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Synthesis of Group 10 Metal Complexes with a New Unsymmetrical PN^3P -Pincer Ligand Through Ligand Post-modification: Structure and Reactivity

Xiufang Wang, Liangfeng Yao, Yupeng Pan, and Kuo-Wei Huang*

KAUST Catalysis Center and Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia
E-mail: hkw@kaust.edu.sa (K.-W. Huang)

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

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

Keywords: Pincer complexes • Ligand post-modification • Coordination chemistry • Organometallics

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 CH₂ groups with NH spacers in the pyridine-based PN³ 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 PN³P pincer complexes by post-modifications to the ligand.

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

The cationic, tetracoordinated, square-planar group-10 (Ni, Pd and Pt) metal complexes **1a-1c** were conveniently synthesized by the coordination of the PN³P-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^tBu 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^tBu 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 ¹H nuclear magnetic resonance (NMR) spectra of **3a-3c** in C₆D₆ show an apparent triplet signal for one hydrogen in the sp² 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: ³¹P{¹H} NMR spectra (δ = 105.4 ppm (d, ²J_{P-P} = 297.7 Hz, 1P), 104.0 ppm (d, ²J_{P-P} = 297.7 Hz, 1P) for **3a**; δ = 116.0 (d, ²J_{P-P} = 398.5 Hz, 1P), 113.5 (d, ²J_{P-P} = 398.5 Hz, 1P) for **3b**; δ = 116.0 (d, with ¹⁹⁵Pt satellites, ²J_{P-P} = 369.0 Hz, ¹J_{Pt-P} = 2580.5 Hz, 1P), 113.5 (d, with ¹⁹⁵Pt satellites, ²J_{P-P} = 371.5 Hz, ¹J_{Pt-P} = 2592.8 Hz, 1P) for **3c**).

Scheme 1. Synthesis of group-10 chloride complexes.

To fully structurally characterize these new complexes, single crystals of **3a-3c** suitable for the X-ray crystallographic analysis 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 Figure 1. In general, the structures of these three complexes are similar and the PN^3P -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 ($[\text{Ph-PNP}]\text{MCl}$, $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$) 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** ($2.3172(7) \text{ \AA}$) is similar to that in an analogous complex, $[\text{Ph-PNP}]\text{PdCl}$ ($2.317 \text{ \AA}$),^[8] indicating that the electron properties of the new PN^3P -pincer ligand and the bis(2-diphenylphosphinophenyl)amide ligand may be comparable.

Figure 2. Molecular structures of complexes **3a-3c** with thermal ellipsoids set at 40% probability. Hydrogen atoms were omitted for clarity.

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)

Scheme 2. Synthesis of methyl complexes (**4a** and **4b**). **Scheme 3.** Synthesis of *n*-butyl complexes (**5a** and **5b**).

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 *n*-butyl lithium), the corresponding methyl complexes, **4a** and **4b** (Scheme 2), and *n*-butyl complexes, **5a** and **5b** (Scheme 3), were obtained.

Figure 3. Molecular structure of complexes **4a** with thermal ellipsoids set at 30% probability. Hydrogen atoms were omitted for clarity.

Table 2. Selected bond distances and angles for **4a**.

Compound	4a
Bond Lengths (Å)	
C1-C2	1.524(3)
C2-C3	1.492(3)
C3-C4	1.325(3)
C4-C5	1.483(3)
N1-C1	1.300(3)
C1-N2	1.371(3)
N3-C5	1.301(3)
C5-N2	1.383(3)
M1-N2	1.929(16)

M1-C12	1.945(2)
M1-P1	2.180(5)
M1-P2	2.183(5)
Bond Angles (°)	
P1-M1-P2	165.58(2)
N2-M1-C12	177.51(11)

The methyl complexes **4a** and **4b** were thermally stable in boiling C₆D₆ overnight, and they showed chemical inertness towards O₂, CO and CO₂. Single crystals of **4a** were obtained from the pentane solution at room temperature and characterized by single-crystal X-ray diffraction. Its solid-state structure is similar to the chloride complex, adopting a slightly distorted square-planar geometry (Fig. 3). The bond distances of Ni1-N2 (1.929(16) Å) is slightly shorter than those in analogous [PNP]NiMe complexes^[9] (1.945(3)~1.967(8) Å), as is the Ni-C bond length (1.945(2) Å) compared to those in the [PNP]NiMe complexes (1.965(4)~1.995(7) Å).

Figure 4. Molecular structures of complexes **5a-5b** with thermal ellipsoids set at 30% probability. Hydrogen atoms were omitted for clarity.

Table 3. Selected bond distances and angles for **5a-5b**.

Compound	5a	5b
Bond Lengths (Å)		
C1-C2	1.534(2)	1.538(6)
C2-C3	1.492(3)	1.496(6)
C3-C4	1.323(3)	1.313(6)
C4-C5	1.482(2)	1.477(6)
N1-C1	1.298(2)	1.291(5)
C1-N2	1.369(2)	1.354(5)
N3-C5	1.289(2)	1.304(5)
C5-N2	1.383(2)	1.381(5)
M1-N2	1.9425(13)	2.077(3)
M1-C12	1.9602(17)	2.200(4)
M1-P1	2.1736(5)	2.3298(10)
M1-P2	2.2291(5)	2.2878(10)
Bond Angles (°)		
P1-M1-P2	164.359(19)	159.38(4)
N2-M1-C12	172.86(7)	176.17(15)

The reactivities of complexes **5a** and **5b** are of interest because only a handful of *n*-alkyl transition-metal complexes have previously been isolated and fully characterized.^[3a,4e, 9] Their reactivities towards O₂, CO and CO₂ are similar to those of methyl complexes. When the *n*-butyl nickel complex **5a** was heated under Ar, no β-H elimination reaction was observed. However, when the *n*-butyl palladium complex **5b** was heated under the same conditions, β-H elimination occurred, but the reaction could not be completed even after being heated in C₆D₆ at 80 °C for 60 h, as indicated by ¹H and ³¹P{¹H} NMR spectroscopy. Similar thermal stability was reported in an analogous butyl pincer palladium complex.^{4e} The molecular structures of **5a** and **5b** also adopt a slightly distorted square-planar geometry (Fig. 4). The bond distance of

Pd-C in **5b** (2.200(4) Å) was relatively longer than that in the [PNP^F]PdMe analog (2.061(2) Å),^[10] suggesting that the *trans* influence of our new pincer ligand is more pronounced on Pd.

In summary, we used a post-modification strategy to prepare a new class of diimine-amido anionic PN³P-pincer ligand-ligated group-10 transition metal complexes. The corresponding alkyl complexes were also synthesized and characterized. The methyl complexes (**4a** and **4b**) and *n*-butyl Ni complex (**5a**) showed excellent thermal stability, while *n*-butyl Pd **5b** underwent slow β-H elimination. Future work will involve the use of less bulky groups on the phosphine donors to evaluate their impact on the reactivity.

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