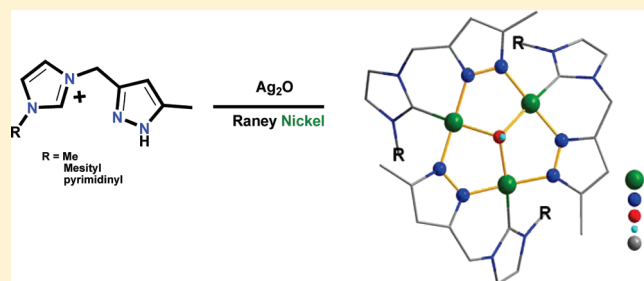


Synthesis and Characterization of Nickel Inverse 9-Metallacrown-3, Palladium–Silver, and Dinuclear Platinum Complexes Containing Pyrazole-Functionalized NHC Ligands

Chao Chen,^{†,‡} Huayu Qiu,^{*,‡} and Wanzhi Chen^{*,†}[†]Department of Chemistry, Zhejiang University, Xixi Campus, Hangzhou 310028, People's Republic of China[‡]College of Materials, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 310036, People's Republic of China

S Supporting Information

ABSTRACT: Three metallacrown nickel complexes $[\text{Ni}_3(\mu\text{-OH})(\text{L}1)_3](\text{PF}_6)_2$ (**1**, $\text{L}1 = 3\text{-}((N\text{-methylimidazolylidenyl})\text{-methyl})\text{-5-methylpyrazolate}$), $[\text{Ni}_3(\mu\text{-OH})(\text{L}2)_3](\text{PF}_6)_2$ (**2**, $\text{L}2 = 3\text{-}((N\text{-mesitylimidazolylidenyl})\text{methyl})\text{-5-methylpyrazolate}$), and $[\text{Ni}_3(\mu\text{-OH})(\text{L}3)_3](\text{PF}_6)_2$ (**3**, $\text{L}3 = 3\text{-}((N\text{-pyrimidin-2-ylimidazolylidenyl})\text{methyl})\text{-5-methylpyrazolate}$) were obtained by the reactions of corresponding silver–NHC complexes with Raney nickel powder at 45 °C. The same reaction at 80 °C afforded $[\text{Ni}_3(\text{L}2)_4](\text{PF}_6)_2$ (**4**). The carbene-transfer reaction of the silver–carbene complex with $[(\eta^3\text{-C}_3\text{H}_5)\text{PdCl}]_2$ yielded the heterotrimetallic complex $[\text{AgPd}_2(\eta^3\text{-C}_3\text{H}_5)_2(\text{L}2)_2](\text{PF}_6)_2$ (**5**), whereas the carbene-transfer reaction with $\text{Pt}(\text{cod})\text{Cl}_2$ gave $[\text{Pt}_2(\text{L}3)_2](\text{PF}_6)_2$ (**6**). All of these complexes have been fully characterized by ESI-MS, NMR spectroscopy, and elemental analysis. The molecular structures of **1–6** were also studied by X-ray diffraction analysis. In **1–3**, three nickel centers are bridged together by three pyrazole–NHC ligands and a hydroxide group, forming a 9-metallacrown-3 topology. Complex **4** is paramagnetic, consisting of two square-planar nickel(II) ions and one tetrahedral nickel ion in which three Ni ions are bridged by four pyrazolate units. In the mixed Pd–Ag complex **5**, two palladium and one silver centers are bridged by two pyrazole–NHC ligands. Complex **5** showed good catalytic activity in the Sonogashira coupling reaction of aryl bromides and phenylacetylene under mild conditions typically catalyzed by Pd–Cu systems.



INTRODUCTION

Pyrazole derivatives have adjacent nitrogen atoms that could incorporate more than one reactive metal atom in close proximity, thus facilitating potentially unique chemical reactivity and physical properties. Many homo- or heterometallic complexes of pyrazole derivatives containing short metal–metal distances have found wide applications in material science,¹ bioinorganic chemistry,² and homogeneous catalysis.³ Although many polynuclear complexes with pyrazoles or pyrazolates are known,⁴ the most notable examples are the trinuclear cyclic complexes of coinage metals. For example, the triangular pyrazole-based copper complexes with a $\text{Cu}_3(\mu\text{-X})_2$ core ($\text{X} = \text{Cl}, \text{Br}$) may relate to the active sites of particulate methane monooxygenase.⁵ The analogous $[\text{Cu}_3(\mu\text{-OH})(\mu\text{-pz})_3]$ complex ($\text{Hpz} = \text{pyrazole}$) acts as a valuable catalyst or catalyst precursor in the peroxidative oxidation of cyclohexane and cyclopentane to the corresponding ketones and alcohols.⁶ Moreover, the macrocyclic structure has a topology of metallacrown, which can be considered as analogous of crown ethers with the repeat unit of $[\text{metal-N-N}]$ —in which the metal atoms are oriented toward the center of the cavity.⁷ Metallacrowns of different sizes are a new class of molecular recognition agents that can selectively encapsulate

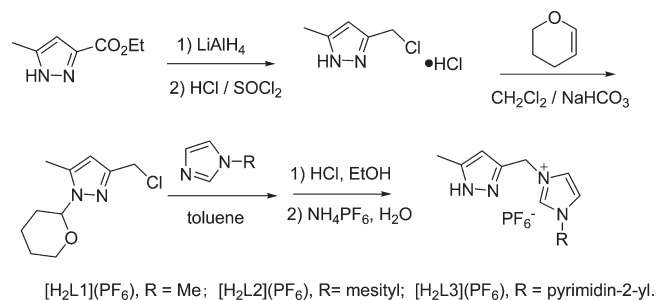
cations and anions in their cavities.⁸ A few well-defined pyrazole-based metallacrown complexes have been reported, and their physical properties have been studied.⁹ However, the metallacrown complexes involving *N*-heterocyclic carbene ligands have not been known so far.

N-Heterocyclic carbenes (NHCs) have been extensively studied as ligands in organometallic chemistry and homogeneous catalysis due to their strong σ -donor properties and ease of preparation.¹⁰ Multidentate NHCs containing additional nitrogen functionalities may significantly improve catalyst stability, and their potential hemilability make ease of generation of vacant coordination sites and catalytically active species. Multidentate NHCs have been used for construction of multinuclear metal complexes showing interesting optophysical properties.¹¹ Transition-metal complexes of multidentate ligands have found wide applications in C–C coupling,¹² hydrosilylation,¹³ polymerization,¹⁴ and hydrogenation reactions.¹⁵ Our interest in this area involves the design and synthesis of metal–NHC complexes bearing various functional groups, such as pyridine,

Received: June 7, 2011

Published: July 27, 2011

Scheme 1. Synthesis of Ligand Precursors



pyrimidine, triazole, and naphthyridine, because such mixed C^N ligands would allow a further fine-tuning of the metal coordination.¹⁶ We have reported that pyrazole-linked bis(NHC) ligands were able to construct multinuclear silver and gold clusters displaying luminescence.¹⁷ The dinuclear nickel complexes containing pyrazole-functionalized bis(NHC) ligands showed remarkable enhancement of catalytic activities in homogeneous catalysis compared to corresponding mononuclear nickel complexes.¹⁸ Other related dinuclear and multinuclear pyrazolate NHC complexes have also been described.¹⁹ In this paper, we describe the synthesis and characterization of a few pyrazole-functionalized NHC ligands, the corresponding three trinuclear metallocrown nickel complexes, [Ni₃(μ-OH)(L1)₃](PF₆)₂ (**1**, L1 = 3-((N-methylimidazolyliidenyl)methyl)-5-methylpyrazolate), [Ni₃(μ-OH)(L2)₃](PF₆)₂ (**2**, L2 = 3-((N-mesitylimidazolyliidenyl)methyl)-5-methylpyrazolate), and [Ni₃(μ-OH)(L3)₃](PF₆)₂ (**3**, L3 = 3-((N-pyrimidin-2-ylimidazolyliidenyl)methyl)-5-methylpyrazolate), and a linear trinuclear nickel complex [Ni₃(L2)₄](PF₆)₂ (**4**). Dinuclear palladium and platinum complexes [AgPd₂(η³-C₃H₅)₂(L2)₂](PF₆) (**5**) and [Pt₂(L3)₂](PF₆)₂ (**6**) are also detailed.

RESULTS AND DISCUSSION

Synthesis of Ligand Precursors. As shown in Scheme 1, 3-(chloromethyl)-5-methylpyrazole hydrochloride salt was synthesized from reduction of ethyl 5-methyl-1H-pyrazole-3-carboxylate and subsequent chlorination. Further reaction of 3-(chloromethyl)-5-methyl-1-(tetrahydro-pyran-2-yl)pyrazole with N-alkylimidazole after removal of tetrahydropyran and anion exchange with NH₄PF₆ gave the corresponding imidazolium salts, 3-(N-methylimidazoliumylmethyl)-5-methyl-1H-pyrazole ([H₂L1](PF₆)), 3-(N-mesitylimidazoliumylmethyl)-5-methyl-1H-pyrazole ([H₂L2](PF₆)), and 3-(N-pyrimidin-2-ylimidazoliumylmethyl)-5-methyl-1H-pyrazole ([H₂L3](PF₆)) as white solids. The three imidazolium salts have been characterized by NMR and elemental analysis. The ¹H NMR spectra of these imidazolium salts in dmsO-d₆ exhibit their acidic imidazolium protons at 9.12, 9.70, and 10.22 ppm as singlets and pyrazole NH protons at 12.67, 12.69, and 12.67 ppm as broad singlets, respectively.

Synthesis and Characterization of [Ni₃(μ₃-OH)(L)₃](PF₆)₂. Direct reaction of metal powders with imidazolium salts is the most convenient procedure for the synthesis of metal–NHC complexes.^{16e} A solution of silver–NHC complexes, resulted from 5-(N-alkylimidazoliumylmethyl)-3-methyl-1H-pyrazole salts in acetonitrile with an equivalent of Ag₂O at 45 °C, was treated with an excess of Raney nickel powder overnight and yielded yellow solutions, and the trinuclear nickel complexes

[Ni₃(μ₃-OH)(L1)₃](PF₆)₂ (**1**), [Ni₃(μ₃-OH)(L2)₃](PF₆)₂, (**2**), and [Ni₃(μ₃-OH)(L3)₃](PF₆)₂ (**3**) were isolated as yellow solids in 22–51% yields (Scheme 2). We have previously reported the synthesis and structure of nickel hydroxide complexes of NHC ligands, and the hydroxide ion is assumed to come from water in solvent.¹⁸ In the case of [H₂L2](PF₆), another trinuclear complex [Ni₃(L2)₄](PF₆)₂ (**4**) was also obtained simultaneously. Complexes **1** and **3** could also be obtained through typical carbene-transfer reactions of silver complexes with Ni-(PPh₃)₂Cl₂, as we previously described in comparable yields.¹⁶ Interestingly, when we applied the same procedure to [H₂L2](PF₆), we found that, at 25 °C, complex **2** was exclusively afforded, whereas at 80 °C, complex **4** was obtained as the sole product. However, we were not able to prepare analogous [Ni₃(L1)₄](PF₆)₂ and [Ni₃(L3)₄](PF₆)₂ even at higher temperature by the carbene-transfer route, and only **1** and **3** could be obtained. Moreover, **2** is stable at 80 °C and could not convert to **4** upon heating. Complexes **1**–**4** have been fully characterized by elemental analysis, NMR, and ESI spectroscopy.

The ¹H NMR spectra of complexes **1** and **3** in dmsO-d₆ and **2** in acetone-d₆ show three singlet signals at 7.62, 7.39, and 6.01 ppm for **1**; 7.85, 7.54, and 5.81 ppm for **2**; and 8.08, 7.87, and 5.56 ppm for **3**, which can be assigned to the imidazolyliene backbone and pyrazole CH protons. The resonance signals of the methylene protons appear as doublets at 5.59 and 5.33 ppm for **1**, 5.65 and 5.37 ppm for **2**, and 5.61 and 5.19 ppm for **3**, respectively, illustrating that the rotation of the methylenes in **1**–**3** is prohibited. The resonances of hydroxide groups are observed at 2.08 and 2.34 ppm for **1** and **3**, respectively. However, the hydroxide group of complex **2** is found at 0.79 ppm. The ¹³C NMR spectra of **1**–**3** exhibit resonance peaks at 152, 154, and 158 ppm, which are ascribed to the carbenic carbon atoms.²⁰ In the ESI-MS spectra (positive ions in CH₃CN), the peaks at 866.89, 1176.65, and 1054.74 amu are ascribed to [Ni₃(μ-OH)(L)₃(PF₆)]⁺ and the peaks at 717.24, 1029.15, and 909.03 amu are ascribed to [Ni₃(μ-OH)(L)₃]²⁺ fragments. The existence of hydroxide ions is also supported by their IR spectra with broad absorptions at 3398, 3431, and 3422 cm^{−1} for **1**–**3**. Complex **4** shows unusual ¹H NMR and ¹³C NMR spectra. Although all the ¹H NMR peaks are sharp and their intensities are consistent with the formulation of **4**, they appeared in the range of −3.44 to 10.69 ppm, whereas ¹³C NMR resonances appear in the range of 12.0–200.2 ppm due to its paramagnetic nature induced by the tetrahedral nickel(II) ion. In the ESI-MS spectrum (positive ions, CH₃CN) of **4**, the peaks at 1347.12 and 646.45 amu are ascribed to [Ni₃(L2)₄(PF₆)]⁺ and [Ni₃(L2)₄]²⁺ fragments.

The structures of **1**–**3** were identified by X-ray single-crystal diffraction analysis. The single crystals suitable for X-ray diffraction were grown by slow diffusion of Et₂O into their CH₃CN and DMSO solutions. The three complexes have the same structures consisting of a triangular Ni₃ core in which three nickel ions are linked by three NHC ligands and a μ₃-OH group, and therefore, only the structure of **1** is shown in Figure 1. The structures of **2** and **3** are given in the Supporting Information. In the structure of **1**, each two nickel(II) ions are bridged by a pyrazolate ion, forming a nine-membered ring capped by a hydroxide. Each nickel(II) center is coordinated by two pyrazolates, one NHC, and one OH group, displaying typical square-planar geometry. Two pyrazolates coordinated to the same metal are trans-arranged. The hydroxide ion is equally bonded to the three metals in η³ fashion with an average Ni–O distance of 1.93 Å and is 0.620 Å out of the plane defined by three metal centers.

Scheme 2. Synthesis of the Nickel–Carbene Complexes

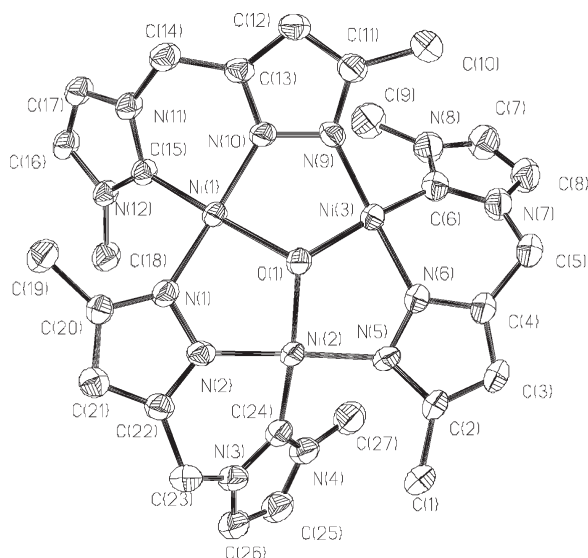
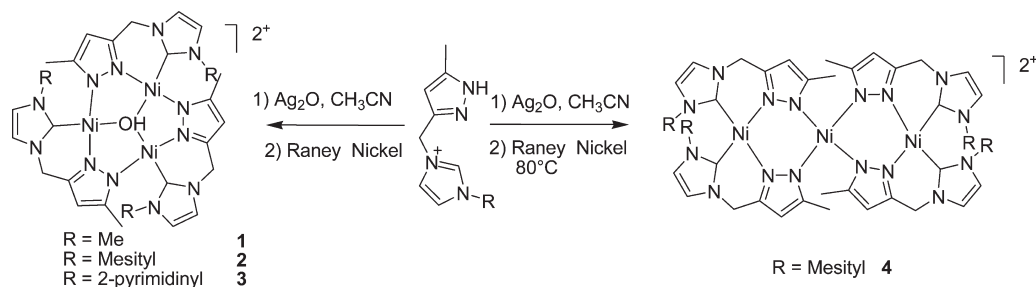


Figure 1. Cationic structure of **1** represented by thermal ellipsoids at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ni(1)–N(10) 1.852(7), Ni(1)–N(1) 1.855(8), Ni(1)–C(15) 1.862(9), Ni(1)–O(1) 1.938(6), Ni(2)–O(1) 1.929(6), Ni(2)–N(2) 1.833(8), Ni(2)–N(5) 1.869(8), Ni(2)–C(24) 1.879(12), Ni(3)–N(9) 1.857(8), Ni(3)–N(6) 1.858(9), Ni(3)–C(6) 1.871(12), Ni(3)–O(1) 1.933(6), Ni(2)–O(1)–Ni(3) 110.9(3), Ni(2)–O(1)–Ni(1) 110.0(3), Ni(3)–O(1)–Ni(1) 110.2(3), N(10)–Ni(1)–N(1) 169.7(4), N(2)–Ni(2)–N(5) 169.9(4), N(9)–Ni(3)–N(6) 170.0(4), C(15)–Ni(1)–O(1) 168.2(4), C(24)–Ni(2)–O(1) 168.9(4), C(6)–Ni(3)–O(1) 169.8(4).

The Ni–Ni distance is 3.174 Å, showing no metal–metal interaction. The Ni–C and Ni–N bond distances fall in the ranges of 1.862–1.879 and 1.833–1.869 Å, respectively, which are normal for square-planar nickel(II)–NHC complexes.²⁰ The distances between the three nickel ions and μ_3 -OH are similar [Ni(1)–O(1) = 1.938(6), Ni(2)–O(1) = 1.929(6), and Ni(3)–O(1) = 1.933(6)] and longer than those reported for other triangular complexes containing the [Ni₃(μ_3 -O)] core.²¹ The three pyrazole rings extend to the same side of the Ni₃ plane with dihedral angles between the pyrazole rings and the Ni₃ plane being 16.46, 13.51, and 15.85°, respectively, whereas the three NHC moieties extend to the other side of the Ni₃ plane.

Complexes **1–3** represent rare examples of inverse 9-metallacrown-3 with three repeating [Ni–N–N] units supported by NHC ligands. The center of the metallacycle accommodated a triply bridging hydroxide. The most common metallacrown structures containing three [M–N–N] units rely on the group

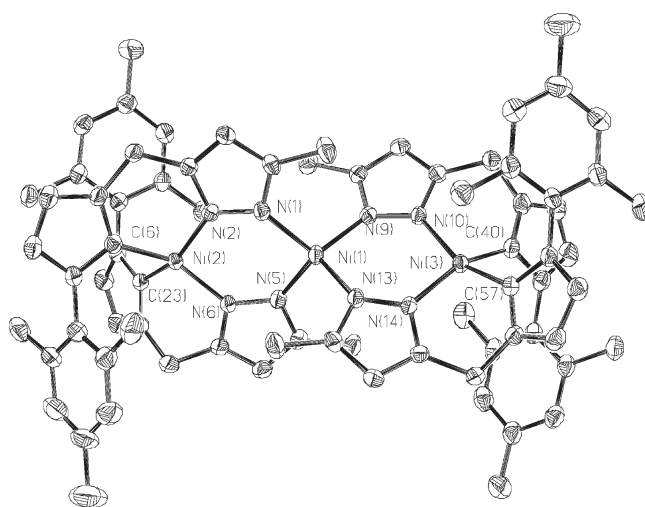


Figure 2. Cationic structure of **4** represented by thermal ellipsoids at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ni(1)–N(5) 1.954(5), Ni(1)–N(9) 1.969(5), Ni(1)–N(13) 1.971(5), Ni(1)–N(1) 1.977(5), Ni(2)–C(23) 1.861(6), Ni(2)–C(6) 1.869(6), Ni(2)–N(2) 1.922(5), Ni(2)–N(6) 1.930(5), Ni(3)–C(40) 1.860(6), Ni(3)–C(57) 1.865(6), Ni(3)–N(14) 1.927(4), Ni(3)–N(10) 1.927(5), N(5)–Ni(1)–N(9) 116.6(2), N(5)–Ni(1)–N(13) 107.3(2), N(9)–Ni(1)–N(13) 102.47(19), N(5)–Ni(1)–N(1) 102.81(19), N(9)–Ni(1)–N(1) 112.84(19), N(13)–Ni(1)–N(1) 115.16(19), C(23)–Ni(2)–C(6) 89.4(2), C(23)–Ni(2)–N(2) 156.2(2), C(6)–Ni(2)–N(2) 89.4(2), C(23)–Ni(2)–N(6) 87.8(2), C(6)–Ni(2)–N(6) 156.0(2), N(2)–Ni(2)–N(6) 102.51(19), C(40)–Ni(3)–C(57) 89.8(2), C(40)–Ni(3)–N(14) 157.9(2), C(57)–Ni(3)–N(14) 88.3(2), C(40)–Ni(3)–N(10) 88.4(2), C(57)–Ni(3)–N(10) 156.0(2), N(14)–Ni(3)–N(10) 101.92(19).

11 elements copper, silver, and gold.^{7,22} The tetracoordinated nickel(II) complex with a pyramidal μ_3 -OH core is hard to achieve considering the square-planar framework compared with other hexacoordinated nickel(II) compounds with the similar structure.

The molecular structure of **4** is shown in Figure 2. X-ray analysis reveals that **4** contains a linearly arranged trinuclear nickel moiety supported by four pyrazolate–NHC ligands. The central Ni(II) ion is linked to each terminal Ni(II) ion through two pyrazolate groups, forming a Ni₂N₄ ring with a twisted chair conformation. The two terminal nickel(II) ions are coordinated by two nitrogen atoms of pyrazoles and two carbon atoms of imidazolylidenes, respectively, forming a distorted square-planar

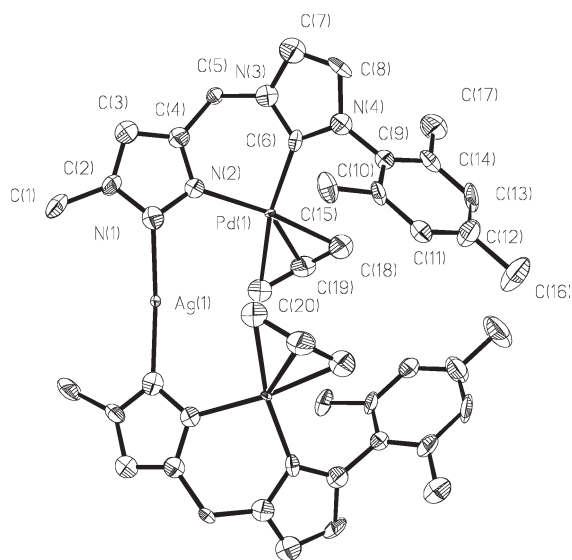
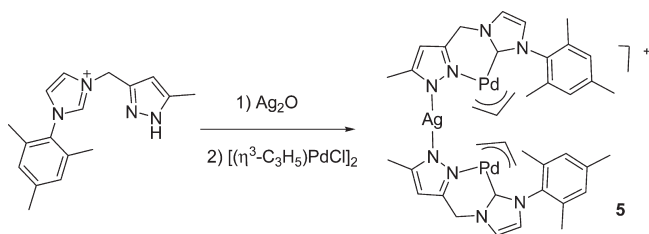
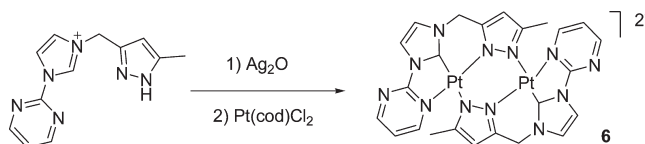
Scheme 3. Synthesis of **5**

Figure 3. Structure of **5** represented by thermal ellipsoids at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Pd(1)–C(6) 2.052(6), Pd(1)–N(2) 2.086(5), Pd(1)–C(18) 2.112(7), Pd(1)–C(19) 2.144(7), Pd(1)–C(20) 2.206(7), Ag(1)–N(1) 2.081(5), C(6)–Pd(1)–N(2) 86.5(2), C(6)–Pd(1)–C(18) 100.2(2), N(2)–Pd(1)–C(18) 172.9(2), C(6)–Pd(1)–C(19) 132.3(3), N(2)–Pd(1)–C(19) 137.1(2), C(18)–Pd(1)–C(19) 37.9(3), C(6)–Pd(1)–C(20) 168.8(2), N(2)–Pd(1)–C(20) 104.7(2), C(18)–Pd(1)–C(20) 68.6(3), C(19)–Pd(1)–C(20) 37.8(3), N(1)–Ag(1)–N(1)#1 176.1(3). Symmetry code: #1 $-x + 2, y, -z + 1/2$.

geometry. The bond distances of Ni–C [1.860(6)–1.869(6) Å] and Ni–N [1.922(5)–1.930(5) Å] and the bond angles between adjacent donating atoms (within the bond angles from 87.8° to 102.51° for Ni(2) and 88.3° to 101.92° for Ni(3)) are in the normal range as compared to many known nickel–NHC complexes having a square-planar geometry.²⁰ The central Ni(II) ion is coordinated by four pyrazolate nitrogen atoms. Unlike the two terminal nickel ions, the central nickel ion adopts a distorted tetrahedral geometry with N–Ni1–N bond angles of 102.47–116.59°. The steric hindrance of methyl groups on the pyrazole rings prevents a typical square-planar structure. The tetrahedral coordination geometry of nickel ion confirmed its paramagnetic nature due to the presence of two unpaired electrons. The bond distances of Ni(1)–N are in the range of 1.954(5)–1.977(5) Å, which are significantly longer than other Ni–N distances around the square-planar Ni(II) ions.

Synthesis and Characterization of [AgPd₂(η³-C₃H₅)₂-(L₂)₂](PF₆). The reactions of the in situ generated silver–NHC

Scheme 4. Synthesis of [Pt₂(L₃)₂](PF₆)₂ (**6**)

complexes from the pyrazole-imidazolium salts with Pd(cod)Cl₂ or Pd(CH₃CN)₂Cl₂ yielded pale-yellow solutions after removal of AgCl. Unfortunately, we were not able to isolate Pd–NHC complexes because they quickly decomposed to palladium black. When [(η³-C₃H₅)PdCl]₂ was used, a mixed palladium–silver complex **5** was obtained (Scheme 3). The complex was characterized by ¹H and ¹³C NMR spectra, elemental analysis, and ESI spectroscopy. In its ¹H NMR spectrum, the imidazolylidene backbone and pyrazole CH protons appear at 7.78, 7.45, and 6.18 ppm as three singlets. The ¹³C NMR spectrum exhibits a resonance peak at 175 ppm ascribed to the carbenic carbon atoms. In the ESI-MS spectrum (positive ions, CH₃CN), the peaks at 962.99 and 427.21 amu were ascribed to [AgPd₂(η³-C₃H₅)₂(L₂)₂]⁺ and [Pd(η³-C₃H₅)L₂]⁺ fragments.

Single crystals of **5** were obtained by slow evaporation of its acetonitrile solution. As shown in Figure 3, the structure of **5** consists of two tetracoordinated Pd(II) and one bicoordinated Ag(I) atom. The coordination geometry around Pd is distorted square-planar with one carbene, one pyrazole, and an ally group. The Pd(1)–C(6) distance (2.052(6)) is normal as compared to those of known palladium–NHC complexes (1.8–2.1 Å).²³ The Ag atom is linked by two pyrazoles in linear geometry with a N–Ag–N of 176.1(3)°. The Ag–N distance (2.081(5) Å) is also in the normal range of other silver complexes.²⁴

Synthesis and Characterization of [Pt₂(L₃)₂](PF₆)₂. As shown in Scheme 4, the carbene-transfer reaction with [Pt(cod)Cl₂] in acetonitrile gave [Pt₂(L₃)₂](PF₆)₂ (**6**) as a yellow solid. The cationic section of **6** is depicted in Figure 4. The two platinum(II) ions were linked by two pyrazolates, forming a Pt₂N₄ ring with a boat conformation, and the molecule as a whole displays a beautiful saddle-like conformation. Each Pt(II) ion is coordinated by two pyrazoles, one pyrimidine, and one NHC carbon in a square-planar geometry. The dihedral angle between the two pyrazole planes is 40.9°. The pyrimidine, pyrazole, and imidazolylidene rings of the same ligand are roughly coplanar. In the ESI-MS spectrum (positive ions, CH₃CN), the peaks at 1012.85 and 434.61 amu were ascribed to [Pt₂(L₃)₂](PF₆)⁺ and [PtL₃]⁺ fragments.

Catalytic Studies. Transition metal–NHC complexes have proven to be useful catalysts in various C–C coupling reactions. The mixed Pd–Ag complex offers us an opportunity to examine its efficiency for Sonogashira coupling. Although the Pd–Cu system is more frequently used, the Pd–Ag system is also a choice.²⁵ The well-defined Pd–Ag catalyst would be superior to the commonly used two-component catalysts taking account of practical convenience. Under the conditions we previously used,²⁶ we examined the catalytic activity of **5**. A brief investigation showed that **5** alone is inefficient for the coupling reaction of *p*-acetylphenyl bromide and phenylacetylene. Activation of the Pd–Ag catalyst was achieved by addition of 1 mol % of PPh₃. Phosphine is believed to stabilize low valent palladium species, which is the actual catalyst. A survey of the reaction of aryl halides with phenylacetylene using 1 mol % of **5** in the presence of Cs₂CO₃ at 80 °C was done, and the results are given in Table 1. The palladium–silver complex was found to be good for the

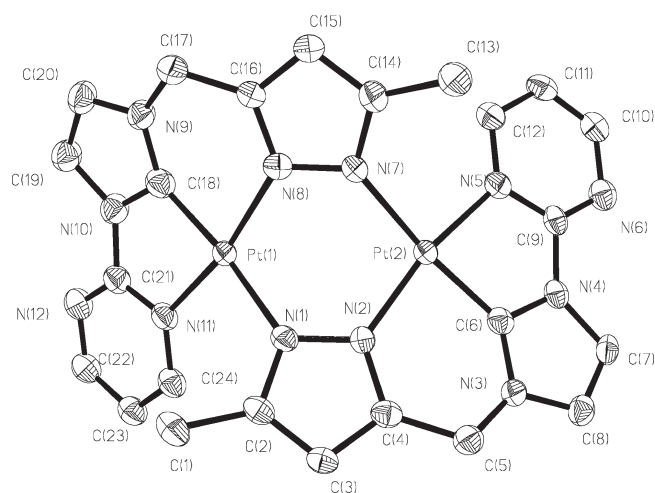


Figure 4. Molecular structure of **6** represented by thermal ellipsoids at a 30% level. Selected bond lengths (Å) and angles (deg): Pt(1)–C(18) 1.915(14), Pt(1)–N(8) 1.982(10), Pt(1)–N(11) 2.074(10), Pt(1)–N(1) 2.096(10), Pt(2)–C(6) 1.912(13), Pt(2)–N(2) 1.970(10), Pt(2)–N(5) 2.049(11), Pt(2)–N(7) 2.061(10), C(18)–Pt(1)–N(8) 86.7(5), C(18)–Pt(1)–N(11) 79.0(5), N(8)–Pt(1)–N(11) 164.2(4), C(18)–Pt(1)–N(1) 170.5(5), N(8)–Pt(1)–N(1) 95.2(4), N(11)–Pt(1)–N(1) 100.1(4), C(6)–Pt(2)–N(2) 88.2(5), C(6)–Pt(2)–N(5) 78.7(5), N(2)–Pt(2)–N(5) 164.7(4), C(6)–Pt(2)–N(7) 170.3(4), N(2)–Pt(2)–N(7), 95.4(4) N(5)–Pt(2)–N(7) 98.8(4).

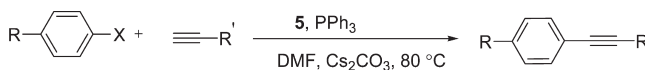
coupling of aryl bromides bearing electron-withdrawing or electron-donating substituents and phenylacetylene in good-to-excellent yields (entries 1–5). The catalyst system is also efficient for the coupling reaction of heteroaryl bromides, and the target products could be obtained in nearly quantitative yields (entries 6–8), although the reaction time is longer. Aliphatic alkynes show lower activity than aromatic alkynes (entries 9–10). The Sonogashira reaction of 4-chloroacetophene is also successful, giving a moderate yield within 24 h (entry 11).

In summary, we have synthesized and fully characterized a few nickel-, palladium-, and platinum–NHC complexes of pyrazole–NHC ligands. Nickel complexes **1–3** have a topology of inverse 9-metallacrown-3 with three repeated [Ni–N–N] units, and the metallacycles host a triply bridging hydroxide representing the first examples of metallacrown complexes supported by NHC ligands. A linearly arranged Ni₃ complex was obtained at higher temperature. The same ligand forms a dinuclear platinum complex showing versatile coordination behavior of pyrazole–NHC ligands. The heterobimetallic complex **5** contains palladium and silver ions and shows good catalytic activity in Sonogashira coupling reactions of aryl bromides and phenylacetylene.

EXPERIMENTAL SECTION

General Procedures. All chemicals were of reagent grade quality obtained from commercial sources and used as received. Ethyl 3-methylpyrazole-5-carboxylate,²⁷ [(η³-C₃H₅)PdCl]₂,²⁸ and Pt(cod)Cl₂²⁹ were synthesized according to the reported methods. NMR spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer, 400 MHz for ¹H and 100 MHz for ¹³C. Chemical shifts (δ) were expressed in parts per million downfield to TMS at δ = 0 ppm, and coupling constants (*J*) were expressed in Hz. ESI-mass spectral data were acquired using a Waters Micromass ZQ mass spectrometer (+ mode, ESI source). Elemental analyses were performed on a Flash EA 1112 instrument.

Table 1. Sonogashira Coupling Reactions Catalyzed by **5**^a



entry	R	X	R'	time (h)	yield %
1	<i>P</i> -C(O)CH ₃	Br	phenyl	8	100 (95)
2	H	Br	phenyl	8	95
3	<i>P</i> -CH ₃	Br	phenyl	8	97 (92)
4	<i>P</i> -OCH ₃	Br	phenyl	8	100
5	<i>P</i> -Cl	Br	phenyl	8	100
6	2-bromothiophene	Br	phenyl	8	79
7	2-bromothiophene	Br	phenyl	16	98 (90)
8	2-bromopyridine	Br	phenyl	16	100 (87)
9	<i>P</i> -C(O)CH ₃	Br	1-butyl	24	80 (76)
10	<i>P</i> -C(O)CH ₃	Br	1-hexyl	24	75
11	<i>P</i> -C(O)CH ₃	Cl	phenyl	24	60 (44)

^a Reaction conditions: aryl halide, 1.0 mmol; alkyne, 1.2 mmol; complex **5**, 1.0 mol %; PPh₃, 1.0 mol %; Cs₂CO₃, 1.2 mmol; DMF, 3 mL; 80 °C. GC yields and isolated yields are given in parentheses.

3-(Chloromethyl)-5-methylpyrazole hydrochloride. The compound was synthesized from ethyl 3-methylpyrazole-5-carboxylate according to the literature method.³⁰ Yield: 11.0 g, 66%. ¹H NMR (CDCl₃): 13.20 (br, NH, 2H), 6.40 (s, pyrazole CH, 1H), 4.73 (s, CH₂, 2H), 2.54 (s, CH₃, 3H). ¹³C NMR (CDCl₃): 145.2, 144.5, 106.6, 33.6, 11.1. HRMS (TOF MS EI⁺) *m/z*: [M – HCl] calcd for C₅H₇ClN₂ 130.0298. Found 130.0299.

3-(Chloromethyl)-5-methyl-1-(tetrahydro-pyran-2-yl)-pyrazole. 1,2-Dihydropyran (9.22 g, 110 mmol) was added to a solution of 3-(chloromethyl)-5-methylpyrazole hydrochloride (8.3 g, 50 mmol) in 500 mL of dichloromethane at room temperature. After stirring overnight, the mixture was concentrated to 100 mL and washed with a solution of 25 g of sodium bicarbonate in 400 mL of water, and the separated organic phase was dried over MgSO₄. The solvent was evaporated, and the residue was recrystallized from petroleum ether to give a white solid. Yield: 9.4 g, 88%. ¹H NMR (CDCl₃): 6.11 (s, pyrazole CH, 1H), 5.20 (dd, *J* = 2.0 and 10 Hz, thp CH, 1H), 4.57 (d, *J* = 12 Hz, CH₂, 1H), 4.53 (d, *J* = 12 Hz, CH₂, 1H), 4.03 (d, *J* = 7.2 Hz, thp CH, 1H), 3.62 (m, thp CH₂, 1H), 2.39 (m, thp CH₂, 1H), 2.31 (s, CH₃, 3H), 2.08 (m, thp CH₂, 1H), 1.90 (m, thp CH₂, 1H), 1.68 (m, thp CH₂, 2H), 1.56 (m, thp CH₂, H). ¹³C NMR (CDCl₃): 148.3, 140.6, 105.7, 84.5, 67.9, 39.3, 29.5, 24.9, 22.8, 11.0. HRMS (TOF MS EI⁺) *m/z*: calcd for C₁₀H₁₅ClN₂O 214.0873. Found 214.0870.

3-(*N*-Methylimidazoliumylmethyl)-5-methyl-1*H*-pyrazole hexafluorophosphate ([H₂L1](PF₆)). A solution of 3-(chloromethyl)-5-methyl-1-(tetrahydro-pyran-2-yl)pyrazole (2.14 g, 10 mmol) and *N*-methylimidazole (1.23 g, 15 mmol) in toluene (10 mL) was refluxed overnight. The resulting solid was dissolved in ethanol (25 mL) and filtered. To the filtrate was added concentrated hydrochloric acid (1.5 mL), and it was stirred for 3 h. The solvent was removed, the residue was redissolved in water (25 mL), and then a saturated NH₄PF₆ aqueous solution (30 mL) was added dropwise. The resulting precipitate was washed with water, ethanol, and ether. Yield: 2.51 g, 78%. Anal. Calcd for C₉H₁₃F₆N₄P: C, 33.55; H, 4.07; N, 17.39. Found: C, 33.86; H, 4.06; N, 17.31. ¹H NMR (dms-*d*₆): 12.67 (s, NH, 1H), 9.12 (s, NCHN, 1H), 7.71, 7.67 (both s, NCHCHN, each 1H), 6.09 (s, pyrazole CH, 1H), 5.31 (s, CH₂, 2H), 3.65 (s, CH₃, 3H), 2.22 (s, CH₃, 3H). ¹³C NMR (dms-*d*₆): 145.7, 140.7, 136.9, 124.1, 122.9, 103.8, 46.7, 36.2, 10.9.

3-(*N*-Mesitylimidazoliumylmethyl)-5-methyl-1*H*-pyrazole hexafluorophosphate ([H₂L2](PF₆)). According to the same

Table 2. Summary of X-ray Crystallographic Data for 1 and 4–6

	1·2CH ₃ CN·DMSO	4·2CH ₃ CN	5·CH ₃ CN	6·2CH ₃ CN
formula	C ₃₁ H ₄₃ F ₁₂ N ₁₃ Ni ₃ P ₂ O ₂ S	C ₇₂ H ₈₂ F ₁₂ N ₁₈ Ni ₃ P ₂	C ₄₄ H ₅₄ AgF ₆ N ₁₀ Pd ₂ P	C ₂₈ H ₂₈ F ₁₂ N ₁₄ Pt ₂ P ₂
fw	1127.91	1665.63	1188.61	1240.76
crystal system	triclinic	triclinic	monoclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	10.9545(12)	13.2854(14)	20.3269(8)	9.7764(9)
<i>b</i> /Å	15.3178(18)	19.085(2)	22.2835(8)	12.1843(16)
<i>c</i> /Å	15.4704(19)	19.144(2)	11.0602(5)	16.3997(19)
β /deg	106.440(2)	92.2230(10)	107.703(4)	86.770(2)
<i>V</i> /Å ³	2360.5 (5)	3958.2(7)	4772.5(3)	1862.7(4)
<i>Z</i>	2	2	4	2
<i>D</i> /g cm ^{−3}	1.587	1.398	1.654	2.212
cryst size/mm	0.22 × 0.17 × 0.10	0.41 × 0.38 × 0.35	0.32 × 0.25 × 0.23	0.37 × 0.30 × 0.21
reflns collected	12 510	20 735	16 103	9742
ind reflns, <i>R</i> _{int}	8193, 0.1097	13 765, 0.0232	4168, 0.0716	6474, 0.0323
goodness of fit on <i>F</i> ²	1.057	1.044	1.032	1.035
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0948, 0.2265	0.0638, 0.1727	0.0645, 0.1708	0.0495, 0.1159
<i>R</i> 1, <i>wR</i> 2 (all data)	0.1882, 0.2614	0.1152, 0.2238	0.0705, 0.1794	0.0868, 0.1396

procedure as for compound [H₂L1](PF₆), [H₂L2](PF₆) was obtained as a white solid. Yield: 3.54 g, 83%. Anal. Calcd for C₁₇H₂₁F₆N₄P: C, 47.89; H, 4.96; N, 13.14. Found: C, 47.41; H, 4.92; N, 12.75. ¹H NMR (dmso-*d*₆): 12.69 (br, NH, 1H), 9.50 (s, NCHN, 1H), 8.00, 7.91 (both d, *J* = 1.6 Hz, NCHCHN, each 1H), 7.15 (s, mesityl CH, 2H), 6.12 (s, pyrazole CH, 1H), 5.45 (s, CH₂, 2H), 2.33 (s, CH₃, 3H), 2.24 (s, mesityl CH₃, 3H), 2.01 (s, mesityl CH₃, 6H). ¹³C NMR (dmso-*d*₆): 145.8, 141.0, 137.6, 134.7, 131.4, 130.0, 129.7, 124.5, 123.63, 103.7, 65.4, 20.9, 17.3, 10.8.

3-(*N*-Pyrimidin-2-ylimidazoliumylmethyl)-5-methyl-1*H*-pyrazole hexafluorophosphate ([H₂L3](PF₆)). [H₂L3](PF₆) was prepared similarly as [H₂L1](PF₆). Yield: 3.54 g, 83%. Anal. Calcd for C₁₂H₁₃F₆N₆P: C, 37.32; H, 3.39; N, 21.76. Found: C, 37.01; H, 3.34; N, 20.46. ¹H NMR (dmso-*d*₆): 12.67 (br, NH, 1H), 10.22 (s, NCHN, 1H), 9.03 (d, *J* = 5.2 Hz, *o*-C₄H₃N, 2H), 8.43, 7.92 (both s, NCHCHN, each 1H), 7.74 (t, *J* = 4.8 Hz, *m*-C₄H₃N, 1H), 6.16 (s, pyrazole CH, 1H), 5.48 (s, CH₂, 2H), 2.21 (s, CH₃, 3H). ¹³C NMR (dmso-*d*₆): 160.4, 152.4, 144.9, 141.0, 135.9, 124.2, 122.9, 119.8, 104.2, 47.3, 10.8.

Synthesis of [Ni₃(μ-OH)(L1)₃](PF₆)₂ (1). A solution of [H₂L1](PF₆) (128 mg, 0.4 mmol) in CH₃CN (5 mL) was treated with Ag₂O (96 mg, 0.4 mmol). After the mixture was stirred at 45 °C for 2 h, an excess of Raney nickel powder (ca. 100 mg) was added and stirred for 24 h. After filtration through a plug of Celite, the solution was concentrated to ca. 1.0 mL. Addition of diethyl ether (10 mL) afforded 1 as a yellow solid. Yield: 78 mg, 51%. Anal. Calcd for C₂₇H₃₇F₁₂N₁₂Ni₃OP₂: C, 32.15; H, 3.40; N, 16.66. Found: C, 32.41; H, 3.44; N, 16.17. ¹H NMR (dmso-*d*₆): 7.61 (s, NCHCHN, 3H), 7.39 (s, NCHCHN, 3H), 6.01 (s, pyrazole CH, 3H), 5.59, 5.32 (both d, *J* = 16.8 Hz, CH₂, 6H), 3.23 (s, CH₃, 9H), 2.08 (s, OH, 1H), 1.51 (s, CH₃, 9H). ¹³C NMR (dmso-*d*₆): 152.3 (Ni–C), 145.8, 125.2, 124.1, 104.5, 47.0, 36.7, 13.6.

Synthesis of [Ni₃(μ-OH)(L2)₃](PF₆)₂·Et₂O (2) and [Ni₃(L2)₄](PF₆)₂ (4). According to the same procedure as described for 1, complexes 2 and 4 were obtained simultaneously and isolated by fractional crystallization. For 2: yellow solid. Yield: 38 mg, 22%. Anal. Calcd for C₅₅H₆₈F₁₂N₁₂Ni₃O₂P₂: C, 47.35; H, 4.91; N, 12.05. Found: C, 47.29; H, 5.18; N, 12.30. ¹H NMR (acetone-*d*₆): 7.85, 7.54 (both s, NCHCHN, each 3H), 7.09 (s, mesityl CH, 3H), 6.65 (s, mesityl CH, 3H), 5.81 (s, pyrazole CH, 3H), 5.65, 5.37 (both d, *J* = 18.0 Hz, CH₂, 6H), 4.01 (s, CH₃, 9H), 2.12 (s, mesityl CH₃, 9H), 2.12 (s, mesityl CH₃,

9H), 1.93 (s, mesityl CH₃, 9H), 1.81 (s, mesityl CH₃, 9H), 0.79 (s, OH, 1H). ¹³C NMR (dmso-*d*₆): 154.0 (Ni–C), 147.4, 146.6, 137.4, 134.3, 134.1, 132.8, 129.1, 128.9, 126.7, 123.5, 103.4, 47.7, 23.1, 20.6, 18.3, 15.9. For 4: tan-yellow solid. Yield: 65 mg, 41%. Anal. Calcd for C₆₈H₇₆F₁₂N₁₆Ni₃P₂: C, 51.58; H, 4.84; N, 14.15. Found: C, 51.64; H, 4.85; N, 14.33. The compound is paramagnetic. ¹H NMR (acetone-*d*₆): 10.69 (s, 4H), 6.62 (s, 4H), 5.14 (s, 4H), 4.96 (s, 4H), 4.82 (s, 4H), 2.89 (s, 8H), 2.06 (s, 24H), −1.72 (s, 12H), −3.44 (s, 12H). ¹³C NMR (acetone-*d*₆): 200.2, 138.6, 132.8, 130.5, 129.5, 129.4, 127.5, 127.1, 123.0, 122.8, 65.2, 19.5, 13.5, 12.0.

Synthesis of [Ni₃(μ-OH)(L3)₃](PF₆)₂ (3). Complex 3 was prepared similarly as for 1 and isolated as a yellow solid. Yield: 48 mg, 30%. Anal. Calcd for C₃₆H₃₄F₁₂N₁₈Ni₃OP₂: C, 36.01; H, 2.85; N, 21.00. Found: C, 35.79; H, 2.79; N, 20.86. ¹H NMR (dmso-*d*₆): 8.95 (d, *J* = 5.2 Hz, *o*-C₅H₄N₂, 6H), 8.08, 7.87 (all s, NCHCHN, each 3H), 6.95 (d, *J* = 4.8 Hz, *m*-C₅H₄N₂, 3H), 5.56 (s, pyrazole CH, 3H), 5.61, 5.19 (both d, *J* = 16.4 Hz, CH₂, 6H), 2.34 (s, OH, 1H), 1.43 (s, CH₃, 9H). ¹³C NMR (dmso-*d*₆): 158.3 (Ni–C), 156.0, 151.2, 145.4, 141.7, 135.2, 124.1, 122.7, 103.3, 47.5, 14.6.

Synthesis of [AgPd₂(η³-C₃H₅)₂(L2)₂](PF₆) (5). A solution of [H₂L2](PF₆) (170 mg, 0.4 mmol) in CH₃CN (5 mL) was treated with Ag₂O (96 mg, 0.4 mmol). The mixture was stirred at 45 °C for 2 h. [(η³-C₃H₅)PdCl]₂ (74 mg, 0.2 mmol) was then added to the solution at room temperature and stirred for another 2 h. After filtration through a plug of Celite, the filtrate was concentrated to ca. 2 mL. Addition of diethyl ether (30 mL) gave 5 as a white solid. Yield: 169 mg, 76%. Anal. Calcd for C₄₀H₄₈AgF₆N₈Pd₂P·H₂O: C, 42.72; H, 4.48; N, 9.96. Found: C, 42.21; H, 4.24; N, 9.50. ¹H NMR (dmso-*d*₆): 7.78, 7.74 (both s, NCHCHN, each 2H), 7.02 (s, mesityl CH, 2H), 6.94 (s, mesityl CH, 2H), 6.18 (s, pyrazole CH, 2H), 5.31 (d, *J* = 15.6 Hz, CH₂, 4H), 5.14 (m, CH₂ + C₃H₅, 4H), 4.20 (d, *J* = 7.6 Hz, C₃H₅, 2H), 3.30 (s, C₃H₅, 2H), 3.17 (d, *J* = 13.6 Hz, C₃H₅, 2H), 2.60 (br, C₃H₅, 2H), 2.32 (s, CH₃, 6H), 2.29 (s, mesityl CH₃, 6H), 1.92 (s, mesityl CH₃, 6H), 1.85 (s, mesityl CH₃, 6H). ¹³C NMR (dmso-*d*₆): 175.4 (Pd–C), 148.9, 145.2, 138.8, 136.8, 135.3, 134.9, 129.2, 129.0, 123.3, 122.3, 118.1, 102.5, 68.8, 65.3, 47.5, 21.0, 18.5, 17.9, 15.6, 14.5.

Synthesis of [Pt₂(L3)₂](PF₆)₂ (6). A solution of [H₂L3](PF₆) (154 mg, 0.4 mmol) in CH₃CN (5 mL) was treated with Ag₂O (96 mg, 0.4 mmol) at 45 °C for 2 h. Pt(cod)Cl₂ (114 mg, 0.4 mmol) was then added to the solution at room temperature and stirred for 2 h.

The resulting mixture was filtered through a plug of Celite to remove AgCl, and the filtrate was concentrated to ca. 2 mL. Compound **6** was obtained as a pale yellow solid after addition of 20 mL of diethyl ether. Yield: 129 mg, 56%. Anal. Calcd for $C_{24}H_{22}F_{12}N_{12}Pt_2P_2$: C, 24.88; H, 1.91; N, 14.51. Found: C, 24.63; H, 2.21; N, 14.63. 1H NMR (dmsd- d_6): 9.19 (d, $J = 4.8$ Hz, m - $C_5H_4N_2$, 2H), 8.38, 7.98 (both s, NCHCHN, each 2H), 8.17 (d, $J = 5.6$ Hz, m - $C_5H_4N_2$, 2H), 7.68 (t, $J = 5.2$ Hz, o - $C_5H_4N_2$, 2H), 6.75 (s, pyrazole CH, 2H), 5.92, 5.85 (both d, $J = 17.6$ Hz, CH_2 , 4H), 2.31 (s, CH_3 , 6H). ^{13}C NMR (dmsd- d_6): 161.9 (Pt–C), 159.5, 157.8, 152.0, 146.5, 143.5, 123.5, 121.1, 108.3, 48.7, 14.7.

X-ray Diffraction Analysis. Single-crystal X-ray diffraction data for **1–4** and **6** were collected at 298(2) K on a Siemens Smart/CCD area-detector diffractometer with a Mo K α radiation ($\lambda = 0.71073$ Å), and **5** was measured at 153(2) K on a Gemini Ultra Atlas/CCD area-detector diffractometer with Cu K α radiation ($\lambda = 1.54184$ Å) by using an ω -2 θ scan mode. Unit-cell dimensions were obtained with least-squares refinement. Data collection and reduction were performed using the SMART and SAINT software or Oxford Diffraction CrysAlisPro software.³¹ All structures were solved by direct methods and refined against F^2 by the full-matrix least-squares techniques.³² All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in their calculated positions. Details of the X-ray experiments and crystal data are summarized in Table 2.

■ ASSOCIATED CONTENT

S Supporting Information. Structural parameters for **1–6** as CIF files and the structural drawings of **2** and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: chenwzz@zju.edu.cn. Fax: 0086-571-88273314.

■ ACKNOWLEDGMENT

We gratefully acknowledge the financial support of the National Natural Science Foundation of China (20872129 and 21072170) and the Fundamental Research Fund for the Central Universities (2010QNA3004) for financial support.

■ REFERENCES

- (1) (a) Rawashdeh-Omary, M. A.; Rashdan, M. D.; Dharanipathi, S.; Elbjairami, O.; Ramesh, P.; Dias, H. V. R. *Chem. Commun.* **2011**, 47, 1160. (b) Hou, L.; Shi, W.-J.; Wang, Y.-Y.; Wang, H.-H.; Cui, L.; Chen, P.-X.; Shi, Q.-Z. *Inorg. Chem.* **2011**, 50, 261. (c) Jozak, T.; Sun, Y.; Schmitt, Y.; Lebedkin, S.; Kappes, M.; Gerhards, M.; Thiel, W. R. *Chem.—Eur. J.* **2011**, 17, 3384. (d) Fujisawa, K.; Ishikawa, Y.; Miyashita, Y.; Okamoto, K. *Inorg. Chim. Acta* **2010**, 363, 2977. (e) Wang, K.-W.; Chen, J.-L.; Cheng, Y.-M.; Chung, M.-W.; Hsieh, C.-C.; Lee, G.-H.; Chou, P.-T.; Chen, K.; Chi, Y. *Inorg. Chem.* **2010**, 49, 1372.
- (2) (a) Fensch, L. K.; Pröpper, K.; John, M.; Demeshko, S.; Brückner, C.; Meyer, F. *Angew. Chem., Int. Ed.* **2011**, 50, 1420. (b) Dougan, S. J.; Melchart, M.; Habtemariam, A.; Parsons, S.; Sadler, P. J. *Inorg. Chem.* **2006**, 45, 10882. (c) Kelly, M. E.; Dietrich, A.; Gómez-Ruiz, S.; Kalinowski, B.; Kaluderović, G. N.; Müller, T.; Paschke, R.; Schmidt, J.; Steinborn, D.; Wagner, C.; Schmidt, H. *Organometallics* **2008**, 27, 4917. (d) Kennedy, A. R.; Florence, A. J.; McInnes, F. J.; Wheate, N. J. *Dalton Trans.* **2009**, 7695. (e) Sun, R. W.-Y.; Ng, M. F.-Y.; Wong, E. L.-M.; Zhang, J.; Chui, S. S.-Y.; Shek, L.; Lau, T.-C.; Che, C.-M. *Dalton Trans.* **2009**, 10712.
- (3) (a) Penkova, L. V.; Maciag, A.; Rybak-Akimova, E. V.; Haukka, M.; Pavlenko, V. A.; Iskenderov, T. S.; Kozzowski, H.; Meyer, F.; Fritsky,

I. O. *Inorg. Chem.* **2009**, 48, 6960. (b) Contaldi, S.; Nicola, C. D.; Garau, F.; Karabach, Y. Y.; Martins, L. D. R. S.; Monari, M.; Pandolfo, L.; Pettinari, C.; Pombeiro, A. J. L. *Dalton Trans.* **2009**, 4928. (c) Sachse, A.; Demeshko, S.; Dechert, S.; Daebel, V.; Langeb, A.; Meyer, F. *Dalton Trans.* **2010**, 3903. (d) Kashiwame, Y.; Kuwata, S.; Ikariya, T. *Chem.—Eur. J.* **2010**, 16, 766.

(4) For reviews, see: (a) Sadimenko, A. P.; Basson, S. S. *Coord. Chem. Rev.* **1996**, 147, 247. (b) Klingele, J.; Dechert, S.; Meyer, F. *Coord. Chem. Rev.* **2009**, 253, 2698. (c) Kuwata, S.; Ikariya, T. *Chem.—Eur. J.* **2011**, 17, 3542.

(5) Boča, R.; Dlhán, L.; Mezei, G.; Ortiz-Pérez, T.; Raptis, R. G.; Telsler, J. *Inorg. Chem.* **2003**, 42, 5801.

(6) Nicola, C. D.; Karabach, Y. Y.; Kirillov, A. M.; Monari, M.; Pandolfo, L.; Pettinari, C.; Pombeiro, A. J. L. *Inorg. Chem.* **2007**, 46, 221.

(7) Mezei, G.; Zaleski, C. M.; Pecoraro, V. L. *Chem. Rev.* **2007**, 107, 4933.

(8) (a) Kayser, L.; Pattacini, R.; Rogez, G.; Braunstein, P. *Chem. Commun.* **2010**, 46, 6461. (b) Zhang, J.; Teo, P.; Pattacini, R.; Kermagoret, A.; Welter, R.; Rogez, G.; Hor, T. S. A.; Braunstein, P. *Angew. Chem., Int. Ed.* **2010**, 49, 4443. (c) Angaridis, P. A.; Baran, P.; Boča, R.; Cervantes-Lee, F.; Haase, W.; Mezei, G.; Raptis, R. G.; Werner, R. *Inorg. Chem.* **2002**, 41, 2219.

(9) (a) Casarin, M.; Cingolani, A.; Nicola, C. D.; Falcomer, D.; Monari, M.; Pandolfo, L.; Pettinari, C. *Cryst. Growth Des.* **2007**, 7, 677. (b) Halcrow, M. A. *Dalton Trans.* **2009**, 2059. (c) Pérez, J.; Riera, L. *Eur. J. Inorg. Chem.* **2009**, 4913. (d) Jones, L. F.; Kilner, C. A.; Halcrow, M. A. *Chem.—Eur. J.* **2009**, 15, 4667. (e) Jones, L. F.; Barrett, S. A.; Kilner, C. A.; Halcrow, M. A. *Chem.—Eur. J.* **2008**, 14, 223. (f) Viciano-Chumillas, M.; Tanase, S.; de Jongh, L. J.; Reedijk, J. *Eur. J. Inorg. Chem.* **2010**, 3403.

(10) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, 47, 3122.

(11) (a) Catalano, V. J.; Malwitz, M. A.; Etogo, A. O. *Inorg. Chem.* **2004**, 43, 5714. (b) Catalano, V. J.; Malwitz, M. A. *Inorg. Chem.* **2003**, 42, 5483. (c) Hu, X.; Tang, Y.; Gantzel, P.; Meyer, K. *Organometallics* **2003**, 22, 612. (d) Rit, A.; Pape, T.; Hepp, A.; Hahn, F. E. *Organometallics* **2011**, 30, 334.

(12) (a) Liu, A.; Zhang, X.; Chen, W. *Organometallics* **2009**, 28, 4868. (b) Ellul, C. E.; Reed, G.; Mahon, M. F.; Pascu, S. I.; Whittlesey, M. K. *Organometallics* **2010**, 29, 4097. (c) Chiu, P. L.; Lai, C.-L.; Chang, C.-F.; Hu, C.-H.; Lee, H. M. *Organometallics* **2005**, 24, 6169.

(13) (a) Poyatos, M.; Maise-François, A.; Bellemin-Lapponnaz, S.; Gade, L. H. *Organometallics* **2006**, 25, 2634. (b) Lv, C.; Gu, S.; Chen, W.; Qiu, H. *Dalton Trans.* **2010**, 39, 4198.

(14) Li, W.; Sun, H.; Chen, M.; Wang, Z.; Hu, D.; Shen, Q.; Zhang, Y. *Organometallics* **2005**, 24, 5925.

(15) Fogler, E.; Balaraman, E.; Ben-David, Y.; Leitens, G.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2011**, 30, 3826.

(16) (a) Xi, Z.; Zhang, X.; Chen, W.; Fu, S.; Wang, D. *Organometallics* **2007**, 26, 6636. (b) Zhang, X.; Liu, A.; Chen, W. *Org. Lett.* **2008**, 10, 3849. (c) Liu, B.; Zhang, Y.; Xu, D.; Chen, W. *Chem. Commun.* **2011**, 47, 2883. (d) Gu, S.; Xu, H.; Zhang, N.; Chen, W. *Chem.—Asian J.* **2010**, 5, 1677. (e) Liu, B.; Xia, Q.; Chen, W. *Angew. Chem., Int. Ed.* **2009**, 48, 5513.

(17) Zhou, Y.; Chen, W. *Organometallics* **2007**, 26, 2742.

(18) (a) Zhou, Y.; Xi, Z.; Chen, W.; Wang, D. *Organometallics* **2009**, 27, 5911. (b) Xi, Z.; Zhou, Y.; Chen, W. *J. Org. Chem.* **2008**, 73, 8497.

(19) (a) Scheele, U. J.; John, M.; Dechert, S.; Meyer, F. *Eur. J. Inorg. Chem.* **2008**, 373. (b) Jeon, S.-J.; Waymouth, R. M. *Dalton Trans.* **2008**, 437. (c) Scheele, U. J.; Georgiou, M.; John, M.; Dechert, S.; Meyer, F. *Organometallics* **2008**, 27, 5146. (d) Zhou, Y.; Zhang, X.; Chen, W.; Qiu, H. *J. Organomet. Chem.* **2008**, 693, 205. (e) Liu, B.; Liu, B.; Zhou, Y.; Chen, W. *Organometallics* **2010**, 29, 1457.

(20) (a) Li, F.; Hu, J. J.; Koh, L. L.; Hor, T. S. A. *Dalton Trans.* **2010**, 5231. (b) Ray, S.; Shaikh, M. M.; Ghosh, P. *Eur. J. Inorg. Chem.* **2009**, 13, 1932. (c) Zhang, C.; Wang, Z. *Organometallics* **2009**, 28, 6507. (e) Berding, J.; van Dijkman, T. F.; Lutz, M.; Spekb, A. L.; Bouwman, E. *Dalton Trans.* **2009**, 6948. (f) Zhang, X.; Liu, B.; Liu, A.; Xie, W.; Chen,

W. *Organometallics* **2009**, *28*, 1336. (g) Varonka, M. S.; Warren, T. H. *Organometallics* **2010**, *29*, 717.

(21) Biswas, B.; Pieper, U.; Weyhermüller, T.; Chaudhuri, P. *Inorg. Chem.* **2009**, *48*, 6781.

(22) (a) Mohamed, A. A. *Coord. Chem. Rev.* **2010**, *254*, 1918. (b) Tsupreva, V. N.; Titov, A. A.; Filippov, O. A.; Bilyachenko, A. N.; Smol'yakov, A. F.; Dolgushin, F. M.; Agapkin, D. V.; Godovikov, I. A.; Epstein, L. M.; Shubina, E. S. *Inorg. Chem.* **2011**, *50*, 3325.

(23) (a) Frey, G. D.; Schütz, J.; Herdtweck, E.; Herrmann, W. A. *Organometallics* **2005**, *24*, 4416. (b) Li, F. W.; Bai, S.; Andy Hor, T. S. *Organometallics* **2008**, *27*, 672. (c) Dyson, G.; Frison, J.; Simonovic, S.; Whitwood, A. C.; Douthwaite, R. E. *Organometallics* **2008**, *27*, 281. (d) Viciu, M. S.; Stevens, E. D.; Petersen, J. L.; Nolan, S. P. *Organometallics* **2004**, *23*, 3752.

(24) Garrison, J. C.; Youngs, W. J. *Chem. Rev.* **2005**, *11*, 105.

(25) Chinchilla, R.; Nájera, C. *Chem. Rev.* **2007**, *107*, 874.

(26) Gu, S.; Chen, W. *Organometallics* **2009**, *28*, 909.

(27) Skinner, P. J.; Cherrier, M. C.; P. Webb, J.; Shin, Y.-J.; Gharbaoui, T.; Lindstrom, A.; Hong, V.; Tamura, S. Y.; Dang, H. T.; Pride, C. C.; Chen, R.; Richman, J. G.; Connolly, D. T.; Semple, G. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 5.

(28) Dent, W. T.; Long, R.; Wilkinson, A. J. *J. Chem. Soc.* **1964**, 1585.

(29) McDermott, J. X.; White, J. F.; Whitesides, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521.

(30) Schenck, T. G.; Downes, J. M.; Milne, C. R. C.; Mackenzie, P. B.; Boucher, T. G.; Whelan, J.; Bosnich, B. *Inorg. Chem.* **1985**, *24*, 2334.

(31) (a) SMART-CCD Software, version 4.05; Siemens Analytical X-ray Instruments: Madison, WI, 1996. (b) CrysAlisPro; Oxford Diffraction Ltd.: Oxford, U.K., 2008.

(32) Sheldrick, G. M. *SHELXTL*, version 5.1; Bruker AXA Inc.: Madison, WI, 1998.