic moments, elemental analysis, and ESI MS. In addition, some compounds are characterized by X-ray crystallography. In a preliminary study, these complexes catalyze the oxidative homo-coupling of aryl Grignard reagents in the presence of MeI as oxidizing agents to give symmetrical biaryls, but are inactive in Kumada cross-coupling reactions. The reactivity of V(III), Cr(III), Cr(II) and Mn(II) is compared with related Fe(II) and Co(II) complexes of the types [Fe(PNP-*i*Pr)Cl_2], and [Co(PNP-*i*Pr)Cl_2]. In all cases, good to excellent isolated yields are obtained. However, since the respective metal chlorides in the absence of PNP ligands exhibited comparable reactivities, the new PNP complexes offer no real advantage for this type of coupling reactions.

1. Introduction

Among the many ligand systems that can be found in the chemical literature pincer ligands play an important role and their complexes have attracted tremendous interest due to their high stability, activity and variability [1]. These tridentate ligands are often planar scaffolds consisting of neutral central pyridine backbone tethered to two, mostly bulky, two-electron donor groups by different spacers. In this family of ligands steric, electronic, and also stereochemical parameters can be manipulated by modifications of the substituents at the donor sites and/or the spacers. Accordingly, many applications of mostly precious second and third row transition metal pincer complexes in the fields of catalysis, molecular recognition and supramolecular chemistry were discovered turning this area into an intensively investigated subject in organometallic chemistry. As non-precious first-row transition metals are concerned, the chemistry of neutral pyridine-based iron [2–7] and cobalt [8,9] PNP complexes experienced an impressive upswing in recent years. Reports on chromium [10], nickel [11,12], and copper [13] PNP pincer complexes are still rare, while vanadium, manganese, and titanium PNP pincer complexes appear to be unknown as yet.

We are currently focusing on the chemistry of non-precious metal complexes containing PNP pincer ligands based on the 2,6-diaminopyridine scaffold, where the pyridine ring and the phosphine moieties are connected via NH, N-alkyl, or N-aryl linkers (Scheme 1) [14].

Herein we report on the synthesis, characterization and reactivity of a series of new vanadium, chromium, and manganese PNP complexes of the types [M(PNP)Cl_3] (M = V, Cr) and [M(PNP)Cl_2] (M = Cr, Mn). In a preliminary study, these complexes were found to catalyze the homo-coupling of PhMgBr in the presence of MeI or atmospheric oxygen as oxidizing agents, but were inactive for cross coupling reactions.

2. Results and discussion

Treatment of [$MCl_3(THF)_3$] (M = V, Cr) with the PNP ligands **1a**–**g** in THF affords the six-coordinate 14e and 15e complexes [V(PNP)Cl_3] (**2a**–**e**,**2g**) and [Cr(PNP)Cl_3] (**3a**–**f**) in high isolated yields (93–99%), respectively (Scheme 2). Likewise, the reaction of anhydrous MCl_2 (M = Cr, Mn) with 1 equiv of the PNP ligands **1a**–**g** in THF at room temperature afforded the five-coordinate 14e and 15e complexes [Cr(PNP)Cl_2] (**4a**–**f**) and [Mn(PNP)Cl_2] (**5a**–**e**,**5g**) in 92–98% isolated yields (Scheme 3). All complexes display large paramagnetic shifted and very broad ^1H NMR signals and thus were not

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http://dx.doi.org/10.1016/j.ica.2016.02.064
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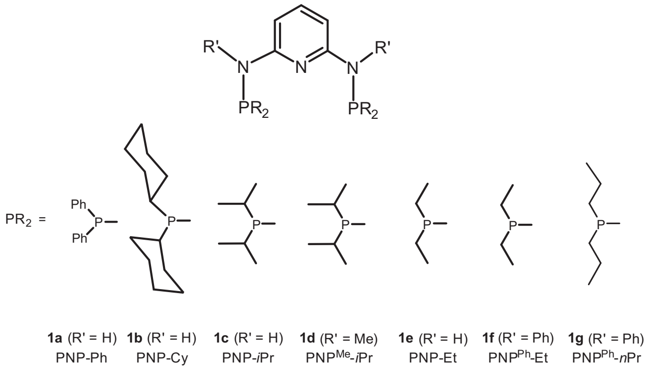
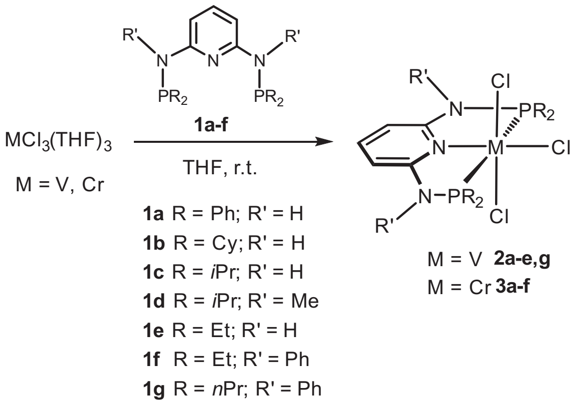


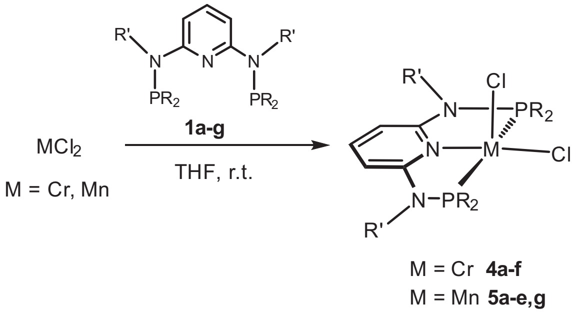
Scheme 1. PNP ligands used in this work (labeling of complexes refers to letters of ligands depicted here).



Scheme 2. Synthesis of V(III) and Cr(III) complexes [V(PNP)Cl_3] (**2**) and [Cr(PNP)Cl_3] (**3**).

very informative. $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR could not be detected at all. Complexes **2–5** exhibit solution magnetic moments μ_{eff} of 2.7–2.9 μ_B, 3.9 μ_B, 4.9–5.0 μ_B, and 5.9–6.0 μ_B (Evans method, in CH_3OH) [15], in agreement with d^2, d^3, high spin d^4, and high spin d^5 electron configurations, respectively.

In order to unequivocally establish the ligand arrangement around the metal centers, the solid state structure of complexes [V(PNP-Ph)Cl_3] (**2a**), [V(PNP^{Ph}-*n*Pr)Cl_3] (**2g**), [Cr(PNP-*i*Pr)Cl_3] (**3d**), [Cr(PNP^{Me}-*i*Pr)Cl_2] (**4d**), and [Mn(PNP-*i*Pr)Cl_2] (**5c**) was determined by X-ray diffraction. Representations of these molecules are shown in Figs. 1–5 with selected metrical parameters given in Table 1. The structures of **2a**, **2g** and **3d** show a distorted-octahedral trivalent vanadium and chromium center surrounded by three meridionally placed donor atoms of the PNP ligand. The three chlorine atoms



Scheme 3. Synthesis of Cr(II) and Mn(II) complexes [Cr(PNP)Cl_2] (**4**) and [Mn(PNP)Cl_2] (**5**).

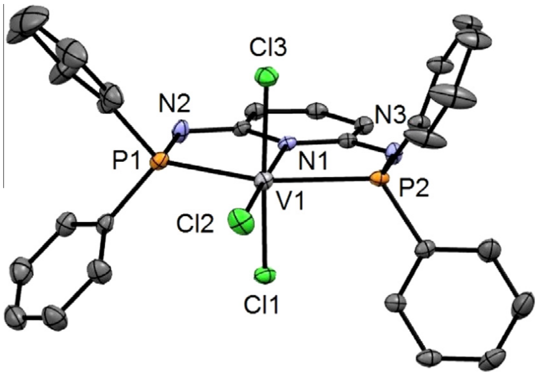


Fig. 1. Structural view of [V(PNP-Ph)Cl_3]·3.5$(CH_3)_2CO$ (**2a**·3.5$(CH_3)_2CO$) showing 50% displacement ellipsoids (H atoms and solvent molecules omitted for clarity).

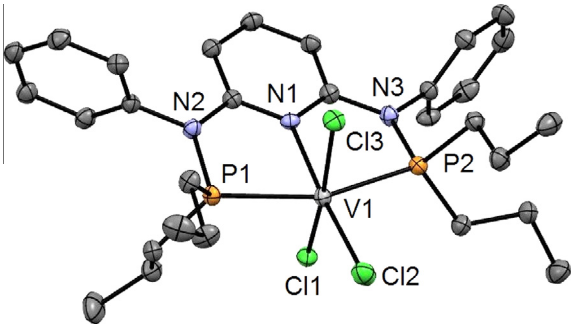


Fig. 2. Structural view of [V(PNP^{Ph}-nPr)Cl_3] (**2g**) showing 50% displacement ellipsoids (H atoms omitted for clarity).

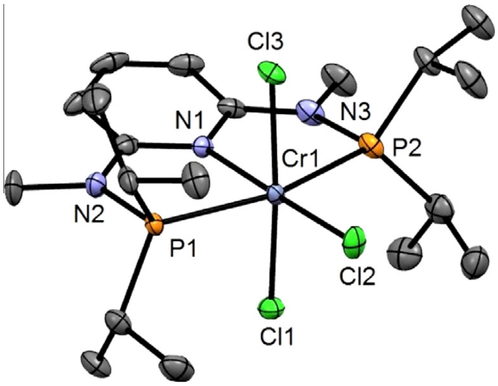


Fig. 3. Structural view of [Cr(PNP^{Me}-*i*Pr)Cl_3] (**3d**) showing 50% displacement ellipsoids (H atoms and a second independent complex are omitted for clarity).

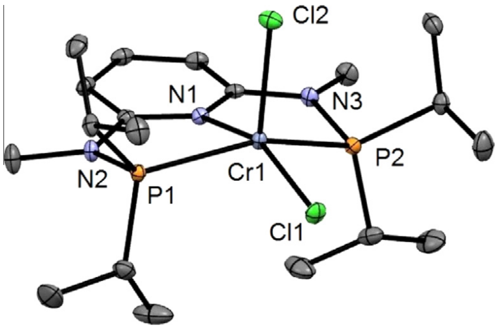


Fig. 4. Structural view of [Cr(PNP^{Me}-*i*Pr)Cl_2]·0.5CH_2Cl_2 (**4d**·0.5CH_2Cl_2) showing 50% displacement ellipsoids (H atoms and solvent molecules omitted for clarity).

Please cite this article in press as: M. Mastalir et al., Inorg. Chim. Acta (2016), http://dx.doi.org/10.1016/j.ica.2016.02.064