

η^6 -Coordination of a Ruthenium(II) Organometallic Fragment to the Arene Ring of N,C,N-Pincer Metal Complexes

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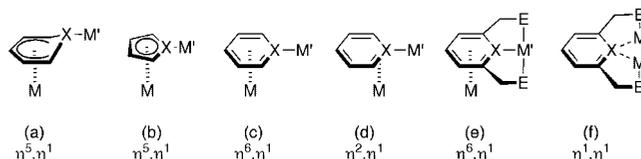
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Summary: Stable heterobimetallic complexes of the type $[MX(NCN)Ru(C_5R_5)]^+$ ($R = H$ or Me), where the phenylene ring of an NCN-pincer ligand coordinates first to a platinum or palladium center via a σ -bond, and second to a ruthenium organometallic fragment via a π -bond, are synthesized in a single step involving electrophilic attack of a cationic Ru species on the aryl metal complex. X-ray crystal structures and solution NMR agree on the simultaneous presence of orthogonal η^6 - and η^1 -coordination axes. ^{195}Pt NMR and electrochemistry show that the η^6 -coordinated ruthenium fragment has a strong electron-withdrawing effect on the pincer metal, which leads to a diminished nucleophilicity of the platinum center toward electrophiles such as SO_2 .

Heteroarenes such as pyridines¹ and phosphinines² share with cyclic aromatic carbanions the ability to simultaneously coordinate via a σ -bond between the electron-rich atom $X = N, P,$ or C^- to one metal center and via a delocalized π -bond between the aromatic ring and another metal (Scheme 1). Unlike pyridine and phosphinines, which usually lose the aromaticity of the heterocycle when coordinated to two metal centers at the same time (Scheme 1a), cyclic aromatic carbanions can share both types of bonding without disrupting the aromaticity of the cycle, leading to geometries where one carbon atom of the cycle coordinates at the same time in a π - and σ -fashion to two different metal centers (Scheme 1b–d). Although most reported structures of type 1c are homometallic, a number of heterobimetallic compounds have been characterized by X-ray crystallography. In all reported examples, π -coordination of the aromatic ligand was realized first, followed by σ -coordination of a second metal, which was realized either by nucleophilic substitution,³ C–H activation,⁴ oxidative insertion,⁵ or transmetalation⁶ aimed at one sp^2 carbon atom of the η^6 -coordinated aromatic ring. Pfeffer and Djukic,⁷ notably, experienced difficulties in selective metal η^1 -coordination to η^6 -coordinated arene rings because of their altered properties compared to unmetalated rings.

In contrast to these methods, we report here the first successful results of a so far unexplored, but straightforward synthetic route

Scheme 1. Different Binding Modes for Aromatic Cycles ($X = C^-, N, P$)



to structures of type 1e. In this new route, σ -coordination is realized first, followed by π -coordination of an electrophilic arenophile that leaves the σ carbon-to-metal bond untouched. This methodology leads to stable, heterobimetallic σ – π -bonded structures, in which the σ - and π -bonded metals share a unique phenyl anion ligand. These new complexes might be good models for the initial step of electrophilic attack that goes beyond the η^6, η^1 or η^2, η^1 stage (Scheme 1c–e) and leads to η^1, η^1 structures (Scheme 1f) or to transmetalation. Structures of type 1f have indeed been characterized by X-ray crystallography⁸ ($M = M' = Cu^I$ or Li^I ; $M = Ta^V$ and $M' = Zn^{II}$) and proposed as transition states for electrophilic transmetalation reactions⁹ ($M = Pd^{II}$ or Pt^{II} , $M' = SiMe_3$).

In this work, the starting σ -bond is realized by selective bis-ortho cyclometalation of a NCN-pincer arene to give $[MX-$

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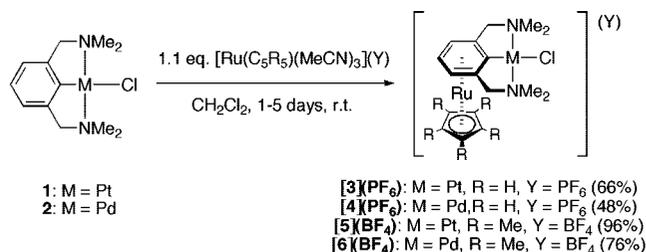
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Scheme 2. Synthesis of Heterobimetallic Complexes 3⁺–6⁺

(NCN)] complexes **1** (M = Pt) and **2** (M = Pd, NCN = [2,6-C₆H₂(CH₂NMe₂)₂]).¹⁰ Reaction of **1** and **2** with the electrophile [Ru(C₅R₅)(MeCN)₃]⁺ (R = H or Me),¹¹ at room temperature in dichloromethane, smoothly yields heterobimetallic complexes 3⁺–6⁺ in moderate to excellent isolated yields (Scheme 2). The obtained heterobimetallic complexes 3⁺–6⁺ form air-stable, off-white powders that can be separated from the starting materials by chromatography.¹² Such stability contrasts to previous work,^{13,14} where for example η¹-coordination of C₅H₅[−] to the ruthenium center in complex [RuCl(NCN)(PPh₃)] led to 1,3-migration of the [Ru(C₅H₅)(PPh₃)]⁺ fragment over the arene ring of the NCN-pincer ligand.¹⁴

Single crystals of 5⁺ and 6⁺ suitable for X-ray structure determination were obtained by slow vapor diffusion of pentane into dichloromethane. The crystal structures of 5⁺ and 6⁺ are isomorphous (see Figure 1, Table 1, and Experimental Section). The molecular structures confirm their heterobimetallic nature, with a very short Ru–Pt distance of 3.9320(3) Å in 5⁺ and Ru–Pd distance of 3.9150(2) Å in 6⁺, in contrast to previous work.^{15,16} In both complexes, the σ-bonded metal has a distorted square-planar geometry typical for NCN-pincer metal complexes, with the chloride ligand out of the M–C₁–N₁–N₂ plane (distance to plane: 0.1305(6) Å for 5⁺ and 0.1192(4) Å for 6⁺), and small N₁–M–N₂ angles (165.24(7)° in 5⁺, 164.05(5)° in 6⁺). The conformation of the five-membered metallacycles including the Pt or Pd center are puckered in the solid state, with a 11.51(8)° and 11.45(6)° dihedral angle between the

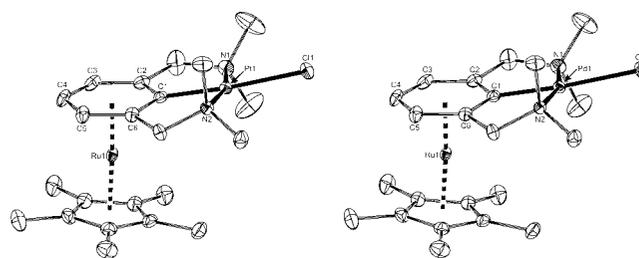


Figure 1. Molecular structures of complexes [5]⁺ (left) and [6]⁺ (right) in the crystal. Hydrogen atoms, BF₄ anions, and CH₂Cl₂ solvent molecules have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

Table 1. Crystal Structure Data for Complexes 5⁺ and 6⁺

| | 5 ⁺ | 6 ⁺ |
|---|---|---|
| formula | [C ₂₂ H ₃₄ ClN ₂ PtRu](BF ₄) · CH ₂ Cl ₂ | [C ₂₂ H ₃₄ ClN ₂ PdRu](BF ₄) · CH ₂ Cl ₂ |
| fW | 829.86 | 741.17 |
| cryst color | colorless | colorless |
| cryst size [mm ³] | 0.36 × 0.18 × 0.12 | 0.63 × 0.30 × 0.21 |
| cryst syst | monoclinic | monoclinic |
| space group | P2 ₁ /c (no. 14) | P2 ₁ /c (no. 14) |
| a [Å] | 9.7601(5) | 9.77336(19) |
| b [Å] | 19.3294(7) | 19.3029(5) |
| c [Å] | 14.7733(5) | 14.73985(19) |
| β [deg] | 91.190(2) | 91.055(1) |
| V [Å ³] | 2786.50(19) | 2780.26(10) |
| Z | 4 | 4 |
| D _x [g/cm ³] | 1.978 | 1.771 |
| μ [mm ^{−1}] | 5.887 | 1.521 |
| abs corr range | 0.19–0.49 | 0.49–0.73 |
| no. of reflns (measd/unique) | 48 675/6395 | 51 109/6382 |
| no. of params/restraints | 338/0 | 337/0 |
| R1/wR2 [I > 2σ(I)] | 0.0155/0.0325 | 0.0166/0.0380 |
| R1/wR2 [all reflns] | 0.0191/0.0337 | 0.0190/0.0391 |
| S | 1.051 | 1.063 |
| extinction coeff | 0.00095(3) | |
| ρ _{min} /max [e/Å ³] | −0.72/0.53 | −0.57/0.53 |

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phenyl ring and the coordination plane of Pt (for 5⁺) and Pd (for 6⁺), respectively. As a consequence, the C₂ symmetry found in the parent pincer metal complexes **1** and **2** is retained for the pincer fragment of 5⁺ and 6⁺. η⁶-Coordination of the [Ru(C₅R₅)]⁺ fragment does not significantly alter the distances around the σ-bonded metal. For example, the values for Pt–Cl and Pt–C₁ do not vary between 5⁺ and **1** (2.4189(5) vs 2.407(1) Å for Pt–Cl, 1.912(2) vs 1.907(5) Å for Pt–C₁).¹⁷

In the solid state, the distance between the Ru atom and the average plane of the arene ring is 1.72788(16) Å in 5⁺ and 1.72304(12) Å in 6⁺, and the Ru–Cp* distance is 1.81299(16) Å in 5⁺ and 1.81396(12) Å in 6⁺. These values are comparable to that found in [Ru(C₅Me₅)(C₆H₅Me)]⁺ (1.7142(5) and 1.7943(5) Å, respectively).¹⁸ The arene and Cp* rings are slightly unparallel however, with a dihedral angle of 6.54(12)° in 5⁺ and 7.35(8)° in 6⁺. Although C₁ formally bears a higher negative charge than C₄, the latter is closer to the ruthenium center than the former (Ru–C₁ is 2.301(2) Å in 5⁺ and 2.2847(14) Å in 6⁺, Ru–C₄ is 2.185(2) Å in 5⁺ and 2.1869(15) Å in 6⁺). This may indicate intramolecular steric repulsion between the bulky Cp* ligand and the methyl groups of the NCN-pincer moiety. Steric interaction might also explain the larger dihedral angle between the C₃–C₄–C₅ and M–C₂–C₁–C₆ planes in 5⁺ and

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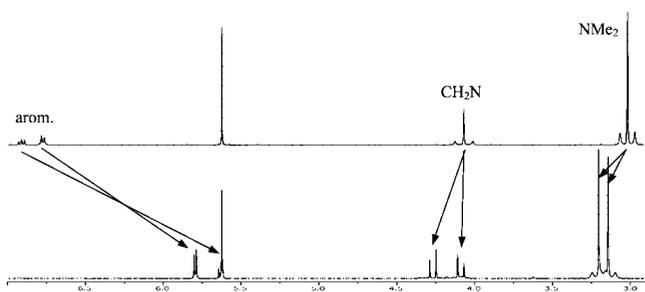


Figure 2. ^1H NMR spectra of **1** (top) and **[3](PF₆)** (bottom) in acetone- d_6 .

6^+ ($8.7(3)^\circ$ and $8.01(18)^\circ$, respectively), compared to the angle found in parent compound **1** ($0.8(5)^\circ$). These angles are however small enough to rule out coordination mode *a* in Scheme 1 where the corresponding angles are typically $\sim 40^\circ$.² In conclusion, the solid-state structures of 5^+ and 6^+ imply an η^6, η^1 -bonding description of the arene ring in these new complexes, as depicted in Scheme 1e.

In solution, ^1H NMR spectra of all complexes $3^+ - 6^+$ show drastic changes compared to **1** and **2**. The aromatic protons of the pincer ligand are ~ 1 ppm upfield shifted after η^6 -coordination of the $[\text{Ru}(\text{C}_5\text{R}_5)]^+$ fragment (see Figure 2). Proton NMR also clearly indicates that the two faces of the pincer have become nonequivalent. In **1** and **2**, wagging of the puckered metallacycles renders the methylene protons, but also the axial and equatorial N-methyl groups, equivalent on the NMR time scale. In $3^+ - 6^+$, wagging of the metallacycle is still taking place, but as the two faces of the pincer fragment have become different due to the presence of the $[\text{Ru}(\text{C}_5\text{R}_5)]^+$ fragment, the methylene protons give an AB system and the N-methyl groups appear as two well-resolved singlets (see Figure 2). Axial dissymmetrization of the pincer fragment in $3^+ - 6^+$ is also directly observed in their carbon NMR spectra.¹² Finally, the persistence of the carbon-to-metal σ -bond after η^6 -coordination is unequivocally shown for complexes 3^+ and 5^+ by $^3J_{\text{H-Pt}}$, $^2J_{\text{C-Pt}}$, and $^3J_{\text{C-Pt}}$ coupling constants, and for all complexes $3^+ - 6^+$ by low-field chemical shifts of the *ipso*-carbon atom.¹⁹ These characteristic observations prove that orthogonal η^1 - and η^6 -coordination, as observed in the solid state for 5^+ and 6^+ , is retained in solution for all complexes $3^+ - 6^+$.

It has been well established¹⁰ that the ^{195}Pt chemical shift δ_{Pt} of *para*-substituted NCN-pincer platinum(II) complexes is linearly correlated to the Hammett constant σ_p of the *para*-substituent, hence to its electron-withdrawing or -donating properties. In a similar approach, we measured the ^{195}Pt NMR spectra of complexes 3^+ and 5^+ ; they both give well-resolved singlets at -2851 and -2994 ppm, respectively.²⁰ Comparison with complex **1** ($\delta = -3159$ ppm) points to the strong electron-withdrawing properties of the $[\text{Ru}(\text{C}_5\text{R}_5)]^+$ fragment when π -coordinated to the phenyl ring of the pincer. By extending the $\delta_{\text{Pt}} = f(\sigma_p)$ linear relationship, known for organic substituents, to η^6 -coordinated organometallic fragments (Figure 3), the electronic effect of these fragments corresponds to Hammett constants of 0.84 for $[\text{Ru}(\text{C}_5\text{Me}_5)]^+$ and 1.68 for $[\text{Ru}(\text{C}_5\text{H}_5)]^+$. Such values are particularly high and illustrate that η^6 -

(19) Coupling constants for 3^+ : $J(^1\text{H}-^{195}\text{Pt}) = 17.9$ Hz (NMe₂), 15.4 and 21.4 Hz (CH₂N) and $J(^{13}\text{C}-^{195}\text{Pt}) = 16.3$ Hz (79 ppm), 22.3 Hz (76 ppm), 8.7 Hz (NMe), and 9.8 Hz (NMe'); for 5^+ : $J(^1\text{H}-^{195}\text{Pt}) = 16.9$ Hz (NMe₂), 28.3 and 27.7 Hz (CH₂N) and $J(^{13}\text{C}-^{195}\text{Pt}) = 16.2$ Hz (80.5 ppm), 22.6 Hz (74.1 ppm), and 7.9 Hz (NMe', 54.3 ppm). δ (^{13}C) of the *ipso*-carbon (C₁) for complexes $3^+ - 6^+$: 108.3 , 118.0 , 113.0 , 122.1 ppm, respectively, in acetone- d_6 , whereas for parent complexes **1** and **2** the corresponding values are 144.5 and 156.4 , respectively, in CDCl₃. See Supporting Information.

(20) Values in acetone using Na₂PtCl₆ in D₂O as an external reference.

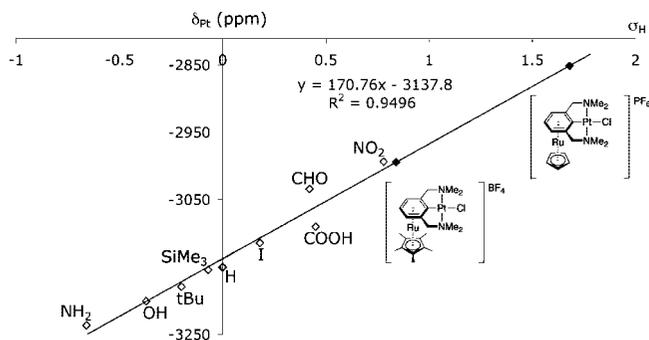


Figure 3. Extension of the $\delta_{\text{Pt}} = f(\sigma_p)$ linear relationship established for *para*-substituted NCN-Pt pincer complexes (open diamonds)^{10c} to η^6 -modified complexes 3^+ and 5^+ (solid diamonds).

Table 2. Electrochemical Data for Complexes $3^+ - 6^+$

| compound | designation | E_{red} (V) ^a | E_{ox}^1 (V) ^a | $\text{M}^{\text{II}} \rightarrow \text{M}^{\text{IV}}$ |
|---|----------------------|-----------------------------------|------------------------------------|---|
| $[(\text{C}_6\text{H}_6)\text{Ru}(\text{C}_5\text{H}_5)]^{+b}$ | | -2.18 | n.o. | |
| $[(\text{C}_6\text{H}_6)\text{Ru}(\text{C}_5\text{Me}_5)]^{+b}$ | | -2.48 | n.o. | |
| [PtCl(NCN)] | 1 | n.o. | +0.65 | |
| [PdCl(NCN)] | 2 | n.o. | +0.68 | |
| [PtCl(NCN)Ru(C ₅ H ₅)] ⁺ | 3⁺ | -2.43 | +1.24 | |
| [PdCl(NCN)Ru(C ₅ H ₅)] ⁺ | 4⁺ | -2.13 | +0.92 | |
| [PtCl(NCN)Ru(C ₅ Me ₅)] ⁺ | 5⁺ | n.o. | +1.15 | |
| [PdCl(NCN)Ru(C ₅ Me ₅)] ⁺ | 6⁺ | -2.18 | +0.93 | |

^a Conditions: 3 mmol/L solution in MeCN, 0.1 M NBu₄PF₆, scan rate = 100 mV/s, $T = 298$ K, Pt working electrode, FeCp₂/FeCp₂⁺ as internal standard. ^b According to ref 21a.

coordination of organometallic "functional groups" like $[\text{Ru}(\text{C}_5\text{R}_5)]^+$ enables obtaining electronic effects that cannot be reached using standard organic substituents.

In acetonitrile solution, complexes $3^+ - 6^+$ undergo fully irreversible oxidation and reduction as observed by cyclic voltammetry (Table 2). Whereas $[\text{Ru}(\text{C}_5\text{R}_5)(\text{arene})]^+$ cations are known to give fully irreversible, one-electron oxidation and reduction waves at very high potentials ($E_{\text{red}} < -2.1$ V and $E_{\text{ox}} > +1.9$ V vs FeCp₂/FeCp₂⁺ in acetonitrile),²¹ [MX(NCN)] pincer metal complexes **1** and **2** give irreversible anodic waves at much lower potentials, which correspond to two-electron oxidations to Pt(IV) or Pd(IV).²² As a consequence, we attribute the reductive features below -2.0 V to Ru(II)-based reductions and the features above $+0.6$ V to Pt(II)- or Pd(II)-based oxidations. The pincer-based oxidations of complexes $3^+ - 6^+$ are shifted toward much higher potentials (240 to 590 mV) than **1** and **2**, while the Ru-based reductions occur at either lower (Pt) or slightly higher (Pd) potentials compared to $[\text{Ru}(\text{C}_5\text{R}_5)(\text{C}_6\text{H}_6)]^+$. These observations unambiguously show the presence of intramolecular electronic interactions between the metal centers and are consistent with the strong electron-withdrawing properties of $[\text{Ru}(\text{C}_5\text{R}_5)]^+$ observed by ^{195}Pt NMR.

NCN-pincer platinum(II) complexes are known for their platinum-based nucleophilicity. Notably, they undergo rapid and

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reversible complexation of SO₂ to the platinum center to yield a bright orange η^1 -SO₂ adduct,²³ or of I₂ to yield the corresponding dark colored η^1 -I₂ adduct.²⁴ Bubbling SO_{2(g)} through dichloromethane and acetone solutions of **3**⁺ and **5**⁺ did not lead to any color change, nor to any modification of the UV-visible or NMR spectra. Similarly, addition of iodine to an acetone solution of [PtI(NCN)Ru(C₅Me₅)]⁺²⁵ did not produce any color change beyond that induced by iodine itself. These observations emphasize the dramatically lowered nucleophilicity of platinum in **3**⁺ and **5**⁺, which results from the strong electron-withdrawing properties of the [Ru(C₅R₅)]⁺ fragment when directly η^6 -coordinated to the arene ring of the pincer complex.

In conclusion, we have presented a new synthetic approach in which η^6 -coordination of the cationic fragment [Ru(C₅R₅)]⁺ is realized directly to a previously metallated NCN-pincer ligand. This is the first report of an electrophilic attack stopping at the η^6, η^1 stage, without further rearrangement of the metal fragments or full transmetalation. This procedure efficiently yields rigid heterobimetallic architectures sharing, in an orthogonal fashion, the σ - and π -electrons of a unique phenyl anion. These σ, π -complexes are highly stable: they withstand chromatography and can be handled in air. ¹H and ¹³C NMR and X-ray crystallography clearly show that the two faces of the pincer fragment have become nonequivalent. Changes in the ¹⁹⁵Pt NMR spectra and electrochemical data show that in such bimetallic complexes the two metals are strongly affecting each other, with the [Ru(C₅R₅)]⁺ fragment acting as a powerful electron-withdrawing group on the σ -bonded pincer metal. Initial chemical reactivity studies corroborate the notion that the σ -bonded metal ion has a severely diminished nucleophilicity and a much higher oxidation potential. Considering the large number of different NCN-, SCS-, and PCP-pincer metal complexes and their applications in, for example, catalysis, our methodology represents a straightforward way to functionalize these pincer complexes in an unprecedented manner. This new methodology might provide access to complexes with otherwise nonachievable electronic properties and with axial dissymmetry. Current investigations in our laboratory aim to investigate these issues.

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(25) Obtained by silver abstraction of Cl⁻ from a solution of **5**⁺ in acetone/water, followed by reaction with 1.0 equiv of NaI in acetone.

Experimental Section

Synthesis of the Complexes. In a typical experiment, 200 μ mol of pincer complex **1** or **2** was mixed with 220 μ mol of Ru(C₅R₅)(CH₃CN)₃(Y) (R = H, Y = PF₆ or R = CH₃, Y = BF₄) in 5.0 mL of freshly distilled dichloromethane, and the mixture was stirred under nitrogen for 1 to 5 days. The solution was directly put on a 50 mL alumina column and flash-eluted with a dichloromethane/methanol (99:1) mixture. Unreacted Ru(II) reagent and traces of uncoordinated NCN-pincer complexes were removed to afford the product, which was reprecipitated from dichloromethane/pentane to yield **3**⁺–**6**⁺ as whitish, air-stable powders.

X-ray Crystal Structure Determinations. Reflections were measured on a Nonius Kappa CCD diffractometer with rotating anode (graphite monochromator, $\lambda = 0.71073$ Å) up to a resolution of $(\sin \theta/\lambda)_{\max} = 0.65$ Å⁻¹. Intensities were integrated with EvalCCD²⁶ using an accurate description of the experimental setup for the prediction of the reflection contours. The reflections were scaled and corrected for absorption using the program SADABS.²⁷ The structure of **5**⁺ was solved with automated Patterson methods using the program DIRDIF.²⁸ The coordinates of **5**⁺ were used as a starting model for the refinement of the isomorphous **6**⁺. The structures were refined with SHELXL-97²⁹ against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. The phenyl hydrogen atoms H3, H4, and H5 of the pincer ligand were refined freely with isotropic displacement parameters; all other hydrogen atoms were refined with a riding model. Geometry calculations and checking for higher symmetry was performed with the PLATON program.³⁰ Further details are given in Table 1.

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Supporting Information Available: Full characterization for complexes **3**⁺–**6**⁺ and spectroscopic data for **1** and **2**. Crystallographic CIF files for **5**⁺ and **6**⁺. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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