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Synthesis of group 10 metal complexes with a new unsymmetrical PN^{3}P-pincer ligand through ligand post-modification: Structure and reactivity

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Dedicated to Professor Gerard van Koten on the occasion of his 75th birthday.

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ABSTRACT

A post-modification strategy is used to synthesize a new class of diimine-amido PN^{3}P-pincer group-10 transition metal complexes. The coordination chemistry and the thermal stabilities of their organometallic derivatives are characterized and investigated.

The nature of the pincer ligands strongly depends on their structures, which can be modified through varying their donor atoms, their spacers, the substituents of their donor groups and their backbones [1]. In transition-metal complexes, the more electron-donating pincer ligands could promote the metal center's activation of inert chemical bonds, and the unsaturation in their backbones can afford rich electronic properties to the resulting complexes. As such, strong electron-donating anionic PNP pincer ligands, containing unsaturated bonds, have been widely studied (Fig. 1) [2–5]. We recently demonstrated that replacing the CH_2 groups with NH spacers in the pyridine-based PN^3 complexes can result in diverse catalytic activities and different thermodynamic and kinetic properties through deprotonation and reprotonation of the NH group [6]. In this communication, we report on how this process also allows us to prepare a new class of PN^{3}P pincer complexes by post-modifications to the ligand.

The cationic, tetracoordinated, square-planar group-10 (Ni, Pd and Pt) metal complexes **1a**-**1c** were conveniently synthesized by the coordination of the PN^{3}P-pincer ligand with a stoichiometric amount of divalent group-10 metal halides according to the literature procedure [7]. The neutral dearomatization complexes **2a**-**2c** were obtained by using one equivalent of KO^{t}Bu to deprotonate one of the amine arms in complexes **1a**-**1c** [6]. Very interesting, upon treatment of complexes **1a**-**1c** or **2a**-**2c** with excess amounts of KO^{t}Bu and ethyl iodide, the pyridine ring could be alkylated with three ethyl groups on the carbon atoms *meta* to the central N donor (Scheme 1), suggesting that these dearomatized pyridine groups react like enamines. This process led to the formation of a series of novel diimine-amido ligated complexes (**3a**-**3c**). The ^{1}H nuclear magnetic resonance (NMR) spectra of **3a**-**3c** in C_6D_6 show an apparent triplet signal for one hydrogen in the sp^2 region (δ = 5.41 ppm (**3a**), 5.46 ppm (**3b**) and 5.44 ppm (**3c**)), indicating that there is only one olefinic hydrogen in the 1,2,3,6-tetrahydropyridine ring for each complex. The existence of two nonequivalent P atoms was supported by an AB system with two doublets: ^{31}P{^{1}H} NMR spectra (δ = 105.4 ppm (d, $^2J_{P\text{-}P}$ = 297.7 Hz, 1P), 104.0 ppm (d, $^2J_{P\text{-}P}$ = 297.7 Hz, 1P) for **3a**; δ = 116.0 (d, $^2J_{P\text{-}P}$ = 398.5 Hz, 1P), 113.5 (d, $^2J_{P\text{-}P}$ = 398.5 Hz, 1P) for **3b**; δ = 116.0 (d, with ^{195}Pt satellites, $^2J_{P\text{-}P}$ = 369.0 Hz, $^1J_{Pt\text{-}P}$ = 2580.5 Hz, 1P), 113.5 (d, with ^{195}Pt satellites, $^2J_{P\text{-}P}$ = 371.5 Hz, $^1J_{Pt\text{-}P}$ = 2592.8 Hz, 1P) for **3c**).

To fully structurally characterize these new complexes, single crystals of **3a**-**3c** suitable for the X-ray crystallographic analysis

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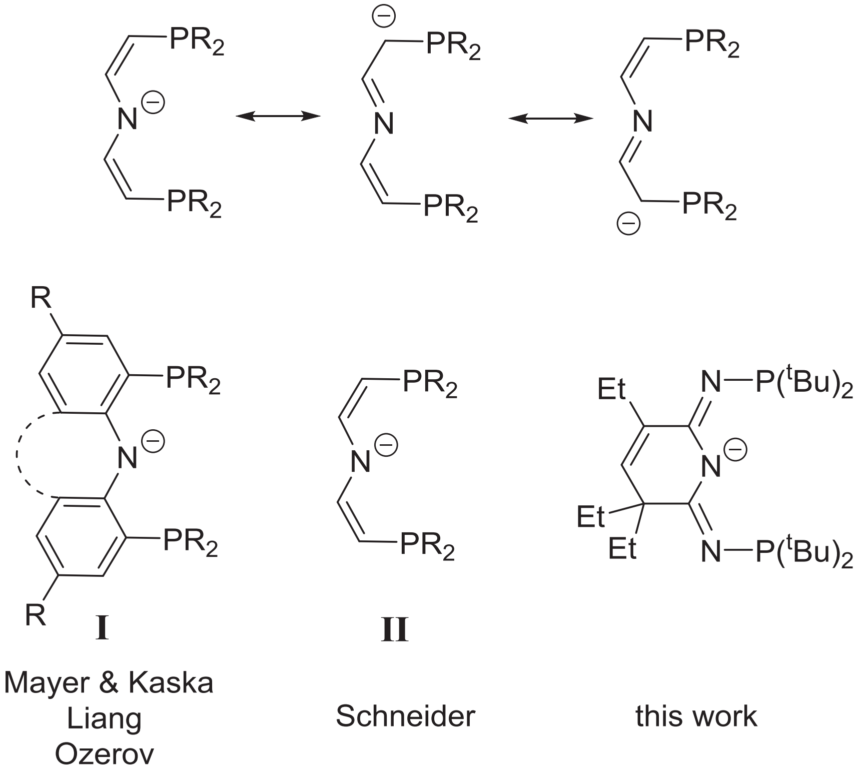
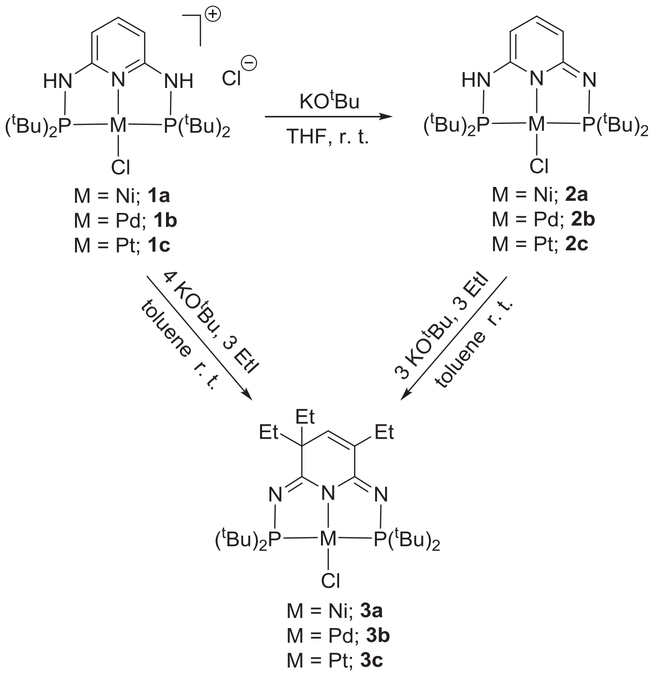


Fig. 1. Examples of anionic PNP pincer ligands with unsaturated arms and selected resonance structures.

were grown from the corresponding concentrated pentane solutions at room temperature. Table 1 summarizes the selected bond distances and angles of the solid-state molecular structures of **3a**-**3c** illustrated in Fig. 2. In general, the structures of these three complexes are similar and the PN^{3}P-pincer ligand is coordinated in a meridional fashion to the central metal ion through the two phosphorus atoms and the one-amido nitrogen atom. The d^8 metal centers adopt a slightly distorted square-planar coordination geometry, similar to those observed for group-10 metal chlorides ([Ph-PNP]MCl, M = Ni, Pd, Pt) supported by the bis(2-diphenylphosphinophenyl)amide (Ph-PNP) ligand [10]. All N2-M-Cl bond angles are close to 180°. The bond distances of C3–C4, N1–C1 and N3–C5 (Table 1) are within the range for typical double bonds, in good agreement with their solution NMR data. The Pd–Cl bond distance of **3b** (2.3172(7) Å) is similar to that in an analogous complex, [Ph-PNP]PdCl (2.317 Å) [8], indicating that the electron properties of the new PN^{3}P-pincer ligand and the bis(2-diphenylphosphinophenyl)amide ligand may be comparable.



Scheme 1. Synthesis of group-10 chloride complexes.

The chloride complexes of **3a** and **3b** were found to be robust in air and water, even at elevated temperatures. When **3a** and **3b** were treated with one equivalent of lithium reagent (methyl lithium or

Table 1
Selected bond distances and angles for **3a**-**c**.

Compound	3a	3b	3c
Bond Lengths (Å)			
C1–C2	1.525(3)	1.525(3)	1.521(4)
C2–C3	1.488(3)	1.488(5)	1.485(5)
C3–C4	1.324(3)	1.317(5)	1.314(5)
C4–C5	1.478(2)	1.476(3)	1.472(4)
N1–C1	1.295(3)	1.296(3)	1.298(4)
C1–N2	1.384(2)	1.383(3)	1.381(4)
N3–C5	1.296(2)	1.293(4)	1.296(4)
C5–N2	1.396(2)	1.395(3)	1.399(4)
M1–N2	1.8858(15)	2.013(2)	2.014(2)
M1–Cl1	2.1594(6)	2.3172(7)	2.3079(8)
M1–P1	2.1935(5)	2.2936(6)	2.2843(7)
M1–P2	2.1952(5)	2.2937(6)	2.2841(7)
Bond Angles (°)			
P1–M1–P2	166.54(2)	161.76(2)	162.12(3)
N2–M1–Cl1	178.01(6)	178.66(7)	179.62.(8)

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