

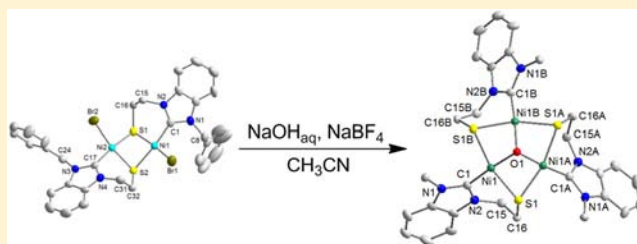
# A Comparative Study on Dinuclear and Multinuclear Ni(II), Pd(II), and Pt(II) Complexes of a Thiolato-Functionalized, Benzannulated *N*-Heterocyclic Carbene Ligand

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## Supporting Information

**ABSTRACT:** Dimeric thiolato-bridged Ni(II) and Pt(II) NHC complexes **2** and **4** have been synthesized from ligand precursor **A** through a combined and in situ deprotonation/hydrolysis protocol of a thioester-functionalized benzimidazolium salt in the presence of the respective metal salts. Reactivity studies of **2** and **4**, and their previously reported Pd(II) analogue **1a** toward either Me<sub>3</sub>OBF<sub>4</sub>, NaOH, or Na<sub>2</sub>S·9H<sub>2</sub>O revealed clear differences. Complex **2** decomposed when treated with Me<sub>3</sub>OBF<sub>4</sub>. On the other hand, its reaction with aqueous NaOH solution in the presence of NaBF<sub>4</sub> yielded trinuclear [Ni<sub>3</sub>S<sub>3</sub>O] complex **6**, which possesses an interesting [Ni<sub>3</sub>S<sub>3</sub>] triangle with a capping μ<sub>3</sub>-oxido ligand. Pt(II) analogue **4** was converted to the tetranuclear [Pt<sub>4</sub>S<sub>4</sub>] macrocycle **5** when treated with Me<sub>3</sub>OBF<sub>4</sub>, in analogy to the result from **1a**, while no defined products could be isolated when **4** was treated with either NaOH or Na<sub>2</sub>S·9H<sub>2</sub>O. Pd(II) analogue **1a** reacted with Na<sub>2</sub>S·9H<sub>2</sub>O to give the tripalladium [Pd<sub>3</sub>S<sub>3</sub>S] complex **7** bearing a capping μ<sub>3</sub>-sulfido ligand.



## INTRODUCTION

Donor-functionalized *N*-heterocyclic carbenes (NHCs) have become the focus of metal carbene chemistry, because they give access to complexes with diverse structures, enhanced stabilities, and versatile catalytic applications.<sup>1</sup> Most commonly, substituents containing *N*-, *O*-, and *P*-donor groups have been introduced at the *N* atoms of NHCs.<sup>2</sup> We have devoted our studies to the exploration of less-common *S*-functionalized NHCs, which can be mainly categorized as thioether-, thiolato-, thiophene-, sulfonate-, and sulfoxide-NHCs.<sup>3,4</sup> Among these, the soft and electron-rich thiolato function forms the strongest *M*–*S* bond, and also gives rise to a diverse coordination chemistry, because of its tendency to bridge metal centers, which particularly attracted our interest.<sup>5</sup>

Reported syntheses of NHC-thiolato complexes require the handling of either air-sensitive free thiols or metal(0) precursors.<sup>6</sup> To circumvent this, we have developed a one-step approach to thiolato-bridged Pd(II)-NHC dimers, which involves the direct reaction of thioester-functionalized azolium salts **A/B** with Pd(OAc)<sub>2</sub> (see Scheme 1). The thioester-functionalized azolium salts function as synthetic equivalents of otherwise air-sensitive thiol-NHCs, which are generated in situ by a combined deprotonation and hydrolysis step.<sup>5</sup> In this method, the handling of air-sensitive materials can be avoided, and the synthetic sequence is also shortened. The resulting complexes **1a/b** with a [Pd<sub>2</sub>S<sub>2</sub>] core showed interesting reactivities toward AgO<sub>2</sub>CCF<sub>3</sub>, thiolates, and the strong electrophile Me<sub>3</sub>OBF<sub>4</sub>. In the latter two cases, tetranuclear [Pd<sub>4</sub>S<sub>4</sub>] molecular squares were isolated, which also demon-

strates the unusual reactivity of Meerwein's salts as a metal-free halido-abstracting agent.<sup>5a</sup>

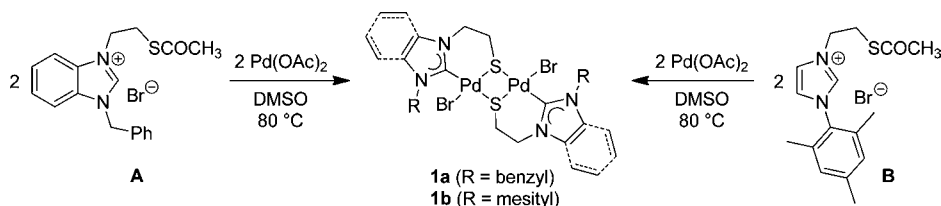
In order to investigate whether the in situ generation of thiolato-NHCs from thioester-NHCs has general application, we explored the syntheses of isoelectronic and isostructural Ni(II) and Pt(II) analogues of **1a**<sup>5a</sup> starting from ligand precursor **A**. Herein, we report different synthetic routes to these metal-NHC dimers and a comparative reactivity study of the respective Ni(II), Pd(II), and Pt(II) NHC complexes toward Me<sub>3</sub>OBF<sub>4</sub>, NaOH, and Na<sub>2</sub>S, which gave rise to a series of multinuclear complexes with different architectures and metal centers highlighting the structural diversity of thiolato-NHC complexes.

## RESULTS AND DISCUSSION

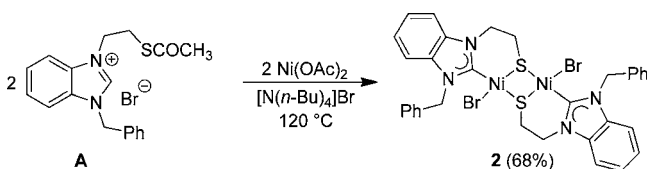
**Synthesis of the Ni(II) Dimeric Complex.** Following our methodology on synthesizing benzimidazol-2-ylidene complexes of Ni(II),<sup>7</sup> benzimidazolium salt **A** bearing a thioester function was heated with Ni(OAc)<sub>2</sub> in molten [N(*n*-Bu)<sub>4</sub>]Br under vacuum at 120 °C (see Scheme 2). In analogy to Pd(II), deprotonation and in situ hydrolysis of the thioester group occurred, giving rise to the formation of the dinuclear Ni(II)-NHC complex **2** with bridging thiolato chelates. The dinuclear complex **2** was isolated as a red solid, which is soluble in chlorinated solvents, CH<sub>3</sub>CN, dimethyl sulfoxide (DMSO), and dimethylformamide (DMF), but insoluble in diethyl ether and

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Scheme 1. Syntheses of Thiolato-Bridged Dimeric Pd(II) NHC complexes 1a/b.<sup>5</sup>

Scheme 2. Synthesis of Thiolato-Bridged Dimeric Ni(II) Benzimidazolin-2-ylidene Complex 2

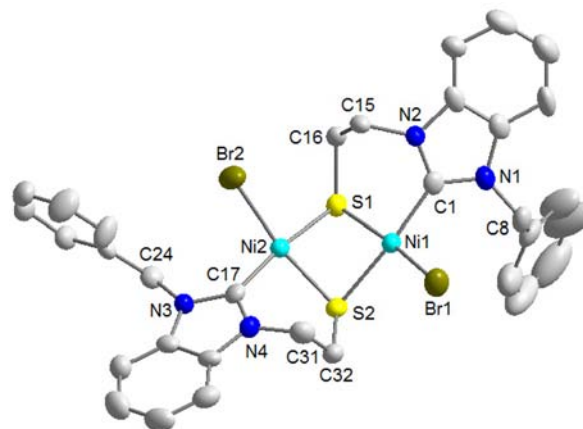


hexane. The formation of **2** is corroborated by its  $^1\text{H}$  NMR spectrum, in which both the downfield  $^1\text{H}$  NMR signal for the acidic NCHN proton and the singlet due to the methylthioester group of ligand precursor **A** are absent. Furthermore, the benzylic protons become diastereotopic upon coordination, giving rise to two doublets with a coupling constant of  $^2J = 15.8$  Hz centered at 6.71 and 5.61 ppm, respectively. Similarly, the diastereotopy of the methylene groups of the bridges results in four pseudo-triplets/doublets in the range of 5.05–1.53 ppm. The carbene signal at 176.1 ppm is shifted downfield compared to that of **1a** (cf. 175.4 ppm),<sup>5a</sup> which may be due to the lower effective nuclear charge of Ni(II), compared to Pd(II). A signal at  $m/z = 733$  in the positive-ion FAB mass spectrum assignable to the  $[\text{M} - \text{Br}]^+$  fragment also supports the formation of **2**.

Single crystals of **2** suitable for X-ray analysis were obtained by slow evaporation of a concentrated  $\text{CH}_2\text{Cl}_2$  solution. The molecular structure depicted in Figure 1 shows that complex **2** is isostructural to its Pd analogue **1a**.<sup>5a</sup> Each Ni(II) center is coordinated by one carbene, two bridging thiolato donors, and one terminal bromido ligand in a square planar fashion. The lengths of the two Ni–C<sub>carbene</sub> bonds are 1.873(6) and 1.892(5) Å, respectively, which are shorter than those in **1a** [cf. 1.977(4) and 1.997(4) Å].<sup>5a</sup> The Ni–S bonds *trans* to the carbenes [2.2329(16) and 2.2398(15) Å] are longer than those *trans* to the bromido ligands [2.1740(17) and 2.1799(16) Å], because of the stronger *trans* influence of the NHCs. The dihedral angles between the  $[\text{NiCSBr}_2]$  coordination plane and NHC planes amount to  $58.3(2)^\circ$  and  $55.8(1)^\circ$ , respectively. As observed for **1a**,<sup>5a</sup> complex **2** is also bent with a similar hinge angle of  $117.43(6)^\circ$ .

**Synthesis of Pt(II) Dimeric Complexes.** Since  $\text{Pt(OAc)}_2$  is not as easily available as  $\text{Pd(OAc)}_2$  or  $\text{Ni(OAc)}_2$ , the synthesis of the thiolato-functionalized Pt(II)-NHC complex was first attempted by reacting ligand precursor **A** with  $\text{PtBr}_2$  and NaOAc as an external base at  $80^\circ\text{C}$ .<sup>8</sup> However, no reaction occurred, and mainly starting materials were recovered. When the temperature was increased to  $160^\circ\text{C}$ , some intractable white solids with a strong odor formed.

To circumvent this problem, a two-step protocol involving precoordination of the thiolato-donors prior to NHC generation was attempted.<sup>9</sup> Thus, ligand precursor **A** was first reacted with  $\text{PtBr}_2$  in boiling  $\text{CH}_3\text{CN}$  (see Scheme 3) yielding an orange precipitate poorly soluble in DMF. Washing of the solid with DMF afforded complex **3** as a yellow powder, which

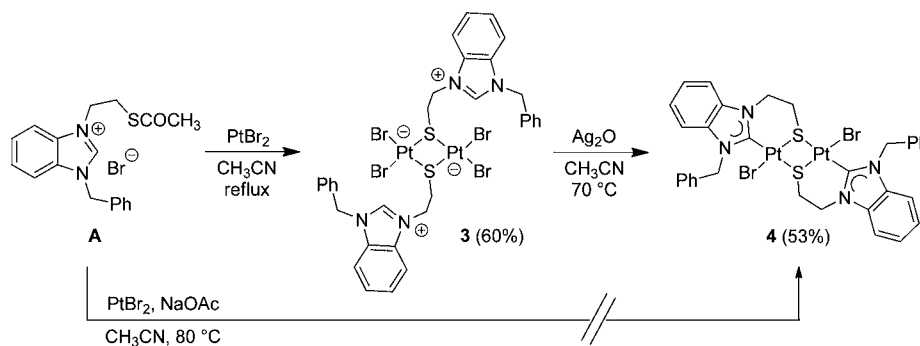


**Figure 1.** Molecular structure of the compound **2** showing 50% probability ellipsoids; H atoms are omitted for clarity. Selected bond lengths and bond angles: Ni1–C1, 1.873(6) Å; Ni1–S1, 2.1740(17) Å; Ni1–S2, 2.2329(16) Å; Ni1–Br1, 2.2979(10) Å; Ni2–C17, 1.892(5) Å; Ni2–S2, 2.1799(16) Å; Ni2–S1, 2.2398(15) Å; Ni2–Br2, 2.3266(10) Å; C1–Ni1–S1,  $92.66(17)^\circ$ ; S1–Ni1–S2,  $78.88(6)^\circ$ ; S2–Ni1–Br1,  $98.38(5)^\circ$ ; Br1–Ni1–C1,  $91.24(17)^\circ$ ; C1–Ni1–S2,  $169.37(18)^\circ$ ; S1–Ni1–Br1,  $167.53(6)^\circ$ ; C17–Ni2–S2,  $92.61(17)^\circ$ ; S2–Ni2–S1,  $78.61(6)^\circ$ ; S1–Ni2–Br2,  $97.19(5)^\circ$ ; Br2–Ni2–C17,  $92.13(16)^\circ$ ; C17–Ni2–S1,  $170.45(17)^\circ$ ; S2–Ni2–Br2,  $168.65(5)^\circ$ ; Ni1–S1–Ni2,  $82.69(6)^\circ$ ; Ni1–S2–Ni2,  $82.72(6)^\circ$ . NiCS<sub>2</sub>Br/NHC dihedral angle =  $58.3(2)^\circ$ ,  $55.8(1)^\circ$ .

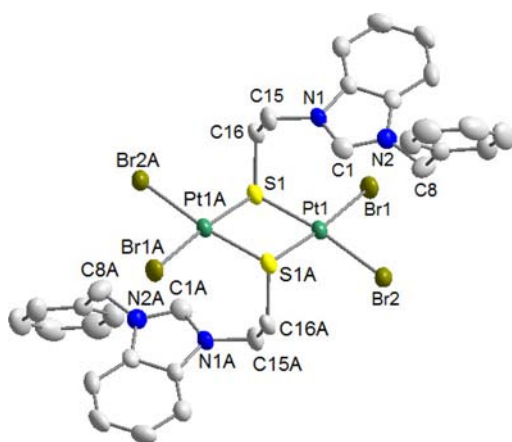
is slightly better soluble in DMSO. Its  $^1\text{H}$  NMR spectrum recorded in  $\text{DMSO-}d_6$  shows two broad singlets narrowly spaced at 10.15 and 10.08 ppm in an approximate 1:1 ratio indicative of benzimidazolium NCHN protons. The three methylene groups also give rise to three broad signals, and coupling could not be resolved. Unfortunately, low-temperature NMR experiments were hampered by the  $\text{DMSO-}d_6$  solvent and the generally poor solubility of the complex. Partial solvolysis of complex **3** may have occurred upon dissolution in DMSO. The replacement of one bromido ligand with the coordinating solvent would lead to inequivalent benzimidazolium moieties, which is also supported by  $^{13}\text{C}$  NMR spectroscopy. Furthermore, it is noteworthy that the signal corresponding to the thioester group of **A** is absent, indicating that hydrolysis took place in wet  $\text{CH}_3\text{CN}$ , and coordination of the resulting thiolato donor to Pt(II) is thus conceivable. Since the electron-rich thiolato-donors tend to bridge two metal centers, a dinuclear complex with a  $[\text{Pt}_2\text{S}_2]$  core and two benzimidazolium moieties can be anticipated. This proposal was supported by a signal at  $m/z = 1244$  in the ESI mass spectrum with the correct isotopic pattern for the  $[\text{M} - \text{Br} + \text{DMSO}]^+$  fragment, which is also consistent with the aforementioned solvolysis.

X-ray diffraction (XRD) analysis on single crystals obtained by diffusing acetone into a DMSO solution provided convincing evidence for the identity of **3**. The molecular

## Scheme 3. Synthesis of Thiolato-Bridged Dimeric Pt(II) Complexes 3 and 4



structure depicted in Figure 2 shows that the thiolato functions have indeed formed and are bridging two Pt(II) centers. The

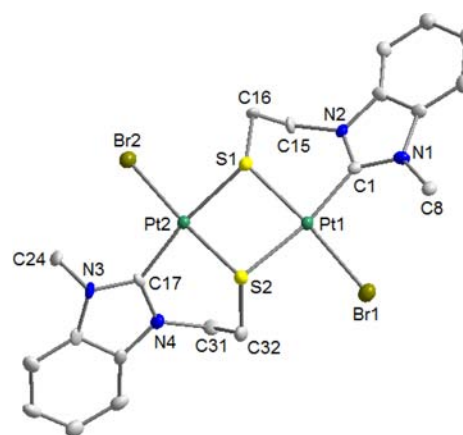


**Figure 2.** Molecular structure of the compound 3·2DMSO, showing 50% probability ellipsoids; H atoms and the DMSO molecule are omitted for the sake of clarity. Selected bond lengths and bond angles: Pt1–S1, 2.2802(16) Å; Pt1–Br1, 2.4619(6) Å; Pt1–Br2, 2.4767(7) Å; Pt1–S1A, 2.2823(14) Å; S1–Pt1A, 2.2824(14); S1–Pt1–Br1, 92.18(4)°; Br1–Pt1–Br2, 93.48(2)°; Br2–Pt1–S1A, 91.51(4)°; S1–Pt1–S1A, 83.03(6)°; Br2–Pt1–S1, 172.99(4)°; S1A–Pt1–Br1, 174.45(4)°; Pt1–S1–Pt1A, 96.97(6)°.

square planar geometry at each Pt(II) is completed by two terminal bromido ligands. The two benzimidazolium moieties remain pendant and balance the overall charge of complex 3. The [Pt<sub>2</sub>S<sub>2</sub>] core is planar with the two benzimidazolium groups located at opposite sides. All bond parameters are in the expected range and do not require further comments.

The desired carbene complex 4 was finally synthesized by treatment of the [Pt<sub>2</sub>S<sub>2</sub>] complex 3 with Ag<sub>2</sub>O in CH<sub>3</sub>CN at 75 °C (see Scheme 2), since no reaction occurred at ambient temperature. Complex 4 was isolated as a yellow powder, which is soluble in CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN, DMF, and DMSO. Its formation is corroborated by a peak at *m/z* = 1045 in the positive ESI mass spectrum corresponding to the [M – Br + CH<sub>3</sub>CN]<sup>+</sup> fragment. Its <sup>1</sup>H NMR spectrum is similar to the Pd(II) and Ni(II) analogues 1a and 2, respectively, showing diastereotopic methylene protons and similar splitting patterns. The carbene carbon atoms resonate at 161.5 ppm in the <sup>13</sup>C NMR spectrum recorded in DMSO-*d*<sub>6</sub>, which is significantly upfield shifted compared to those of 1a<sup>5a</sup> and 2 in CDCl<sub>3</sub> (cf. 1a, 175.4 ppm; 2, 176.1 ppm), which is consistent with the highest effective nuclear charge of Pt(II) in this series.<sup>8</sup>

Single crystals of 4 were obtained by slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub> solution. Figure 3 depicts the molecular structure of



**Figure 3.** Molecular structure of the compound 4·CH<sub>2</sub>Cl<sub>2</sub>, showing 50% probability ellipsoids; H atoms, phenyl rings of N-substituents, and the CH<sub>2</sub>Cl<sub>2</sub> molecule are omitted for clarity. Selected bond lengths and bond angles: Pt1–C1, 1.973(7) Å; Pt1–S1, 2.2887(17) Å; Pt1–S2, 2.3593(18) Å; Pt1–Br1, 2.4711(8) Å; Pt2–C17, 2.004(8) Å; Pt2–S2, 2.2996(17) Å; Pt2–S1, 2.3508(18) Å; Pt2–Br2, 2.4698(8); C1–Pt1–S1, 90.3(2)°; S1–Pt1–S2, 80.32(6)°; S2–Pt1–Br1, 96.00(5)°; Br1–Pt1–C1, 93.3(2)°; C1–Pt1–S2, 170.6(2)°; S1–Pt1–Br1, 174.84(5)°; C17–Pt2–S2, 90.0(2)°; S2–Pt2–S1, 80.27(6)°; S1–Pt2–Br2, 94.87(5)°; Br2–Pt2–C17, 94.9(2)°; C17–Pt2–S1, 170.2(2)°; S2–Pt2–Br2, 174.84(5)°; Pt1–S1–Pt2, 90.03(6)°; Pt1–S2–Pt2, 89.55(6)°. PtCS<sub>2</sub>Br/NHC dihedral angle = 55.8(2)°, 51.7(2)°.

the thiolato-bridged Pt(II) NHC complex 4, which is isostructural to the Pd(II) and Ni(II) analogues 1a and 2, respectively. The Pt–carbene bonds of 1.973(7) and 2.004(8) Å are similar to those in 1a,<sup>5a</sup> but longer than those in 2 (see Table 1). The Pt–S bonds *trans* to the carbenes [2.3593(18) and 2.3508(18) Å] are expectedly longer than those *trans* to the

**Table 1.** Comparison of Selected Parameters Observed in the Isostructural Complexes 1a, 2, and 4

	1a <sup>5a</sup>	2	4
<sup>13</sup> C <sub>carbene</sub> (ppm)	175.4	176.1	161.5
M–C <sub>carbene</sub> bond length (Å)	1.977(4), 1.997(4)	1.873(6), 1.892(5)	1.973(7), 2.004(8)
dihedral angle (°)	55.07(9), 54.21(9)	58.3(2), 55.8(1)	55.8(2), 51.7(2)
hinge angle (°)	119.26(3)	117.43(6)	134.84(3)

Scheme 4. Synthesis of Trinuclear and Tetranuclear NHC Complexes

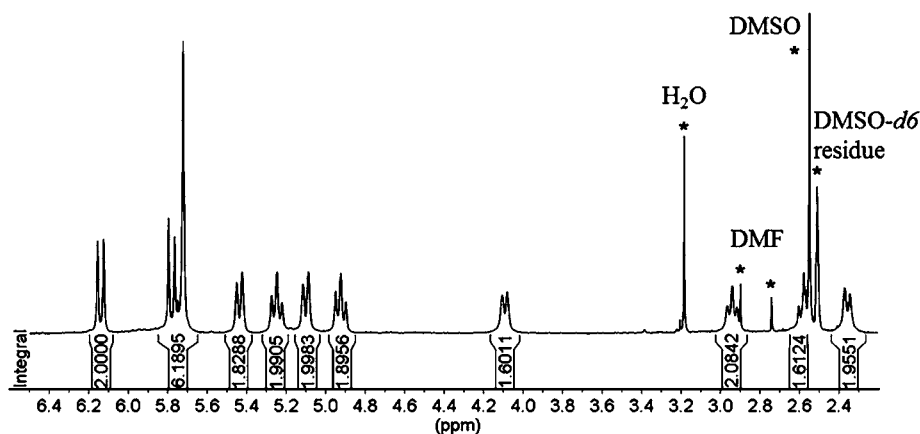
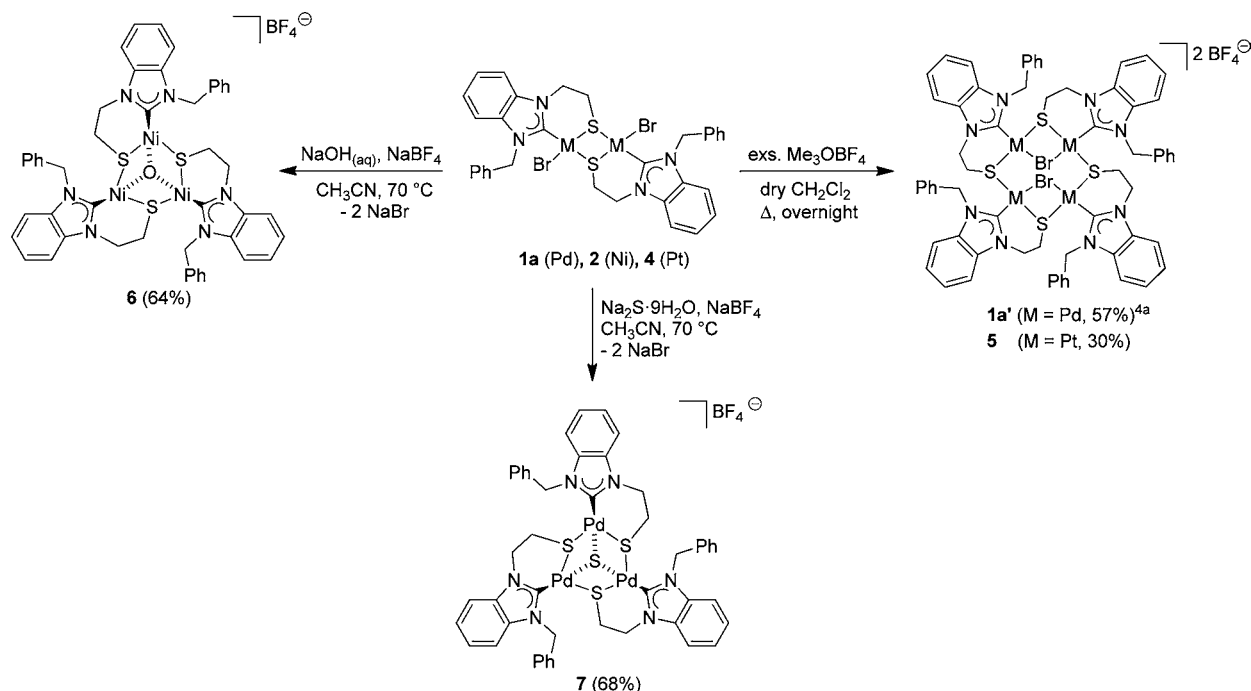


Figure 4.  $^1\text{H}$  NMR spectrum of **5** in the range of 6.50–2.20 ppm. Signals marked with an asterisk (\*) are due to solvents.

bromido ligands [2.2887(17) and 2.2996(17) Å]. The latter are comparable with the Pt–S bonds in **3**. The dihedral angles between the  $[\text{PtCS}_2\text{Br}]$  coordination planes and the NHC planes amount to  $55.8(2)^\circ$  and  $51.7(2)^\circ$ , respectively, which are again similar to the Pd(II) and Ni(II) analogues. Different from the planar  $[\text{Pt}_2\text{S}_2]$  complex **3**, carbene complex **4** is bent with a hinge angle of  $134.84(3)^\circ$ , which is significantly larger than those of its analogues **1a** and **2** (see Table 1).

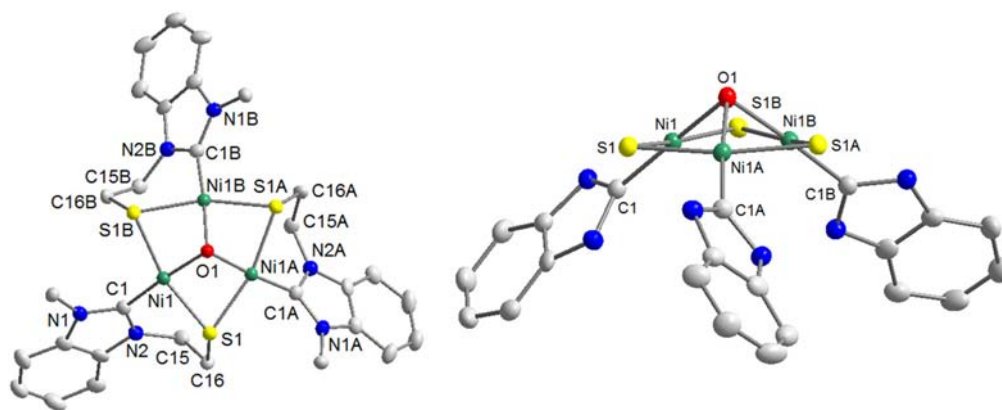
**Synthesis of Multinuclear Group 10 NHC–Thiolato Complexes.** Previously, we reported the preparation of macrocyclic  $[\text{Pd}_4\text{S}_4]$  complexes via the treatment of dimeric Pd(II) complexes **1a** and **1b** with  $\text{Me}_3\text{OBF}_4$ ,  $\text{AgBF}_4$ , or  $\text{NaS}^i\text{Pr}$ , respectively.<sup>5</sup> In analogy, the possibility of synthesizing bigger Ni and Pt aggregates from their respective dimers **2** and **4** was explored. However, the reaction of Ni complex **2** with either  $\text{AgBF}_4$  or  $\text{Me}_3\text{OBF}_4$  in  $\text{CH}_2\text{Cl}_2$  led to severe decomposition, and downfield signals corresponding to benzimidazolium salts appeared in the  $^1\text{H}$  NMR spectra of the products. Apparently, the Ni–C<sub>carbene</sub> bonds were cleaved upon reaction. On the other hand, the reaction of  $\text{Me}_3\text{OBF}_4$  with the Pt(II) complex **4**

was more promising (see Scheme 4), and tetranuclear complex **5** was isolated as an off-white precipitate, which is soluble in DMSO but only sparingly soluble in DMF.

The formation of **5** is supported by ESI MS, which reveals a predominant peak at  $m/z = 1004$  with isotopic intervals of 0.5 in the positive mode corresponding to the  $[\text{M} - 2\text{BF}_4]^{2+}$  fragment. Similar to the Pd(II) analogue **1a'**,<sup>5a</sup> its  $^1\text{H}$  NMR spectrum shows 11 signals for all the methylene groups of the two pairs of inequivalent thiolato–NHC ligands in the range of 6.16–2.35 ppm. Accidental overlap of two methylene groups led to a broad signal at 5.72 ppm (Figure 4). Consistent with this, two carbene signals are observed at 148.8 and 147.1 ppm in the  $^{13}\text{C}$  NMR spectrum. Attempts to obtain single crystals for X-ray analysis met with limited success.

Since both  $\text{AgBF}_4$  and  $\text{Me}_3\text{OBF}_4$  react too harshly with **2**, milder bromide-abstrating reagents were sought. Thus, two equiv of  $\text{NaS}^i\text{Pr}$ , generated in situ from NaOH (in 6.25 M aqueous solution) and  $\text{HS}^i\text{Pr}$ , were used to treat **2** in the presence of  $\text{NaBF}_4$ . Analysis of the reaction mixture revealed that halido abstraction indeed occurred. However, the resulting





**Figure 5.** Molecular structure of the compound **6**-CH<sub>2</sub>Cl<sub>2</sub>, showing 50% probability ellipsoids ((left) top view and (right) side view). H atoms, phenyl rings of N-substituents (left), N-substituents (right), and the CH<sub>2</sub>Cl<sub>2</sub> molecule are omitted for the sake of clarity. Selected bond lengths and bond angles: Ni1–C1, 1.860(5) Å; Ni1–O1, 1.874(4) Å; Ni1–S1, 2.1868(15) Å; Ni1–S1B, 2.1966(15) Å; S1–S1B, 4.3380(25); C1–Ni1–S1, 93.98(16)°; C1–Ni1–S1B, 102.06(16)°; S1B–Ni1–O1, 81.79(4)°; O1–Ni1–S1, 82.05(5)°; S1–Ni1–S1B, 163.49(5)°; C1–Ni1–O1, 175.67(18)°; Ni1–O1–Ni1A, 91.0(2)°. NiCS<sub>2</sub>O/NHC dihedral angle = 47.5(2)°. Ni<sub>3</sub>S<sub>3</sub>/Ni<sub>2</sub>O dihedral angle = 54.1(1)°.

Ni(II)–NHC fragments did not aggregate with the external isopropylthiolato ligands. Instead, the trinuclear complex **6** bearing an interesting cationic [Ni<sub>3</sub>S<sub>3</sub>O] triangle formed as a result of reorganization and concurrent capture of an oxygen atom. The complex charge is balanced by one BF<sub>4</sub><sup>−</sup> counteranion.

Apparently, the thiols were not involved in this reaction, and the O atom is likely to originate from the aqueous NaOH solution. It is anticipated that the bromido are replaced by hydroxido ligands in a first step, and subsequent deprotonation of the intermediate Ni-hydroxo acid afforded a trinuclear species with a central  $\mu_3$ -O<sup>2−</sup> ligand. It is worth noting that the addition of sodium isopropylthiolate to the Pd(II)-imidazolin-2-ylidene analogue **1b** gave rise to a tetrapalladium macrocycle with bridging isopropylthiolato ligands, which nicely demonstrates the very different reactivity of dinickel complex **2** and its Pd(II) analogues **1a/b**.

A control reaction without isopropyl thiol supported this hypothesis, and the reaction of **2** with aqueous NaOH solution and excess NaBF<sub>4</sub> led indeed to the isolation of **6** in a better yield of 64%, in comparison to 40% from the reaction with the thiols (Scheme 4). Complex **6** is soluble in CH<sub>3</sub>CN, DMSO, and DMF, sparingly soluble in CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub>, but insoluble in less-polar solvents such as hexane and diethyl ether. Its positive-mode ESI spectrum shows a base peak at  $m/z = 993$  corresponding to the [M – BF<sub>4</sub>]<sup>+</sup> fragment. In the <sup>1</sup>H NMR spectrum, only one set of ligand signals is observed, which points to a symmetrical molecule. Five pseudo-doublets/triplets resonating in the range of 6.24–1.71 ppm are assigned to the six diastereotopic methylene protons, and consistent with the symmetry, one carbene signal is observed at 179.6 ppm.

Single crystals of **6** were grown from CH<sub>2</sub>Cl<sub>2</sub>, and the molecular structure determined by XRD analysis is shown in Figure 5. There is one six-membered [Ni<sub>3</sub>S<sub>3</sub>] equilateral triangle with an equal side length of 4.3380(25) Å. Above the center of the triangle, one oxido ligand bridges three Ni(II) centers, capping the triangular plane. The dihedral angle between the [Ni<sub>3</sub>S<sub>3</sub>] triangle and each of the Ni<sub>2</sub>O planes is 54.1(1)°. Besides the  $\mu_3$ -oxido ligand, each Ni(II) center is coordinated by one chelating NHC-thiolato ligand and one additional sulfur donor from a neighboring NHC in an essentially square planar manner. Within 3 $\sigma$ , the Ni–C<sub>carbene</sub> bonds [1.860(5) Å] are similar to those in **2** [1.873(6) and

1.892(5) Å], and the same applies to the Ni–S bonds of 2.1868(15) and 2.1966(15) Å [cf. 2.1799(16)/2.2398(15) Å for **2**]. Finally, the dihedral angles between NiCS<sub>2</sub>O and NHC planes are 47.5(2)°.

To further explore this interesting reactivity, dimeric complex **2** was treated with Na<sub>2</sub>S·9H<sub>2</sub>O and NaBF<sub>4</sub> in CH<sub>3</sub>CN or CH<sub>3</sub>CN/H<sub>2</sub>O, for the purpose of preparing the sulfido analogue of **6**. However, the majority of the starting materials were reisolated, and electrospray ionization–mass spectroscopy (ESI MS) analysis of the latter reaction revealed that **6** formed as the major product. The preferred binding of the hard O atom over the soft S atom in this system is very consistent with the HSAB theory.

To compare the reactivity of **2** to its higher analogues further, **1a** and **4** were treated with either NaOH or Na<sub>2</sub>S·9H<sub>2</sub>O, respectively. The Pd(II) dimer **1a** did not react with NaOH and NaBF<sub>4</sub> under various conditions (e.g., excess reagents, increased reaction temperature and prolonged reaction time). On the other hand, the reaction of **1a** with Na<sub>2</sub>S·9H<sub>2</sub>O in the presence of NaBF<sub>4</sub> and CH<sub>3</sub>CN/H<sub>2</sub>O proceeded more easily, and the expected trinuclear [Pd<sub>3</sub>S<sub>3</sub>S] complex **7** was isolated in the yield of 68% (see Scheme 4), as supported by ESI MS, which shows a base peak at  $m/z = 1152$  for the [M – BF<sub>4</sub>]<sup>+</sup> complex cation. Similar to **6**, only one set of signals is observed in the <sup>1</sup>H NMR spectrum of **7**. Two doublets resonate at 6.10 and 5.90 ppm, respectively, which are assignable to the benzylic protons, with a coupling constant of <sup>2</sup>J(H–H) = 15.8 Hz. Four other pseudo-doublets/triplets are observed in the range of 5.12–2.36 ppm, corresponding to the methylene protons of the sulfur chelate. In its <sup>13</sup>C NMR spectrum, one downfield signal at 179.5 ppm is observed for the carbene carbon.

Surprisingly, Pt(II) dimer **4** did not react with either NaOH or Na<sub>2</sub>S·9H<sub>2</sub>O under various reaction conditions.

## CONCLUSION

With the isolation of complex **2** and **4**, we have confirmed that the syntheses of dimeric thiolato-bridged NHC complexes via a combined and in situ deprotonation/hydrolysis pathway of a thioester-functionalized azolium salt can be extended to Ni(II) and Pt(II). The general methodology of masking an NHC–thiol ligand via its thioester-functionalized azolium ligand precursor is likely to find more applications in the coordination

chemistry of NHC/thiolato chelators. Reactivity studies of the aforementioned dimeric complexes and their Pd(II) analogue **1a** toward either Me<sub>3</sub>OBF<sub>4</sub>, NaOH, or Na<sub>2</sub>S·9H<sub>2</sub>O gave different results. Ni(II) dimer **2** decomposed when treated with Me<sub>3</sub>OBF<sub>4</sub>, while Pt(II) analogue **4** reacted in a similar way to Pd(II) dimer **1a**, leading to tetranuclear [Pt<sub>4</sub>S<sub>4</sub>] macrocycle **5**. The reaction of **2** and aqueous NaOH in the presence of NaBF<sub>4</sub> yielded a new trinuclear Ni(II) complex **6** with a [Ni<sub>3</sub>S<sub>3</sub>O] triangle via capture of an μ<sub>3</sub>-oxido ligand. In contrast, the reaction of Pd(II) dimer **1a** with NaOH was sluggish, while the treatment of **1** with Na<sub>2</sub>S·9H<sub>2</sub>O yielded a new trinuclear Pd(II) species [Pd<sub>3</sub>S<sub>3</sub>S] with an capping μ<sub>3</sub>-sulfide ligand. On the other hand, the Pt(II) analogue **4** did not lead to the isolation of any product with either NaOH or Na<sub>2</sub>S·9H<sub>2</sub>O. All complexes have been fully characterized and some of their molecular structures determined by X-ray diffraction (XRD) analyses. Research in our laboratory is currently ongoing to extend our methodology to transition metals beyond group 10. Studies are also underway to explore the preparation of higher NHC/thiolato aggregates by simple halido abstraction as an entry to metallo-based supramolecular chemistry.

## EXPERIMENTAL SECTION

**General Considerations.** Unless otherwise noted, all operations were performed without taking precautions to exclude air and moisture, and all solvents and chemicals were used as-received. Thioester-functionalized benzimidazolium salt **A** and dimeric Pd(II) complex **1a** have been synthesized according to a reported procedure.<sup>5a</sup> <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra were recorded on a Bruker ACF 300 spectrometer or AMX 500 spectrophotometer, and the chemical shifts (δ) were internally referenced to the residual solvent signals relative to tetramethylsilane (<sup>1</sup>H, <sup>13</sup>C) or externally to CF<sub>3</sub>CO<sub>2</sub>H (<sup>19</sup>F NMR). Electrospray ionization–mass spectroscopy (ESI MS) spectra were measured using a Finnigan MAT LCQ spectrometer. Elemental analyses were performed on an Elementar Vario Micro Cube elemental analyzer at the Department of Chemistry, National University of Singapore.

**Dimeric Ni(II) Complex 2.** A mixture of salt **A** (117 mg, 0.3 mmol), Ni(OAc)<sub>2</sub> (53 mg, 0.3 mmol) and [N(*n*-Bu)<sub>4</sub>]Br (0.5 g) was dried under vacuum at 60 °C for 3 h. After slowly heating to 120 °C, the solid melted and the color changed to dark red. The mixture was stirred at this temperature under vacuum overnight. After cooling to ambient temperature, H<sub>2</sub>O (20 mL) and CH<sub>2</sub>Cl<sub>2</sub> (10 mL) were added to the resulting solid. The organic phase was separated, washed with H<sub>2</sub>O (3 × 20 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and passed through a short plug of silica gel. Removal of the solvent in vacuo afforded the product as a red solid (81 mg, 0.10 mmol, 68%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.61 (d, <sup>3</sup>J(H,H) = 7.6 Hz, 4 H, Ar–H), 7.38–7.28 (m, 8 H, Ar–H), 7.24–7.13 (m, 6 H, Ar–H), 6.71 (d, <sup>2</sup>J(H,H) = 15.8 Hz, 2 H, NCHHPh), 5.61 (d, <sup>2</sup>J(H,H) = 15.8 Hz, 2 H, NCHHPh), 5.02 (ps-t, 2 H, NCHH), 4.78 (ps-d, 2 H, NCHH), 3.14 (ps-d, 2 H, CHHS), 1.56 (ps-t, 2 H, CHHS). <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, CDCl<sub>3</sub>): 176.1 (s, NCN), 136.0, 135.0, 134.0, 128.8, 128.0, 127.9, 123.04, 123.02, 111.1, 109.9 (s, Ar–H), 52.7 (s, NCH<sub>2</sub>Ph), 49.4 (s, NCH<sub>2</sub>), 25.6 (s, CH<sub>2</sub>S). Anal. Calcd for C<sub>32</sub>H<sub>30</sub>Br<sub>2</sub>N<sub>4</sub>Ni<sub>2</sub>S<sub>2</sub>: C, 47.34%; H, 3.72%; N, 6.90%. Found: C, 47.47%; H, 3.75%; N, 6.62%. MS (FAB): *m/z* = 733 [M – Br]<sup>+</sup>.

**Dinuclear Pt(II) Complex 3.** Salt **A** (391 mg, 1 mmol) and PtBr<sub>2</sub> (355 mg, 1 mmol) were dissolved in CH<sub>3</sub>CN (5 mL) and heated under reflux overnight. The resulting orange solid was collected by filtration and washed with DMF until the color turned yellow. Complex **3** was obtained after washing with diethyl ether (3 × 5 mL) and drying under vacuum. The DMF solution was left to stand and the second batch of the product was isolated by collecting the yellow precipitate and washing it with diethyl ether (3 × 5 mL) (374 mg, 0.3 mmol, 60%). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): δ 10.15 (br-s, 1 H, NCHN), 10.08 (br-s, 1 H, NCHN), 8.29 (d, <sup>3</sup>J(H,H) = 9.0 Hz, 1 H,

Ar–H), 8.20 (d, <sup>3</sup>J(H,H) = 9.0 Hz, 1 H, Ar–H), 7.93 (s, 2 H, Ar–H), 7.66–7.39 (m, 14 H, Ar–H), 5.80 (br-s, 4 H, CH<sub>2</sub>Ph), 5.33 (br-s, 4 H, NCH<sub>2</sub>), 3.26 (br-s, 4 H, CH<sub>2</sub>S). <sup>13</sup>C{<sup>1</sup>H} NMR (75.47 MHz, DMSO-*d*<sub>6</sub>): 143.1, 143.0 (s, NCHN), 134.2, 134.16, 131.9, 131.7, 131.3, 129.3, 129.1, 128.7, 127.1, 114.3 (s, Ar–C), 50.4 (s, CH<sub>2</sub>Ph), 48.5 (d, <sup>3</sup>J(C,Pt) = 42 Hz, NCH<sub>2</sub>), 30.2 (d, <sup>2</sup>J(C,Pt) = 55 Hz, CH<sub>2</sub>S). Anal. Calcd for C<sub>32</sub>H<sub>32</sub>Br<sub>4</sub>N<sub>4</sub>Pt<sub>2</sub>S<sub>2</sub>: C, 30.83%; H, 2.59%; N, 4.49%. Found: C, 30.60%; H, 2.17%; N, 4.36%. MS (ESI): *m/z* = 1244 [M – Br]<sup>+</sup>.

**Dimeric Pt(II) Complex 4.** Complex **3** (374 mg, 0.3 mmol) and Ag<sub>2</sub>O (70 mg, 0.3 mmol) were suspended in CH<sub>3</sub>CN (10 mL) and heated at 75 °C overnight. The mixture was cooled and filtered over Celite to remove the precipitate. After the solvent of the filtrate was removed in vacuo, the resulting solid was redissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and passed through a short plug of silica gel. Removal of the solvent afforded the product as a yellow solid (172 mg, 0.16 mmol, 53%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 7.86 (d, <sup>3</sup>J(H,H) = 5.0 Hz, 2 H, Ar–H), 7.57–7.52 (m, 6 H, Ar–H), 7.38–7.28 (m, 10 H, Ar–H), 6.48 (d, <sup>2</sup>J(H,H) = 15.8 Hz, 2 H, NCHHPh), 5.68 (d, <sup>2</sup>J(H,H) = 15.8 Hz, 2 H, NCHHPh), 5.03 (ps-d, 2 H, NCHH), 4.31 (ps-d, 2 H, NCHH), 3.76 (ps-d, 2 H, CHHS), 2.24 (ps-t, 2 H, CHHS). <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, DMSO-*d*<sub>6</sub>): 161.5 (s, NCN), 136.7, 133.7, 133.5, 129.1, 128.3, 127.9, 124.3, 124.2, 112.6, 112.3 (s, Ar–H), 51.2 (s, NCH<sub>2</sub>Ph), 50.4 (s, NCH<sub>2</sub>), 23.1 (s, CH<sub>2</sub>S). Anal. Calcd for C<sub>32</sub>H<sub>30</sub>Br<sub>2</sub>N<sub>4</sub>Pt<sub>2</sub>S<sub>2</sub>: C, 35.43%; H, 2.79%; N, 5.17%. Found: C, 35.40%; H, 2.73%; N, 4.79%. MS (ESI): *m/z* = 1045 [M – Br + CH<sub>3</sub>CN]<sup>+</sup>.

**Tetranuclear Pt(II) Complex 5.** A mixture of **4** (54 mg, 0.05 mmol) and Me<sub>3</sub>OBF<sub>4</sub> (22 mg, 0.15 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was heated under reflux overnight. The resulting mixture was filtered and the product was obtained as an off-white powder (17 mg, 0.008 mmol, 30%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 8.02 (d, <sup>3</sup>J(H,H) = 5.0 Hz, 2 H, Ar–H), 7.75 (d, <sup>3</sup>J(H,H) = 5.0 Hz, 4 H, Ar–H), 7.54–7.29 (m, 30 H, Ar–H), 6.14 (d, <sup>2</sup>J(H,H) = 15.1 Hz, 2 H, CHHPh), 5.78 (d, <sup>2</sup>J(H,H) = 15.1 Hz, 2 H, CHHPh), 5.72 (br s, 4 H, CH<sub>2</sub>Ph), 5.44 (ps-d, 2 H, NCHH), 5.25 (ps-d, 2 H, NCHH), 5.10 (ps-t, 2 H, NCHH), 4.92 (ps-t, 2 H, NCHH), 4.05 (ps-d, 2 H, CHHS), 2.94 (ps-t, 2 H, CHHS), 2.60 (ps-t, 2 H, CHHS), 2.36 (ps-d, 2 H, CHHS). <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, DMSO-*d*<sub>6</sub>): 148.8, 147.1 (s, NCN), 135.5, 135.48, 133.8, 133.6, 133.1, 129.4, 129.1, 128.8, 128.4, 127.7, 127.2, 125.2, 125.16, 124.9, 113.1, 113.0, 112.8, 112.5 (s, Ar–H), 51.0, 50.6 (s, CH<sub>2</sub>Ph), 50.3, 49.1 (s, NCH<sub>2</sub>), 33.9, 31.6 (s, CH<sub>2</sub>S). <sup>19</sup>F{<sup>1</sup>H} NMR (282.37 MHz, DMSO-*d*<sub>6</sub>): –72.28 (s, <sup>10</sup>BF<sub>4</sub>), –72.33 (s, <sup>11</sup>BF<sub>4</sub>). Anal. Calcd for C<sub>64</sub>H<sub>60</sub>B<sub>2</sub>Br<sub>2</sub>F<sub>8</sub>N<sub>8</sub>Pt<sub>4</sub>S<sub>4</sub>: C, 35.21%; H, 2.77%; N, 5.13%. Found: C, 35.13%; H, 3.04%; N, 4.79%. MS (ESI): *m/z* = 1004 [M – 2BF<sub>4</sub>]<sup>2+</sup>.

**Trinuclear Ni(II) Complex 6.** A mixture of complex **2** (41 mg, 0.05 mmol), NaOH (6.25 mol/L aqueous solution, 16 μL, 0.1 mmol), and NaBF<sub>4</sub> (6 mg, 0.05 mmol) was stirred in CH<sub>3</sub>CN (5 mL) at 70 °C overnight. The mixture was allowed to cool to ambient temperature and filtered over Celite. The solvent of the filtrate was removed under vacuum, and the resulting red solid was redissolved in CH<sub>3</sub>CN (5 mL) and filtered over Celite again. After the CH<sub>3</sub>CN was removed in vacuo, the red solid was washed with CH<sub>2</sub>Cl<sub>2</sub> (3 × 3 mL) to give complex **6**. The CH<sub>2</sub>Cl<sub>2</sub> solution was left for slow evaporation to obtain red crystals as a second crop of complex **6** (23 mg, 0.02 mmol, 64%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 7.75–7.62 (m, 12 H, Ar–H), 7.42–7.28 (m, 15 H, Ar–H), 6.24 (d, <sup>2</sup>J(H,H) = 15.8 Hz, 3 H, CHHPh), 5.78 (m, 6 H, CHHPh + NCHH), 5.34 (ps-d, 3 H, NCHH), 1.94 (ps-t, 3 H, CHHS), 1.71 (ps-d, 2 H, CHHS). <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, DMSO-*d*<sub>6</sub>): 179.6 (s, NCN), 136.7, 134.6, 134.5, 129.3, 128.6, 127.9, 123.9, 123.7, 111.7, 111.3 (s, Ar–H), 51.1 (s, CH<sub>2</sub>Ph), 49.9 (s, NCH<sub>2</sub>), 28.8 (s, CH<sub>2</sub>S). <sup>19</sup>F{<sup>1</sup>H} NMR (282.37 MHz, DMSO-*d*<sub>6</sub>): –72.28 (s, <sup>10</sup>BF<sub>4</sub>), –72.33 (s, <sup>11</sup>BF<sub>4</sub>). Anal. Calcd for C<sub>48</sub>H<sub>45</sub>BF<sub>4</sub>N<sub>6</sub>Ni<sub>3</sub>OS<sub>3</sub>·3DMSO: C, 49.31%; H, 4.83%; N, 6.39%. Found: C, 49.23%; H, 4.36%; N, 6.59%. MS (ESI): *m/z* = 993 [M – BF<sub>4</sub>]<sup>+</sup>.

**Trinuclear Pd(II) complex 7.** Complex **1a**<sup>5a</sup> (30 mg, 0.033 mmol) was treated with Na<sub>2</sub>S·9H<sub>2</sub>O (8 mg, 0.033 mmol) and NaBF<sub>4</sub> (4 mg, 0.033 mmol) in CH<sub>3</sub>CN (5 mL) and H<sub>2</sub>O (1 mL) at 70 °C for one day. After cooling to ambient temperature, the mixture was filtered

Table 2. Selected X-ray Crystallographic Data for Complexes 2, 3·2DMSO, 4·CH<sub>2</sub>Cl<sub>2</sub>, and 6·CH<sub>2</sub>Cl<sub>2</sub>

	2	3·2DMSO	4·CH <sub>2</sub> Cl <sub>2</sub>	6·CH <sub>2</sub> Cl <sub>2</sub>
formula	C <sub>32</sub> H <sub>30</sub> Br <sub>2</sub> N <sub>4</sub> Ni <sub>2</sub> S <sub>2</sub>	C <sub>32</sub> H <sub>32</sub> Br <sub>4</sub> N <sub>4</sub> Pt <sub>2</sub> S <sub>2</sub> ·2C <sub>2</sub> H <sub>6</sub> OS	C <sub>33</sub> H <sub>32</sub> Br <sub>2</sub> Cl <sub>2</sub> N <sub>4</sub> Pt <sub>2</sub> S <sub>2</sub> ·CH <sub>2</sub> Cl <sub>2</sub>	C <sub>48</sub> H <sub>45</sub> BF <sub>4</sub> N <sub>6</sub> Ni <sub>3</sub> OS <sub>3</sub> ·CH <sub>2</sub> Cl <sub>2</sub>
formula wt, Fw	811.96	1402.81	1169.65	1165.95
color, habit	red, block	yellow, rod	colorless, block	red, block
cryst size [mm]	0.12 × 0.10 × 0.10	0.46 × 0.26 × 0.10	0.26 × 0.10 × 0.10	0.16 × 0.10 × 0.04
temp [K]	296(2)	223(2)	100(2)	100(2)
cryst syst	orthorhombic	monoclinic	orthorhombic	rhombohedral
space group	P2(1)2(1)2(1)	P2(1)/n	Fdd2	R3c
a [Å]	9.7788(4)	13.0288(7)	18.1205(9)	13.6577(12)
b [Å]	15.2048(6)	7.8627(5)	49.575(3)	13.6577(12)
c [Å]	21.1848(8)	21.6471(12)	15.1791(8)	45.745(4)
α [deg]	90	90	90	90
β [deg]	90	107.2210(10)	90	90
γ [deg]	90	90	90	120
V [Å <sup>3</sup> ]	3149.9(2)	2118.1(2)	13635.7(12)	7389.7(11)
Z	4	2	16	6
D <sub>c</sub> [g cm <sup>-3</sup> ]	1.712	2.199	2.279	1.572
radiation used	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ [mm <sup>-1</sup> ]	3.895	10.605	10.854	1.430
θ range [deg]	1.65–27.49	1.64–27.49	1.80–27.50	1.94–27.49
no. of unique data	7215	4860	7820	2856
max., min transmn	0.6968, 0.6522	0.4169, 0.0847	0.4099, 0.1647	0.9450, 0.8034
final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0508, wR <sub>2</sub> = 0.1051	R <sub>1</sub> = 0.0389, wR <sub>2</sub> = 0.0947	R <sub>1</sub> = 0.0295, wR <sub>2</sub> = 0.0726	R <sub>1</sub> = 0.0486, wR <sub>2</sub> = 0.1235
R indices (all data)	R <sub>1</sub> = 0.0828, wR <sub>2</sub> = 0.1156	R <sub>1</sub> = 0.0483, wR <sub>2</sub> = 0.0991	R <sub>1</sub> = 0.0321, wR <sub>2</sub> = 0.0737	R <sub>1</sub> = 0.0521, wR <sub>2</sub> = 0.1261
goodness-of-fit on F <sup>2</sup>	0.989	1.043	1.030	1.121
peak/hole [e Å <sup>-3</sup> ]	0.576/–0.526	1.516/–1.997	2.069/–1.141	0.0914/–0.842

over Celite and the solvent of the filtrate was removed. The resulting yellow solid was redissolved in CH<sub>3</sub>CN (5 mL) and filtered over Celite again. After the solvent was removed in vacuo, the yellow solid was redissolved in MeOH (5 mL) and filtered. Complex 7 was obtained as a yellow solid after removal of the solvent (19 mg, 0.015 mmol, 68%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 7.78–7.73 (m, 6 H, Ar–H), 7.60–7.58 (m, 6 H, Ar–H), 7.41–7.36 (m, 15 H, Ar–H), 6.10 (d, <sup>2</sup>J(H,H) = 15.8 Hz, 3 H, CHHPh), 5.90 (d, <sup>2</sup>J(H,H) = 15.8 Hz, 3 H, CHHPh), 5.12 (ps-d, 2 H, NCHH), 4.13 (ps-t, 3 H, NCHH), 2.36 (ps-d, 2 H, CHHS). The other signal due to CHHS overlaps with the residue signal of *d*<sub>6</sub>-DMSO. <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, DMSO-*d*<sub>6</sub>): 179.5 (s, NCN), 135.8, 133.6, 133.2, 128.9, 128.2, 127.5, 123.9, 112.2, 111.7 (s, Ar–H), 51.3 (s, CH<sub>2</sub>Ph), 50.4 (s, NCH<sub>2</sub>), 30.1 (s, CH<sub>2</sub>S). <sup>19</sup>F{<sup>1</sup>H} NMR (282.37 MHz, DMSO-*d*<sub>6</sub>): –72.28 (s, <sup>10</sup>BF<sub>4</sub>), –72.33 (s, <sup>11</sup>BF<sub>4</sub>). Anal. Calcd for C<sub>48</sub>H<sub>45</sub>BF<sub>4</sub>N<sub>6</sub>Pd<sub>3</sub>S<sub>4</sub>: C, 46.48; H, 3.66; N, 6.78. Found: C, 46.40; H, 3.80; N, 6.79%. MS (ESI): *m/z* = 1152 [M – BF<sub>4</sub>]<sup>+</sup>.

**X-ray Diffraction Studies.** X-ray data for 2, 3·2DMSO, 4·CH<sub>2</sub>Cl<sub>2</sub>, and 6·CH<sub>2</sub>Cl<sub>2</sub> were collected with a Bruker AXS SMART APEX diffractometer, using Mo Kα radiation at 296(2) K (for 2), 223(2) K (for 3·2DMSO), or 100(2) K (for 4·CH<sub>2</sub>Cl<sub>2</sub> and 6·CH<sub>2</sub>Cl<sub>2</sub>) with the SMART suite of Programs.<sup>10</sup> Data were processed and corrected for Lorentz and polarization effects with SAINT,<sup>11</sup> and for absorption effect with SADABS.<sup>12</sup> Structural solution and refinement were carried out with the SHELXTL suite of programs.<sup>13</sup> The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. All H atoms were put at calculated positions. A summary of the most important crystallographic data is given in Table 2.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Crystallographic data for 2, 3·2DMSO, 4·CH<sub>2</sub>Cl<sub>2</sub>, and 6·CH<sub>2</sub>Cl<sub>2</sub> as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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