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Thioamide Pincer Ligands with Charge Versatility

Rowshan Ara Begum, Douglas Powell, and Kristin Bowman-James*

Department of Chemistry, University of Kansas, 1251 Wescoe Hall Drive,
Lawrence, Kansas 66045

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This paper reports the synthesis and characterization of three complexes, two palladium and one platinum, with 2,6-bis-thioamido-phenyl and 2,6-bis-thioamido-pyridine ligands. The ligands show internal charge versatility by losing protons from a phenyl CH (**I**) or from amide NH's (**II** and **III**). The complexes were also examined as Heck catalysts, and the palladacycle, **I**, was found to be more effective compared to the others. The crystal structures of the complexes are also reported.

The incorporation of thioamide functional groups into pincer ligand frameworks has resulted in a class of ligands with an internal charge versatility that adds a new dimension to transition-metal coordination chemistry. The chemistry of thioamides has a lengthy history.[1] In addition to their biological activity, thioamides have been used as therapeutic agents[2] and in transition-metal coordination chemistry.[3−7] More recently, pincer ligands, which hold metal ions in clawlike vices via tridentate coordination, have generated considerable interest among transition-metal chemists as catalysts for carbon−carbon coupling reactions.[8,9] Of these, sulfur-containing pincers have gained recognition because of the added stability that the SCS triad imparts to the catalysts,[9] although there is some debate as to whether these pincers are true or precursor catalysts.[10] In terms of sulfur Lewis base donors, however, thioamides are a relatively unexplored functional group in ligand design strategies. Nonetheless, interest in thioamides is gaining momentum, as is reflected by a number of recent papers reporting on both anion[11] and transition-metal-ion[5,6,12,13] chemistry.

Recently, we reported the first example of a ditopic thioamide-based pincer palladacycle as a catalyst for Heck-type coupling reactions.[12] To our knowledge, that complex represents one of only a few multitopic SCS pincers.[14,15] To further explore the catalytic utility of thioamides in pincer frameworks, we synthesized two simple monotopic pincer ligands, **1** and **2**. Ligand **1**[7] and other *N*,*N*-dialkylthiobenzamide ligands[4,5] have been synthesized by others. However, those investigations primarily focused on understanding the role of sulfur in cyclopalladation reactions[4,5] and using the complexes as precursors to benzothiazoles.[7] An interesting

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* To whom correspondence should be addressed. E-mail: kbjames@ku.edu.

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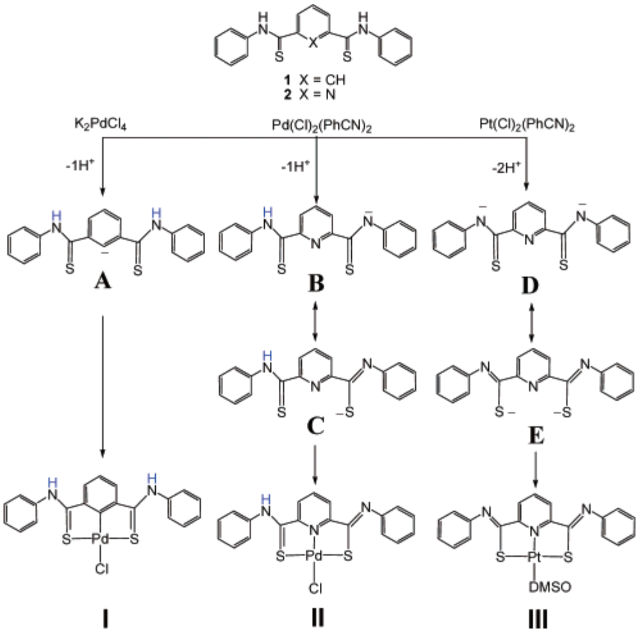
Scheme 1. Synthesis of Thioamide-Based Metal Complexes



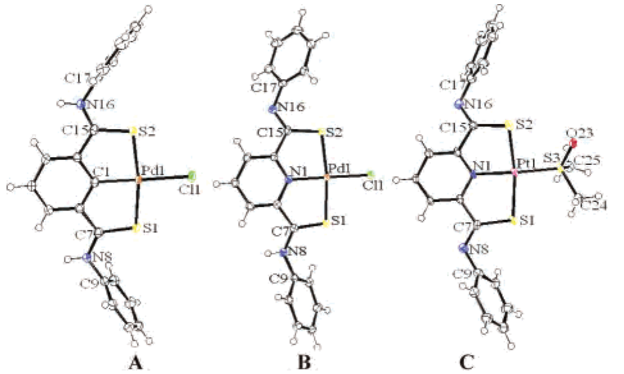


Figure 1. ORTEP plots for (**A**) **I**, (**B**) **II**, and (**C**) **III**. Thermal ellipsoids are drawn at 50% probability.

Table 1. Selected Bond Lengths (Å) for **I**−**III**

	complex			
	I	**II**	**IIIA**	**IIIB**
M1−X	1.958(2)	1.993(16)	1.996(13)	1.985(13)
M1−S1	2.2927(6)	2.2951(6)	2.284(5)	2.284(5)
M1−S2	2.2725(6)	2.2775(6)	2.295(5)	2.285(5)
M1−Y	2.388(8)	2.3122(5)	2.212(4)	2.210(1)
S1−C7	1.707(2)	1.694(2)	1.743(17)	1.738(18)
S2−C15	1.704(2)	1.752(2)	1.738(16)	1.775(16)
C7−N8	1.319(3)	1.323(3)	1.31(2)	1.31(2)
C15−N16	1.325(3)	1.282(3)	1.31(2)	1.28(2)
N8−C9	1.444(3)	1.432(3)	1.41(2)	1.43(2)
N16−C17	1.442(3)	1.413(3)	1.38(2)	1.42(2)

pyrrolidine-containing thioamide pincer complex with platinum that exhibits photoluminescent properties has also been reported.[13] However, **2** has not to our knowledge been previously reported. The SNS pincer ligand was synthesized in order to examine the structural aspects of different donor groups on pincer formation. Herein are reported palladium and platinum complexes of a new SNS pincer (**2**) and structural and catalytic comparisons with the palladium complex of the SCS analogue (**1**; Scheme 1).

The precursor amide ligands have both previously been synthesized.[16,17] Both **1** and **2** were synthesized from the corresponding diamides in good yields using Lawesson's reagent.[18] (The previous synthesis of **1** was by P_2S_5.[7]) The three complexes were obtained by reacting either **1** or **2** in dimethyl sulfoxide (DMSO) with a stoichiometric amount of K_2PdCl_4 or $MCl_2(PhCN)_2$ (M = Pt and Pd) in CH_2Cl_2 (Scheme 1). Crystals suitable for X-ray crystallography were obtained from DMSO for all three complexes. The two palladium complexes, **I** and **II**, crystallized as yellow and red prisms, respectively, while the platinum complex, **III**, was isolated as deep-red crystals.

All three complexes crystallize with the pincer ligand occupying three coordination sites (Figure 1). In **I** and **II**, chloride serves as the fourth ligand, while in **III**, an S-bonded DMSO molecule sits at the remaining site. The negative charge on ligand **1** derives from a deprotonated phenyl hydrogen (Scheme 1, **A**). Ligand **2** becomes either mono- or dinegatively charged as a result of the loss of either one or two of the thioamide NH's, resulting in the existence of two possible resonance structures: either the charge remains on the nitrogen, which would result in an N-bonded ligand, or the charge resonates to the sulfur with the formation of a C═N imine bond (Scheme 1, **B/D** and **C/E**, respectively). In all three cases, however, S-bonded complexes result: in **I**, SCS coordination and, in both **II** and **III**, SNS coordination, with the latter being understood in terms of HSAB binding preferences.[19]

The palladacycle **I** (Figure 1, **A**) crystallizes with two molecules of DMSO hydrogen-bonded with the amide NH's. Bond lengths and angles (Table 1) are comparable to those previously reported for the dipalladium macrocyclic complex[12] and are indicative of N−C═S bonding. The second palladium complex, **II** (Figure 1, **B**), is similar in overall geometry to **I** but is isolated as the monoimine obtained from the resonance structure after deprotonation of one thioamide NH (Scheme 1, **C**), and contains only a single DMSO of crystallization. A shorter C15−N16 bond and longer S2−C15 bond compared with C7−N8 and S1−C7, respectively, confirm this resonance form. The remaining NH forms a hydrogen bond with the DMSO molecule.

The platinum complex, **III**, crystallizes with two crystallographically independent platinum units that form a dimer pair with a shared DMSO of crystallization (Figure 2). The two planar (to within 0.04 Å) $PtNS_3$ coordination groups are within 1.6° of being parallel, with their metals directly above one another at a Pt−Pt distance of 3.702(1) Å. The coordination planes for the two square-planar arrangements are rotated by ~122° about the Pt−Pt vector. The next shortest Pt−Pt separation in the crystal is 5.487(1) Å. In the absence of a coordinated chloride, two negative charges are

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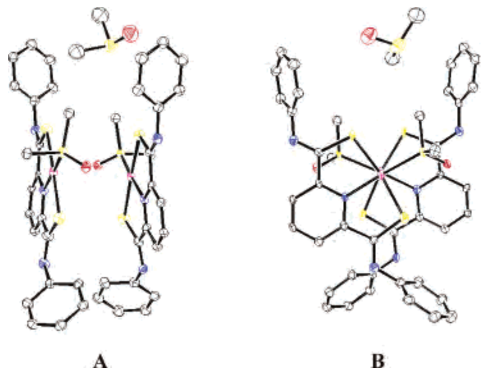

Figure 2. ORTEP plot for the complex **III** showing the dimer pair with one DMSO molecule (**A**) parallel to the metal centers and (**B**) through the metal centers. Thermal ellipsoids are drawn on 50% probability.

Table 2. Heck Coupling of 4-Iodotoluene with Styrene Using Complexes **I**−**III** as Catalysts[a]

entry	catalyst (mol %)	reaction (h)	yield (%) (trans/gem)	TON[b]
1	**I** (1×10^{-3})	18	56/3.5	59500
2	**I** (1×10^{-3})	48	64/6	70000
3	**I** (0.2)	0.25	89/9	490
4	**II** (0.2)	4	26/1.3	137
5	**II** (0.2)	16	53/5.6	293
6	**III** (0.2)	18	*c*/0	

[a] In dimethylacetamide at 165 °C. [b] TON = (moles of product)/(moles of catalyst). [c] Trace.

required for a neutral complex and **2** has lost both thioamide NH's, resulting in a diimine ligand with two negatively charged sulfurs (Scheme 1, **E**, and Figure 1, **C**). In both units **A** and **B**, the two C═N distances are about the same and reasonable for a double bond, given the rather large standard deviations. The C−S bonds are clearly elongated, as was anticipated for single bonds.

The results of coupling reactions between 4-iodotoluene and styrene in the presence of **I**−**III** in air are presented in Table 2. As might have been anticipated, catalysis with the platinum complex **III** was exceedingly slow, yielding only a trace amount of the trans isomer after 18 h. Clearly, **I**, the palladacycle, performed the most efficiently of the two palladium complexes. In the presence of a large excess of elemental mercury ([Hg]:[Pd] = 300:1), catalysis is slowed but still occurs; however, catalyst poisoning is still under investigation. These reactions can also be compared with the ditopic palladacyclic complex, which shows similar catalytic activity, based on the mole percent of Pd.[12]

In summary, these simple thioamide-based ligands provide opportunities for charge versatility as well as pincer ligands with the potential as catalysts for carbon−carbon coupling reactions. In all three cases, SXS binding (X = CH or N) is observed despite the presence of potential amide nitrogen donors, with HSAB issues regulating the preferred resonance form of the ligand.[19] The increased acidity of the thioamide NH bond as opposed to amides could assist in the facile deprotonation of the amide hydrogens in the absence of added base.[20] While it is under debate whether SCS palladacycles are catalysts or precatalysts, these new thioamide-based pincer ligands provide promising new coordination compounds for further chemical and catalytic exploration.

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Supporting Information Available: Detailed synthetic, crystallographic, and catalytic procedures and time-dependent ^{1}H NMR (PDF) and one crystallographic file for the three structures in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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