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π-Back-Bonding Interaction Depending on the Bridging Chain Lengths of Chelated N-Heterocyclic Carbene Platinum Units in Heterometallic Trinuclear Complexes Affecting Their Electrochemical Property

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Supporting Information

ABSTRACT: Newly synthesized heterometallic trinuclear M_2Pt complexes (M = Rh, Ir) containing a platinum moiety having a chelated bis-N-heterocyclic carbene (bisNHC) ligand with a variety of alkylene chain lengths of the bridging part showed two reversible reduction waves in cyclic voltammetry. Only the second reduction potentials were affected by the alkyl chain lengths, which afforded different dihedral angles between the imidazolylidene rings and the platinum coordination plane resulting in the variation of π-back-donation from the platinum center to the carbene carbon atoms.

Trinuclear metal complexes can be used as catalysts in multielectron processes by utilizing their cluster valence electrons (CVEs).[1] Especially, sulfide-containing multinuclear complexes exhibit interesting structures, electronic states, and reactivities because sulfur atoms can coordinate to metal ions in a variety of modes[2] and can adopt a wide range of oxidation states from 2− to 6+, resulting in the rich redox chemistry of sulfide-containing metal complexes.[3] For example, dicationic iridium(III) and rhodium(III) trinuclear complexes with triply bridging sulfido ligands, $[(MCp^*)_3(\mu\text{-S})_2]^{2+}$ (Cp* = η^5-1,2,3,4,5-pentamethylcyclopentadienyl; M = Rh, Ir), have 48 CVEs with three metal−metal bonds. Upon reduction, the CVEs of these sulfide-containing trinuclear complexes change, which causes metal−metal and/or metal−sulfur bond cleavage.[4] These bond cleavages provide reaction sites that can be used to utilize the nucleophilicity of the sulfur atoms and/or electrophilicity of the metal ions. These sulfido-capped trinuclear rhodium and iridium dicationic complexes catalyze the electrochemical reduction of CO_2, affording oxalate, which is a C_2 product.[5] There are only a few examples of electrocatalysts that reduce CO_2 to oxalate.[6]

We planned to develop methodology for modification of the property of such sulfide-containing trinuclear complexes by the introduction of an N-heterocyclic carbene (NHC) unit into the trinuclear system. NHC ligands are strong σ donors, giving more electron density to metal ions, and their complexes containing, e.g., palladium, ruthenium, or iridium, have been used as catalysts in organic reactions such as C−C coupling, hydrogenation, olefin metathesis, and so on.[7] The preparation of NHC ligands with a variety of N-substituents is relatively easy, which allows tuning of the electronic properties and/or steric bulk of their complexes.[8] Furthermore, π-back-bonding from the occupied d orbitals on the metal atom to the formally vacant p orbital of the carbene carbon must change with the orientation of the NHC plane toward the coordination plane of the metal center. The π-back-bonding interaction could be modified using chelating bisNHC ligands because the bridging chain lengths in the bisNHC ligands affect the dihedral angles between a coordination plane of a metal center and two NHC moieties in the ligands.[9]

Although NHC complexes containing sulfido ligands could be useful candidates to construct novel catalysts, only a few examples have been reported.[10] A variety of metal ions can be used in trinuclear complexes to tune their properties, such as their redox potentials; however, construction of sulfide-containing multinuclear frameworks is relatively difficult because sulfido ligands can bridge two, three, or four metal ions.[2] We reported a hydrosulfido complex with a bidentate NHC ligand, *cis*-[Pt(bisNHC-C2)(SH)$_2$] (**1-C2**; bisNHC-C2 = 1,1′-dimethyl-3,3′-ethylene-4-diimidazolyldiylidene),[11] which can be used in the rational synthesis of a variety of sulfido-bridged multinuclear complexes. We report here the syntheses and electrochemical properties of $Pt^{II}M^{III}_2$-type heterometallic trinuclear complexes obtained by reacting hydrosulfidoplatinum complexes with chelate bisNHC ligands having a variety of bridging chains (**1-C1** for the methylene bridge and **1-C2** and **1-C3** for the propylene bridge) and hydroxo-bridged dinuclear rhodium(III) or iridium(III) complexes.

A series of $[(RhCp^*)_2\{Pt(\text{bisNHC-C}n)\}(\mu_3\text{-S})_2](BPh_4)_2$ (n = 1, **2-C1**; n = 2, **2-C2**; n = 3, **2-C3**; Figure 1) complexes were obtained as green solids from the reaction of hydrosulfido complex **1-C1**, **1-C2**, or **1-C3** with $[(RhCp^*)_2(\mu\text{-OH})_3](BPh_4)$[12] in methanol, followed by the addition of $NaBPh_4$. Complexes **2-C*n*** are the first examples of $Pt^{II}Rh^{III}_2$ trinuclear complexes with triply bridging chalcogenido ligands, while a

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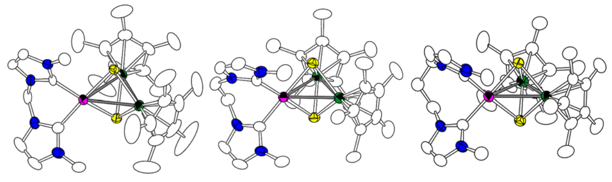

Figure 1. ORTEP drawings of dicationic moieties of **2-C1**(left), **2-C2** (center), and **2-C3** (right) with 50% probability of the thermal ellipsoids. Hydrogen atoms are omitted for clarity.

carbonyl-bridged $Pt^0Rh^I_2$ complex, $[\{Pt(CO)(PPh_3)\}(RhCp^*)_2(\mu_3\text{-}CO)_2]$, has been reported.[13]

The analogous iridium complexes $[\{Pt(bisNHC\text{-}Cn)\}(IrCp^*)_2(\mu_3\text{-}S)_2](BPh_4)_2$ (**3-C1**, **3-C2**, and **3-C3**) were obtained as green solids from similar reactions of the corresponding hydrosulfido complex **1-C1**, **1-C2**, or **1-C3** with $[(IrCp^*)_2(\mu\text{-}OH)_3](BPh_4)$.[12] A few structurally characterized Pt−Ir mixed-metal multinuclear clusters have been reported,[14] and there are only three examples of $PtIr_2$ trinuclear complexes: $[(IrCp^*)_2\{PtCl(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}Se)]^+$,[15] $[(IrCp^*)_2(PtCl_2)(\mu_3\text{-}Se)_2]$,[16] and $[(IrCp^*)_2\{Pt(dppe)\}(\mu_3\text{-}S)_2]^+$ [dppe = 1,2-bis(diphenylphosphino)ethane].[15]

Cyclic voltammetry was examined for a series of Rh_2Pt and Ir_2Pt complexes with methylene (**2-C1** and **3-C1**), ethylene (**2-C2** and **3-C2**), and propylene (**2-C3** and **3-C3**) bridged ligands. Each of the complexes showed two reversible one-electron reduction waves between −0.5 and −1.5 V vs SCE (Figure 2). The lowest unoccupied molecular orbitals (LUMOs) of the complexes obtained from density functional theory (DFT) calculations of the dicationic complexes **2-Cn** and **3-Cn** are mainly located on the M_2PtS_2 cores (see Supporting Information), and the singly occupied (SOMOs) and highest occupied (HOMOs) molecular orbitals of their one- and two-electron-reduction products, respectively, are similar to the LUMOs of the dicationic complexes, which imply that these two-step one-electron-reduction processes take place at the M_2PtS_2 core and no drastic structural changes occurs upon reduction.

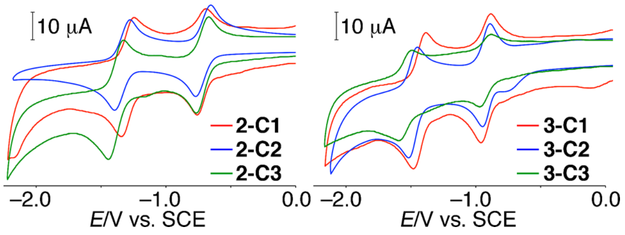

Figure 2. Cyclic voltammograms of heterometallic trinuclear (a) Rh_2Pt and (b) Ir_2Pt complexes with a variety of bridging alkylene chain lengths of bisNHC ligands, recorded at a glassy carbon electrode using solutions of 1.0 mM of the complexes in acetonitrile with 0.1 M $^nBuN_4PF_6$. Scan rate: 100 mV/s.

While the redox potentials of the first reduction for each set of Rh_2Pt and Ir_2Pt complexes are the same, the redox potentials of the second reduction are more negative as the bridging alkylene chains of the NHC ligands become longer (Table 1). These differences in the second reduction potentials are probably attributed to the dihedral angles between the NHC rings and the coordination plane of the platinum center. Variation of the dihedral angles derived from different alkylene chain lengths should affect the π-back-donation from the filled d orbitals of the platinum center to the p orbitals of the carbene carbon atoms.

Table 1. Reduction Potentials (V vs SCE) of Trinuclear Complexes with a Variety of Bridging Alkylene Chains

	Rh_2Pt complexes (**2-C*n***)		Ir_2Pt complexes (**3-C*n***)	
	first reduction	second reduction	first reduction	second reduction
C1	−0.72	−1.30	−0.98	−1.49
C2	−0.71	−1.34	−0.98	−1.54
C3	−0.72	−1.39	−0.98	−1.60

Variation of the dihedral angles was actually observed in the crystallographic analyses for a series of Rh_2Pt complexes showing the dihedral angles 37.1(2)° and 54.5(2)° for **2-C1**, 53.4(3)° and 62.8(3)° for **2-C2**, and 73.0(2)° and 76.5(2)° for **2-C3**. The overlap of the p orbital of the carbene carbon atom and the d_{xy} orbital of the platinum center is maximum when the NHC planes are perpendicular to the coordination plane. In this situation, which nearly occurred with the propylene bridge of the bisNHC ligand, the p orbitals of both of the carbene carbon atoms in the bisNHC ligand interact with the d_{xy} orbital (Figure 3a). On the other hand, when the coordination plane and the two NHC moieties are in the same plane, which is nearly observed for the bisNHC ligand with the methylene bridge, the p orbitals of the two carbene carbon atoms in the bisNHC ligand interact with the d_{yz} and d_{xz} orbitals, respectively (Figure 3b,c). This structural feature on the dihedral angles causes a larger extent of π-back-donation for the methylene-bridged bisNHC ligand than for the propylene-bridged ligand. This difference in π-back-donation leads to less electron density in the case of the ligand with the methylene bridge, resulting in the more positive second reduction potentials for **2-C1** and **3-C1**.

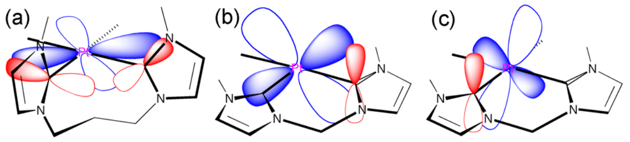

Figure 3. Schematic representation of the overlap of the d orbital of the platinum center and the p orbital of the carbene carbon atom depending on the dihedral angle made up of the coordination and NHC planes.

The C−Pt−C angles are larger for the longer bridging alkyl chains because of steric restrictions [84.8(3)°, 86.4(4)°, 88.1(3)°, 84.5(3)°, and 86.8(4)° for **2-C1**, **2-C2**, **2-C3**, **3-C1**, and **3-C2**, respectively] and are comparable to the reported values for the other platinum complexes with chelated NHC ligands [82.57(10)−84.69(13)° and 83.2(3)−87.66(14)° for the methylene- and ethylene-bridged NHCs, respectively].[11,17] These differences might affect the property of the trinuclear complexes. However, the influence appearing in the reduction potentials by these structural differences is negligible because the differences in the C−Pt−C angles affected σ donation more from the carbenes to the metal center and no differences were found for the first reduction potentials, which should be sensitive to σ donation.

The reason that no differences are observed in the first reduction potentials is probably due to the too small amount of π-back-donation provided from the M_2PtS_2 core in the oxidized form of the complexes due to less electron density on the core with higher oxidation states of metal ions, Pt^{II} and two Rh^{III} or

Ir^{III}. To the best of our knowledge, while some spectroscopic and voltammetric observations for the tuning of π-back-bonding by a variety of substituents on NHC rings have been reported,[18] our results are the first examples for direct observation about control of the π-back-bonding interaction by arrangement of the NHC planes toward the coordination plane appearing in the redox potentials.

In summary, we prepared heterometallic trinuclear complexes containing platinum bisNHC units with a variety of bridging alkyl chains and also demonstrated that possible control of the redox potentials of the trinuclear complexes using variation of the dihedral angles varied with the different lengths of the bridging chains of the bisNHC ligands. Further investigation of the properties of the heterometallic trinuclear complexes and their potential use as electrocatalysts is in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, synthetic procedures, complete experimental details, and DFT calculations. 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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