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Chelated Bis-N-heterocyclic Carbene Platinum and Palladium Units as Tunable Components of Multinuclear Complexes

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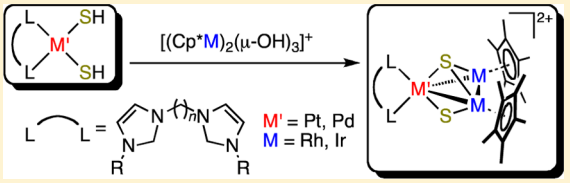
Supporting Information

ABSTRACT: Heterometallic trinuclear M_2M' complexes (M = Rh, Ir; M′ = Pt, Pd) containing a platinum or palladium moiety with chelated bis-N-heterocyclic carbene ligands, $[(MCp^*)_2\{M'(bisNHC\text{-}Cn\text{-}R)\}(\mu_3\text{-}S)_2](BPh_4)_2$ (M = Rh, Ir; M′ = Pt, Pd; bisNHC-C*n*-R = methylene-, ethylene-, or propylene-bridged bis(*N*-alkyl-imidazolylidene)), were synthesized by reacting bis(hydrosulfido)platinum(II) or palladium(II) complexes with bisNHC-C*n*-R and hydroxo-bridged dinuclear complexes $[(MCp^*)_2(\mu\text{-}OH)_3](BPh_4)$, whose dinuclear structures remained intact during the formation of the trinuclear complexes, which was confirmed by using electrospray mass spectrometry and NMR spectroscopy. The heterometallic trinuclear M_2M' complexes with a variety of alkylene bridges in bisNHC-C*n*-R showed two reversible reduction waves in the cyclic voltammogram, and the second reduction potentials were affected by the alkylene chain lengths, which caused different dihedral angles between the imidazolylidene rings and the coordination plane of the platinum or palladium center. The M_2M' complexes, except for those containing the platinum unit with the ethylene-bridged bisNHC ligands, showed dynamic behavior in solution due to the flapping wing motion of the NHC ligand moieties. Although activation parameters obtained from line-shape analyses on variable-temperature NMR spectra of the complexes suggested that the flapping wing motion occurred without bond cleavage, large negative $\Delta S^{\ddagger}$ values were obtained for the complexes with the palladium unit with the ethylene-bridged ligand, suggesting that the Pd−$C_{carbene}$ bond cleavage, accompanied by coordination of solvent molecules, occurred.



INTRODUCTION

N-Heterocyclic carbene (NHC) ligands are strong σ-donors, giving a large amount of electron density to metal ions, making NHC complexes useful as catalysts in organic reactions.[1] A variety of N-substituents can be introduced onto the NHC ligands to modify their σ-donating ability and steric bulk around the reaction sites in their metal complexes.[2] Moreover, NHC ligands are π-acceptors, meaning that they can back-bond with metal ions.[3] A formally vacant p orbital (actually, it accepts π electrons from the neighboring N atoms to some extent) of the carbene carbon atom of an NHC ligand is perpendicular to the NHC ring. Thus, the π back-donation from the metal center to the carbene carbon atom should be affected by the orientation of the NHC rings in relation to the coordination plane, which can be controlled by using chelated bisNHC ligands with a variety of alkylene bridges (bisNHC-C*n*-R).[4]

Therefore, we were inspired to use bisNHC-C*n*-R ligands to tune the properties of metal cluster compounds. Multinuclear cluster compounds can be used as catalysts in multielectron processes and can have multiple reaction sites. For example, dicationic Ir^{III} and Rh^{III} trinuclear complexes with triply bridging sulfido ligands, $[(MCp^*)_3(\mu_3\text{-}S)_2]^{2+}$ (Cp^* = η^5-1,2,3,4,5-pentamethylcyclopentadienyl; M = Rh and Ir), have 48 cluster valence electrons (CVEs)[5] 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.[6] Bond cleavage opens up new reaction sites, from which the nucleophilicity of the S atoms and/or electrophilicity of the metal ions can be utilized. These sulfido-capped trinuclear rhodium and iridium dicationic complexes catalyze the electrochemical reduction of CO_2 affording oxalate, which is a C_2 product.[7] There are only a few examples of electrocatalysts that reduce CO_2 to oxalate.[8]

To tune the properties of such trinuclear complexes, modification of the Cp* ligands is required. However, it is relatively hard and limited when compared to the NHC ligand system. Thus, we replaced one of the {MCp*} units in $[(MCp^*)_3(\mu_3\text{-}S)_2]^{2+}$ with a variety of chelated bisNHC platinum or palladium units {M′(bisNHC)} and investigated the effects of the N-substituents and alkylene bridges on the properties of the trinuclear complexes. In this study, we synthesized a series of heterometallic trinuclear complexes containing Pt- and Pd-bisNHC-C*n*-R units with Me, *i*Pr, and Bn groups as N-substituents and methylene, ethylene, and propylene bridges (Scheme 1).

RESULTS AND DISCUSSION

Syntheses and Structures of the Heterometallic Trinuclear Complexes. Hydrosulfido complexes with a bidentate NHC ligand, $[Pt(bisNHC\text{-}Cn\text{-}R)(SH)_2]$ (**1-C*n*-R**, *n* = 1−3, R = Me, *i*Pr, Bn), were used to synthesize a variety of

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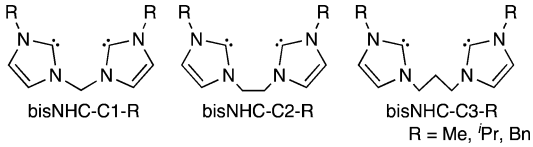
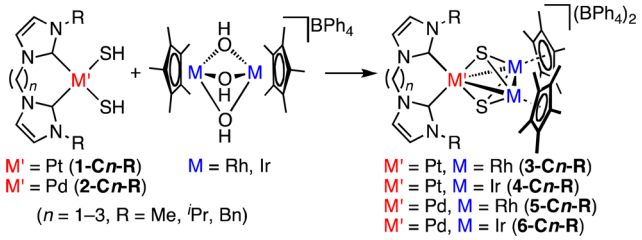
Scheme 1. A Series of Chelated BisNHC Ligands with a Variety of N-Substituents and Bridging Part



sulfido-bridged trinuclear complexes.[9] $[(MCp^*)_2\{Pt(bisNHC\text{-}Cn\text{-}R)\}(\mu_3\text{-}S)_2](BPh_4)_2$ (M = Rh, **3-C*n*-R**; M = Ir, **4-C*n*-R**; *n* = 1−3; R = Me, *i*Pr, Bn) were obtained as green solids from the reactions of **1-C*n*-R** with $[(MCp^*)_2(\mu\text{-}OH)_3](BPh_4)$[10] in methanol, followed by the addition of $NaBPh_4$ (Scheme 2).

Scheme 2. Syntheses of Sulfido-Bridged Heterometallic Trinuclear Complexes with Chelated BisNHC Metal Unit



However, isolation of the corresponding palladium hydrosulfido complexes with methyl N-substituents (**2-C*n*-Me**) was unsuccessful, although on the basis of ^{1}H NMR spectroscopy, the complexes form quantitatively from the reactions of the corresponding dichloro complexes $[Pd(bisNHC\text{-}Cn\text{-}Me)Cl_2]$ (*n* = 1−3) with excess NaSH in dimethyl sulfoxide (DMSO). Heterometallic trinuclear complexes containing the bisNHC palladium units, namely, **5-C*n*-Me** and **6-C*n*-Me**, were synthesized using DMSO solutions of the hydrosulfido palladium complexes obtained by mixing the chloro complexes and NaSH in DMSO.

Structures of **3-C*n*-Me** are shown in Figure 1. All of the structurally characterized heterometallic trinuclear complexes

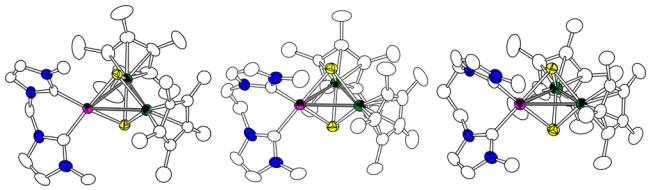


Figure 1. ORTEP drawings of the Rh_2Pt complexes with methyl N-substituents, **3-C1-Me** (left), **3-C2-Me** (center), **3-C3-Me** (right) with 50% probability of thermal ellipsoids. One of the disordered Cp* ligands in **3-C1-Me** and hydrogen atoms are omitted for clarity.

are isostructural and have trianglular cores with one Pt or Pd and two Ir or Rh ions capped by two triply bridging sulfido ligands. The crystals of **3-C1-Me** and **4-C1-Me**, **3-C2-Me** and **4-C2-Me**, **3-C1-*i*Pr** and **4-C1-*i*Pr**, and **5-C1-Me** and **6-C1-Me** are isomorphous, respectively, due to the similarity of atomic radii of the Rh and Ir atoms. However, Pt and Pd complexes having the same Rh or Ir units and bisNHC ligand, **3-C1-Me** and **5-C1-Me**, for example, did not give isomorphous crystals under similar conditions. A few structurally characterized Pt−Ir mixed-metal multinuclear clusters have been reported,[11] and there are only three and five examples of Ir_2Pt and Ir_2Pd trinuclear complexes, respectively: $[(IrCp^*)_2\{M'(dppe)\}(\mu_3\text{-}S)_2]^+$ (M′ = Pd, Pt; dppe =1,2-bis(diphenylphosphino)-ethane),[12] $[(IrCp^*)_2\{PtCl(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}Se)]^+$,[13] $[(IrCp^*)_2(PtCl_2)(\mu_3\text{-}Se)_2]$,[13] $[(IrCp^*)_2\{PdCl(PPh_3)\}(\mu_3\text{-}S)_2]^+$,[12,14] and $[(IrCp^*)_2\{Pd(R\text{-}py)_2\}(\mu_3\text{-}S)_2]^+$.[15] In the case of the Rh_2Pt and Rh_2Pd complexes, **3-C*n*-R** and **5-C*n*-R** are the first examples of $Rh^{III}_2Pt^{II}$ and $Rh^{III}_2Pd^{II}$ trinuclear complexes with triply bridging chalcogenido ligands, although a carbonyl-bridged $Pt^0Rh^I_2$ complex, $[\{Pt(CO)(PPh_3)\}(RhCp^*)_2(\mu_3\text{-}CO)_2]$, has been reported.[16]

The Rh−Rh and Ir−Ir bond lengths (2.8686(8)−2.9302(12) Å) slightly decreased with an increase in the length of the alkylene bridges in the bisNHC-C*n*-R ligands (Table 1). The

Table 1. Metal−Metal Bond Lengths (Å) in M_2Pt Complexes

R	M	C*n*	M−M	M−Pt(CH$_2$)[a]	M−Pt(R)[b]
Me	Rh	C1	2.9067(13)	2.8823(11)	3.0229(10)
		C2	2.8737(13)	2.9718(11)	2.9593(10)
		C3	2.8686(8)	2.9326(7)	3.0335(6)
	Ir	C1	2.9069(8)	2.9053(8)	3.0617(7)
		C2	2.8802(6)	3.0096(6)	2.9908(6)
*i*Pr	Rh	C1	2.9241(9)	2.9095(6)	2.9933(7)
	Ir	C1	2.9204(8)	2.9268(10)	3.0221(9)
Bn	Rh	C1	2.9281(10)[c]	2.9065(10)[c]	3.0678(9)[c]
			2.9302(12)[c]	2.9392(8)[c]	2.9784(10)[c]

[a]M−Pt bonds near the alkylene bridges of the bisNHC ligands. [b]M−Pt bonds near the N-substituents. [c]Two crystallographically independent complexes were observed.

M−Pt bond lengths varied in the range of 2.8823(11)−3.0678(9) Å, and the Pt−M bonds near the alkylene bridges (2.8823(11)−3.0096(6) Å) and the N-substituents (2.9593(10)−3.0678(9) Å) are similar. The M−M distances were found to vary slightly even in crystals of **3-C1-Bn**, in the unit cell of which there were two crystallographically independent complex cations with different Rh−Rh and Rh−Pt bond distances. This fact suggests that the M−M and M−M′ bonds are flexible and are affected by the surrounding environment, such as the crystal packing.

The M−M distances in the M_2Pd complexes are similar to those found in the M_2Pt complexes, and the M−M bond lengths increase in order of the ethylene, methylene, and propylene bridges (Table 2). Similar to the M_2Pt complexes, no trends in the M−Pd bond lengths were found, implying that the M−M bonds are sensitive to the environment surrounding the complexes.

Most striking differences in structures of the heterometallic complexes appeared in the dihedral angles (DHAs) between the NHC rings and the coordination planes of the Pt and Pd centers, which increase with an increase in length of the alkylene bridges (Table 3). Although the DHAs in each

Table 2. Metal−Metal Bond Lengths (Å) in M_2Pd Complexes

R	M	C*n*	M−M	M−Pd(CH$_2$)[a]	M−Pd(R)[b]
Me	Rh	C1	2.8706(8)	2.9732(9)	3.0179(8)
		C2	2.8901(10)	2.9575(11)	2.9776(11)
	Ir	C1	2.8731(5)	2.9881(7)	3.0421(6)

[a]M−Pd bonds near the alkylene bridges of the bisNHC ligands. [b]M−Pd bonds near the N-substituents.

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Table 3. Dihedral Angles (deg) between NHC Rings and Coordination Planes in M_2M' Complexes

Cn	M′	R	Rh_2M'	Ir_2M'
C1	Pt	Me	36.8(2), 54.4(2)	36.8(2), 55.0(2)
		*i*Pr	41.4(3), 45.3(3)	40.7(3), 45.2(3)
		Bn	36.6(3), 43.0(3)[a]	N. A.[b]
			41.0(3), 45.0(3)[a]	
	Pd	Me	41.0(2), 45.5(2)	40.8(2), 45.5(2)
C2	Pt	Me	53.4(3), 62.8(3)	53.9(3), 62.4(3)
	Pd	Me	53.4(2), 69.6(2)	52.3(4), 70.0(4)
C3	Pt	Me	72.8(2), 76.5(2)	N. A.[b]

[a]Two crystallographically independent complexes were observed. [b]Single crystals suitable for X-ray analyses were not obtained.

complex varied in the solid state, only an averaged vibration was observed in solution and, the ^{1}H NMR spectra, only one set of the imidazolylidene signals was observed. The signals of the alkylene bridges appeared as two doublets with geminal coupling for the methylene, two AA′BB′ multiplets for the ethylene, and four multiplets with 1:1:2:2 ratio for the propylene bridges attributed to the fixed endo- and exoprotons in the alkylene bridges. Moreover, the results suggest that the structures of the complexes are symmetrical in solution. The differences in DHAs observed in the solid state are ascribed to the crystal packing, which locks the complexes into stable structures in the solid state.

Formation reactions of the heterometallic trinuclear complexes were examined using [Pt(bisNHC-C2-Me)$(SH)_2$] (**1-C2-Me**) as a starting material. The reactions of hydrosulfido complex **1-C2-Me** with the Rh and Ir hydroxo complexes depended on the solvents. In methanol, only **3-C2-Me** and **4-C2-Me** formed. No other trinuclear complexes, such as $[\{Pt(bisNHC\text{-}C2\text{-}Me)\}_3(\mu_3\text{-}S)_2]^{2+}$, $[(MCp^*)\{Pt(bisNHC\text{-}C2\text{-}Me)\}_2(\mu_3\text{-}S)_2]^{2+}$, and $[(MCp^*)_3(\mu_3\text{-}S)_2]^{2+}$, formed. On the other hand, in acetonitrile, other trinuclear complexes, such as $[(MCp^*)\{Pt(bisNHC\text{-}C2\text{-}Me)\}_2(\mu_3\text{-}S)_2]^{2+}$, formed. These results indicate that the dimeric structures of the Rh and Ir Cp* complexes are maintained in methanol and that the dimeric units break in coordinating solvents, such as acetonitrile. In electrospray ionization (ESI) mass spectra of a mixture of the Rh and Ir hydroxo complexes in acetonitrile, peaks appeared for a heterometallic dimer complex, whereas in methanol, only those for homometallic dimeric complexes were observed, supporting the results described above (see Supporting Information).

Dynamic Behavior of the Trinuclear Complexes in Solution. Although two protons of each methylene group of the alkylene bridges in the ligand precursors are equivalent, they are inequivalent in the complexes affording two different signals (exo- and endoproton signals) with coupling in ^{1}H NMR spectra due to the bent structure of the ligand, which was confirmed by X-ray crystallography. In addition, the two MCp* units in each complex are inequivalent because of the unsymmetrical Pt- and Pd-bisNHC units, and two singlet signals for the Cp*-methyl protons are observed.

The two ^{1}H NMR signals for the methyl protons of the Cp* ligands in the complexes with methylene- or propylene-bridged NHC ligands in DMSO-d_6 merged into one sharp signal at high temperature. However, the complexes with the ethylene-bridged bisNHC ligand showed no dynamic behavior even at 400 K. The observed dynamic behaviors of the complexes with the methylene- and propylene-bridged ligands are attributed to flapping wing motion of the bisNHC ligands. Similar dynamic behavior has been reported for rhenium carbonyl complexes with bisNHC ligands with methylene or ethylene bridges.[17] In this report, no such flapping wing motion was observed for the ethylene-bridged bisNHC complexes.

To investigate the dynamic behavior in detail, temperature-dependent NMR experiments and line-shape analyses were performed. ^{1}H NMR spectra of the Rh_2Pt and Ir_2Pt complexes with a methylene-bridged bisNHC ligand with methyl N-substituents in DMSO-d_6 and simulated spectra in the temperature ranges of 293−363 K for Rh_2Pt **3-C1-Me** and 293−393 K for Ir_2Pt **4-C1-Me** are shown in Figures 2 and 3, respectively. Line-shape analyses for the other complexes, namely, **3-C1-R**, **3-C3-R**, **4-C1-R**, and **4-C1-R**, are shown in the Supporting Information.

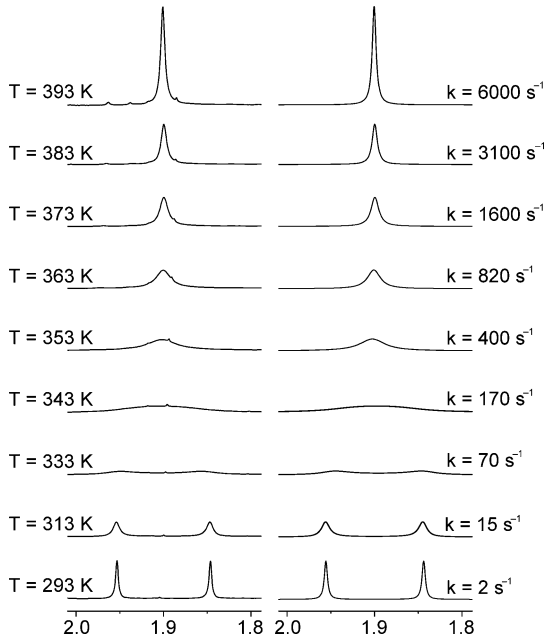

Figure 2. Observed (left) and simulated (right) ^{1}H NMR spectra for the Rh_2Pt complex **3-C1-Me** in DMSO-d_6.

Eyring plots for the M_2Pt complexes using the kinetic parameters obtained from the line shape analyses are shown in Figure 4. The activation parameters for the flapping wing motion of the Rh_2Pt and Ir_2Pt complexes having the same N-substituents and alkylene bridges are similar to each other and show no dependency on the Cp*M units (Table 4). These results clearly show that the dynamic behavior occurs at the platinum bisNHC units. The $\Delta S^{\ddagger}$ values, which generally contain relatively large errors from line shape analyses, were slightly different. The negative or small positive values of $\Delta S^{\ddagger}$ suggest that no bond cleavage occurs during the dynamic process.

For the heterometallic complexes with the Pt-bisNHC unit containing a methylene bridge, inversion at the CH_2 must occur in the flapping wing motion of the bisNHC ligand. In the case of the complexes with the propylene bridge, the propylene bridge seems to be more flexible than those with the methylene bridge, and two of the three CH_2 units in the propylene bridge can move almost freely, whereas the third CH_2 group in the propylene bridge must invert to achieve the flapping wing motion. Since similar activation parameters were obtained for

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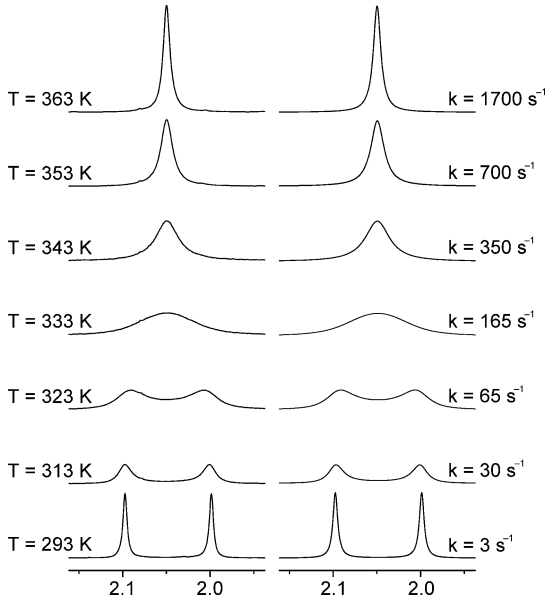

Figure 3. Observed (left) and simulated (right) ^{1}H NMR spectra for the Ir_2Pt complex **4-C1-Me** in DMSO-d_6.

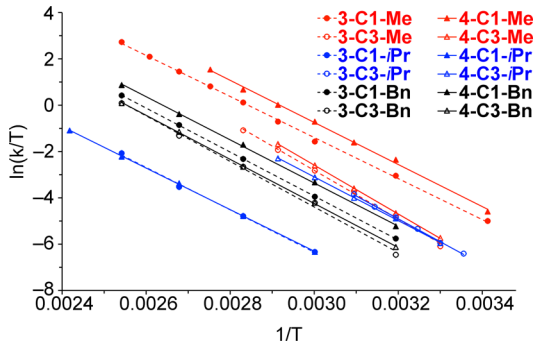

Figure 4. Eyring plots for the M_2Pt complexes **3-C1-R**, **3-C3-R**, **4-C1-R**, and **4-C1-R** using kinetic constants obtained from line shape analyses.

Table 4. Activation Parameters for Flapping Wing Motion of the M_2Pt Heterometallic Trinuclear Complexes[a]

C*n*	R	M	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal mol^{-1}K^{-1})	$\Delta G^{\ddagger}_{298\ K}$ (kcal mol^{-1})
C1	Me	Rh	17.6(2)	3.0(6)	16.8(3)
		Ir	18.1(4)	5.6(11)	16.4(5)
	*i*Pr	Rh	18.2(6)	−5(5)	19.8(16)
		Ir	17.9(2)	−6.1(4)	19.7(3)
	Bn	Rh	18.9(1)	1.7(1)	18.4(1)
		Ir	18.6(3)	1.8(18)	18.0(6)
C3	Me	Rh	20.9(2)	10.0(15)	17.9(5)
		Ir	21.0(1)	11(5)	17.8(14)
	*i*Pr	Rh	19.7(5)	6.0(13)	17.9(6)
		Ir	18.8(2)	3(4)	17.9(13)
	Bn	Rh	19.6(6)	2.8(12)	18.7(7)
		Ir	18.9(2)	1.2(8)	18.6(3)

[a]Values in parentheses represent standard deviations in the last figures of the activation parameters.

the complexes with the methylene and propylene bridges, we concluded that inversion at one CH_2 moiety in the bridges occurred. On the other hand, the ethylene bridges in the complexes must undergo simultaneous inversions at the both of CH_2 moieties, which is extremely difficult.

Lineshape analyses were also applied to the spectra for M_2Pd complexes **5-C*n*-Me** and **6-C*n*-Me**. Although only the M_2Pt complexes with the methylene and propylene bridges exhibited dynamic behavior, all of the M_2Pd complexes showed dynamic behavior. Temperature-dependent ^{1}H NMR spectra of **6-C1-Me** and **6-C2-Me** are shown in Figures 5 and 6, respectively.

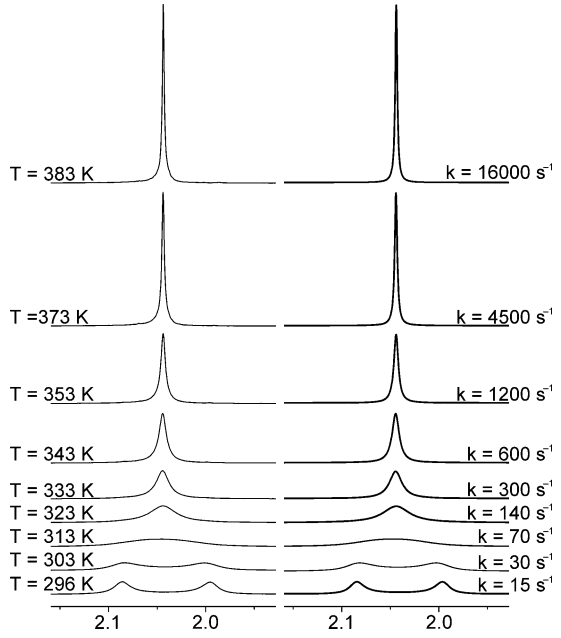

Figure 5. Observed (left) and simulated (right) ^{1}H NMR spectra for the Ir_2Pd complex **6-C1-Me** with the methylene-bridged bisNHC ligand in DMSO-d_6.

Activation parameters of (Table 5) and Eyring plots for (Figure 7) the complexes with the methylene and propylene bridges are

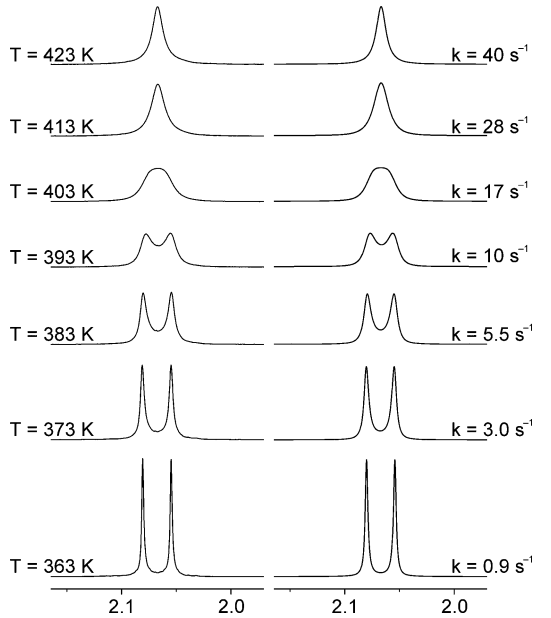

Figure 6. Observed (left) and simulated (right) ^{1}H NMR spectra for the Ir_2Pd complex **6-C2-Me** with the ethylene-bridged bisNHC ligand in DMSO-d_6.

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Table 5. Activation Parameters for Flapping Wing Motion of the M_2Pd Heterometallic Trinuclear Complexes[a]

R	Cn	M	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal mol^{-1}K^{-1})	$\Delta G^{\ddagger}_{298\ K}$ (kcal mol^{-1})
Me	C1	Rh	15.5(1)	−1.8(4)	16.1(2)
		Ir	15.6(2)	−0.4(6)	15.7(4)
	C2	Rh	14.9(2)	−17.1(5)	20.0(3)
		Ir	15.7(3)	−14.7(6)	20.1(4)
	C3	Rh	16.8(3)	−0.5(9)	17.0(6)
		Ir	16.8(2)	−0.6(6)	17.0(4)

[a]Values in parentheses represent standard deviations in the last figures of the activation parameters.

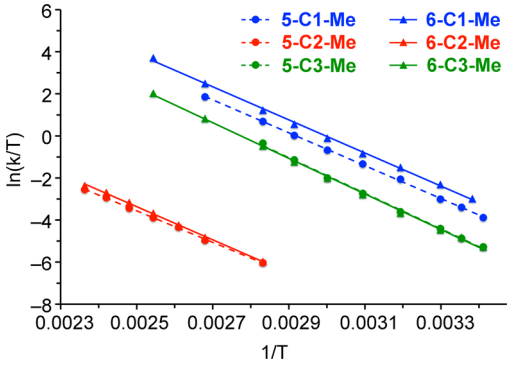

Figure 7. Eyring plots for the M_2Pd complexes **5-C*n*-R** and **6-C*n*-R** using kinetic constants obtained from line-shape analyses.

similar to each other. The small negative values of $\Delta S^{\ddagger}$ show that the dynamics are due to the flapping wing motion without bond cleavage similar to the M_2Pt complexes with the methylene and propylene bridges. On the other hand, different activation parameters were obtained for the M_2Pd complexes with the ethylene bridges, suggesting that they undergo different dynamic processes in solution. Since the activation parameters for the Rh_2Pd and Ir_2Pd complexes were similar, we concluded that the dynamic motion occurred at the Pd-bis NHC units. The large negative $\Delta S^{\ddagger}$ values imply that the process involves Pd−$C_{carbene}$ bond cleavage and coordination of a solvent molecule. This dynamic behavior was not observed for the M_2Pt complexes with the ethylene bridges since the platinum center is inert, supporting Pd−C bond cleavage.

Absorption Spectra for the Trinuclear Complexes. All of the M_2M' complexes have intense colors, and in their absorption spectra, absorption bands between 550−650 nm were observed. Absorption spectra of **3-C*n*-Me** and **4-C*n*-Me** are shown in Figure 8. Similar absorption spectra for $[(IrCp^*)_2\{M'L_2\}(\mu_3\text{-}S)_2]^+$ (M′ = Pd and Pt; L_2 = $(PPh_3)_2$, dppe), which are purple, have been reported.[12]

Time-dependent density functional theory (TD-DFT) calculations on the heterometallic trinuclear complexes showed that the absorptions were due to a transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of each complex. Since the HOMOs and LUMOs of the heterometallic trinuclear complexes are similar to each other, those of **4-C2-Me** are shown in Figure 9 as an example. The HOMO, which has M−M antibonding and M−S bonding characters, and the LUMO, which has M−M bonding and M−S antibonding characters, are mainly located on the M_2PtS_2 core, meaning that the absorption is due to a cluster-center transition. The absorption

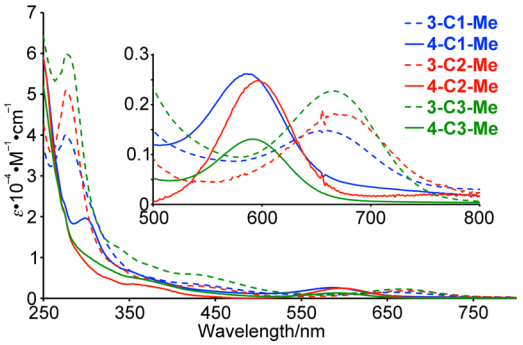

Figure 8. Absorption spectra for the M_2Pt complexes with methyl N-substituents, **3-C*n*-Me** and **4-C*n*-Me**.

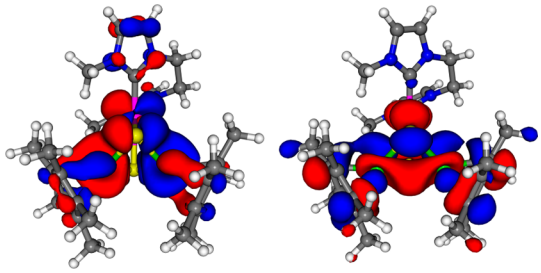

Figure 9. HOMO (left) and LUMO (right) of the Ir_2Pt complex **4-C2-Me** with the optimized structure obtained by DFT calculation at the B3LYP/LanL2DZ level for Ir and Pt atoms and 6-31G(d,p) for the other atoms.

maxima for the heterometallic trinuclear complexes depend on M and M′ in the M_2M' cores (Tables 6 and 7). This fact shows that all of the metal ions in the core contribute to the HOMO and/or LUMO, which is consistent with the results of the DFT calculations.

Table 6. Observed and Calculated Absorption Maxima (nm) for the Cluster-Center Transitions of the M_2Pt Complexes

		Rh_2Pt		Ir_2Pt	
R	Cn	obs	calcd[a]	obs	calcd[a]
Me	C1	658	684	586	570
	C2	673	700	595	581
	C3	666	694	591	578
*i*Pr	C1	659	697	588	579
	C2	672	707	597	586
	C3	665	705	593	585

[a]Obtained by TD-DFT calculations using optimized structures at the B3LYP/LanL2DZ level for Rh, Ir, and Pt atoms and 6-31G(d,p) for the others.

Table 7. Observed and Calculated Absorption Maxima (nm) for the Cluster-Center Transitions of the M_2Pd Complexes

		Rh_2Pd		Ir_2Pd	
R	Cn	obs	calcd[a]	obs	calcd[a]
Me	C1	622	645	562	542
	C2	630	657	569	550.5
	C3	627	655	567	549.7

[a]Obtained by TD-DFT calculations using optimized structures at the B3LYP/LanL2DZ level for Rh, Ir, and Pt atoms and 6-31G(d,p) for the others.

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Moreover, the absorption maxima depend on the bridging alkylenes but not on the N-substituents. The absorption maxima increase in the order of the methylene-, propylene-, and ethylene-bridged bisNHC complexes regardless of the N-substituents and metals. This trend for the absorptions was reproduced by using TD-DFT calculations, although the differences were minute (Tables 6 and 7).

Electrochemical Properties of the Heterometallic Trinuclear Complexes. In the cyclic voltammograms (CVs) of the heterometallic trinuclear complexes, except for the Ir_2Pd complexes **6-C*n*-Me**, two reversible redox waves for the $[M_2M']^{2+/+}$ and $[M_2M']^{+/0}$ couples, which are similar to the $[M_3]^{2+/+}$ and $[M_3]^{+/0}$ couples observed for $[(MCp^*)_3(\mu\text{-}S)_2]^{2+}$ ($[M_3]^{2+}$),[7,18] were observed (Figure 10).

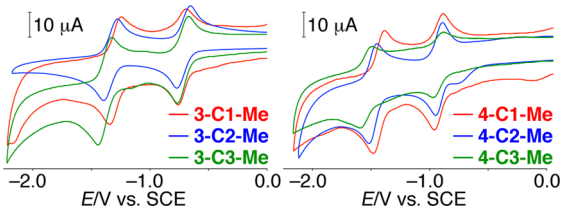

Figure 10. Cyclic voltammograms for Rh_2Pt, **3-C*n*-Me**, (left) and Ir_2Pt, **4-C*n*-Me**, complexes.

The CVs for the Ir_2Pd complexes **6-C*n*-Me** are different from those of the other heterometallic trinuclear complexes. The reduction waves in the CVs for **6-C1-Me** and **6-C3-Me** were irreversible, minor waves were observed, and the reduction current for **6-C3-Me** was large. Moreover, the CVs depended on the concentrations (Figure 11). These differences were attributed to the instability of the reduced species of the complexes under the conditions used. In other words, the reduced species either decomposed or reacted with the solvent. Although **6-C2-Me** in a 1.0 mmol/L solution showed a CV similar to those of the other M_2M' complexes, the second reduction wave was split into two waves and was irreversible in a 0.2 mmol/L solution.

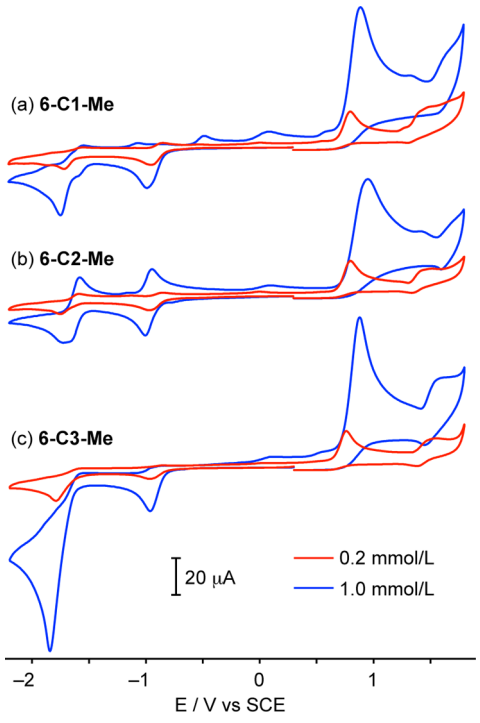

Figure 11. Cyclic voltammograms for the Ir_2Pd complexes with methyl N-substituents. Red and blue lines represent CVs for 0.2 mmol/L or 1.0 mmol/L solutions of the complexes, respectively.

Because the CVs for Ir_2Pd complexes were different from those of the other complexes, they were excluded from further discussion on the electrochemical properties of the heterometallic trinuclear complexes. The $[M_2M']^{2+/+}$ and $[M_2M']^{+/0}$ couples appeared at more negative potentials ($E_{1/2}$) than those for $[M_3]^{2+/+}$ and $[M_3]^{+/0}$ couples (Table 8). Differences in the

Table 8. First and Second Reduction Potentials (*V* vs SCE) of the M_2M' Complexes

M′	M	Rh			Ir		
R	C*n*	C1	C2	C3	C1	C2	C3
Pd	first	−0.71	−0.70	−0.70	−0.90	−0.98	−0.92
Me	second	−1.39	−1.41	−1.43	−1.63	−1.63	−1.80
Pt	first	−0.72	−0.71	−0.72	−0.98	−0.98	−0.98
Me	second	−1.29	−1.33	−1.38	−1.49	−1.54	−1.60
Pt	first	−0.71	−0.71	−0.68	−0.96	−0.96	−0.94
*i*Pr	second	−1.30	−1.37	−1.36	−1.49	−1.56	−1.62
Pt	first	−0.68	−0.68	−0.69	−0.94	−0.95	−0.95
Bn	second	−1.27	−1.31	−1.34	−1.47	−1.51	−1.55
Cp^*M_3	first	−0.52[a]			−0.83[a]		
	second	−0.91[a]			−0.98[a]		

[a]Obtained from refs 6 and 17.

$E_{1/2}$ values of $[M_2M']^{+/0}$ and $[M_3]^{+/0}$ couples are significantly larger than those of the $[M_2M']^{2+/+}$ and $[M_3]^{2+/+}$ couples, meaning that the $[M_2M']^{+}$ state is stabilized against disproportionation.

The reversibility of the reduction couples suggests that only the small structural changes occur during the reduction. The results of DFT calculations on the M_2M' complexes also support our conclusions that only small structural changes occur. Moreover, the $1e^-$- and $2e^-$-reduced species were found to have similar LUMOs, SOMOs, and HOMOs (Figure 12), meaning that the two-step $1e^-$-reduction processes occur at the $M_2M'S_2$ core.

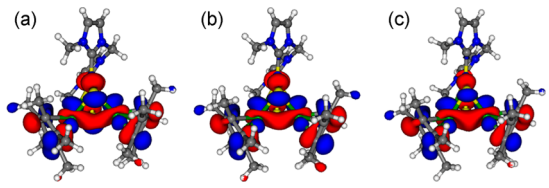

Figure 12. (a) LUMO of the dicationic Rh_2Pt complex **3-C1-Me**, (b) SOMO of the $1e^-$-reduced complex, and (c) HOMO of $2e^-$-reduced complex.

The first $E_{1/2}$ values are barely affected by the N-substituents and the alkylene bridges in the bisNHC ligands. On the other hand, the second $E_{1/2}$ values depended on the alkylene bridges. We have reported that the differences in the second $E_{1/2}$ values among the M_2Pt complexes with methyl N-substituents are attributed to the DHAs between the NHC rings and the coordination plane of the Pt center, which depend on the π back-bonding interactions between the Pt center and the $C_{carbene}$ atoms.[19] The complexes with the isopropyl and benzyl N-substituents also showed the same trend in the $E_{1/2}$ values

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(Figure 13). The reason that no differences are observed in the first $E_{1/2}$ values is because the amount of π back-donation from

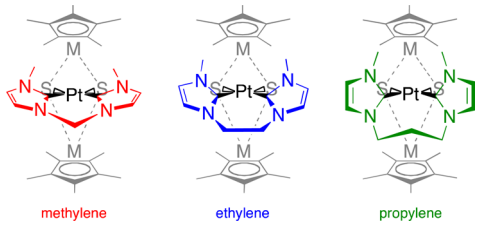

Figure 13. Schematic representation of the dependence of the dihedral angles on the alkylene bridges.

the Pt center of the M_2PtS_2 core in the oxidized form of the complexes is decreased due to smaller amount of electron density on the core at higher oxidation states of the metal ions, that is, Pt^{II} and Rh^{III} or Ir^{III}. Some spectroscopic and voltammetric results concerning the tuning of the π back-bonding via different substituents on the NHC rings have been reported.[20]

Furthermore, the C−Pt−C angles vary in the range of 82.0(7)°−88.1(3)° and are comparable to the reported values for the other Pt 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).[9,21] These differences have an effect on the properties of the trinuclear complexes. However, the effects of the angles on the first $E_{1/2}$ values are negligible because the differences in the C−Pt−C angles affect the σ-donation from the $C_{carbene}$ atoms to the metal center, but, in fact, no differences in the first $E_{1/2}$ values were found.

CONCLUSIONS

A bottom-up method employing hydrosulfido platinum and palladium complexes, [M′(bisNHC-C*n*-R)(SH)$_2$] (M′ = Pt and Pd) was used to construct sulfide-bridged multinuclear complexes with N-heterocyclic carbene ligands. From X-ray structural analyses on the trinuclear complexes, the M−M bond lengths varied and were affected by the environment around the complexes, such as the crystal packing.

The formation of trinuclear complexes in relation to the structures of the hydroxo-bridged dinuclear complexes in solution were investigated, and M_2M'-type heterometallic trinuclear complexes, [(MCp*)$_2${M′(bisNHC-C*n*-R)}(μ_3-S)$_2$]-(BPh$_4$)$_2$ (M = Rh and Ir; M′ = Pt and Pd), were synthesized by reacting the hydrosulfido complexes with hydroxo-bridged dinuclear Rh and Ir complexes, whose dimeric structures remained intact in methanol during the formation of the trinuclear complexes. Reactions of the hydroxo dinuclear complexes with the hydrosulfido complexes in acetonitrile gave different products from those obtained in methanol due to a monomer−dimer equilibrium involving the starting Rh and Ir hydroxo complexes in acetonitrile. The monomeric complexes in acetonitrile reacted with the hydrosulfido Pt complex to afford MPt_2-type trinuclear complex along with the M_2Pt complex.

In the CVs of the heterometallic trinuclear complexes, two reversible reduction peaks were observed, and only the second $E_{1/2}$ values were affected by the lengths of the alkylene bridges in the bisNHC ligands. In the absorption spectra of the complexes, peaks in the ranges of 620−680 and 560−600 nm for the Rh_2M' and Ir_2M' complexes, respectively, were observed, and the absorption maxima did not depend on the N-substituents. However, they slightly depended on the length of the alkylene bridge in the bisNHC ligands, which were reproduced via TD-DFT calculations.

The heterometallic complexes, except for those containing a Pt unit with an ethylene-bridged bisNHC ligand, showed dynamic behavior in solution, which was attributed to a flapping wing motion of the NHC ligands. Activation parameters obtained from line-shape analyses on variable-temperature ^{1}H NMR spectra of the complexes suggested that the flapping wing motion occurred without bond cleavage for the complexes with methylene and propylene bridges and that the motion for the complexes with a Pd unit with an ethylene-bridged ligand occurred with Pd−$C_{carbene}$ bond cleavage, accompanied by coordination of solvent molecules.

EXPERIMENTAL SECTION

Materials and Methods. All chemicals were purchased from Aldrich, Nacalai Tesque, and Wako Pure Chemical and used without further purification. 1,1′-Dialkyl-α,ω-alkylene-diimidazolium dihalide ([bisNHC-C*n*-R]X$_2$) and [Pt(bisNHC-C*n*-R)(SH)$_2$] **1-C*n*-Me** were prepared by modifying procedures reported previously.[9] [(RhCp*)$_2$(μ-OH)$_3$](BPh$_4$) and [(IrCp*)$_2$(μ-OH)$_3$](BPh$_4$) were synthesized by using reported procedures.[10] ^{1}H and ^{13}C NMR spectra were recorded on a JEOL Lambda 300, Lambda 400, or Bruker AVANCE 300 FT-NMR spectrometer. Chemical shifts are expressed in ppm referenced to $SiMe_4$ using solvent peaks. ESI mass spectrometric measurements were performed on an Applied Biosystem Mariner time-of-flight mass spectrometer using HPLC-grade solvents. Absorption spectra were measured on a Shimadzu MultiSpec-1500 spectrometer using acetonitrile as a solvent. Elemental analyses were performed on a J-Science Lab JM-10 or FISONS Instrument EA108 elemental analyzer by the Analytical Research Center at Osaka City University.

[(RhCp)$_2${Pt(bisNHC-C1-Me)}(μ_3-S)$_2$](BPh$_4$)$_2$,* ***3-C1-Me.*** A solution of [Pt(bisNHC-C1-Me)(SH)$_2$] **1-C1-Me** (22.7 mg, 0.052 mmol) in 15 mL of methanol was added to a solution of [(RhCp*)$_2$(μ-OH)$_3$](BPh$_4$) (42.3 mg, 0.050 mmol) in 10 mL of methanol. A solution of NaBPh$_4$ (100.0 mg, 0.29 mmol) in methanol (20 mL) was added to the solution. A dark green solid was collected by filtration and washed with methanol. The obtained solid was dissolved in acetonitrile, and diethyl ether was added to the solution to give a green solid. The solid was collected by filtration and washed with methanol. Addition of diethyl ether into a solution of the crude product in a mixture of dichloromethane and acetonitrile afforded microcrystals of the complex. Yield: 68%. Single crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a solution of the complex in dichloromethane. Anal. Calcd for $C_{77}H_{82}B_2N_4Pt\,Rh_2S_2\cdot CH_2Cl_2\cdot 1/2CH_3CN$: C, 57.31; H, 5.21; N, 3.81. Found: C, 57.02; H, 5.30; N, 3.75%. ^{1}H NMR (DMSO-d_6, 300 MHz, 298 K): δ 7.51 (d, $^3J_{H-H}$ = 1.4 Hz, 2H, 4-Im), 7.38 (d, $^3J_{H-H}$ = 1.9 Hz, 2H, 5-Im), 7.18 (m, 16H, BPh$_4$-*o*-Ph), 6.92 (t, $^3J_{H-H}$ = 7.4 Hz, 16H, BPh$_4$-*m*-Ph), 6.78 (t, $^3J_{H-H}$ = 7.1 Hz, 8H, BPh$_4$-*p*-Ph), 6.15 (d, $^2J_{H-H}$ = 13.2 Hz, 1H, N−CH$_2$), 5.34 (d, $^2J_{H-H}$ = 13.1 Hz, 1H, N−CH$_2$), 3.73 (s, 6H, N-Me), 1.94 (s, 15H, Cp*-Me), 1.84 (s, 15H, Cp*-Me). ^{13}C NMR (DMSO-d_6, 75 MHz, 298 K): δ 163.4 (q, $^1J_{C-B}$ = 49.4 Hz, C−B), 152.7 (2-Im), 135.6 (q, $^2J_{C-B}$ = 1.3 Hz, *o*-Ph), 125.4 (q, $^3J_{C-B}$ = 2.6 Hz, *m*-Ph), 122.9 (4-Im), 121.6 (*p*-Ph), 121.0 (5-Im), 102.3 (d, $^1J_{C-Rh}$ = 7.7 Hz, Cp*-ring), 102.2 (d, $^1J_{C-Rh}$ = 7.1 Hz, Cp*-ring), 62.3 (N−CH$_2$), 37.7 (N-Me), 10.6 (Cp*-Me), 10.5 (Cp*-Me).

[(RhCp)$_2${Pt(bisNHC-C2-Me)}(μ_3-S)$_2$](BPh$_4$)$_2$,* ***3-C2-Me.*** Complex **3-C2-Me** was prepared analogously to **3-C1-Me**. Addition of diethyl ether into a solution of the crude product in a mixture of dichloromethane and acetonitrile afforded microcrystals of the complex. Yield: 38%. Single crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a solution of the complex in dichloromethane. Anal. Calcd for $C_{78}H_{84}B_2N_4PtRh_2S_2\cdot H_2O$: C, 59.21; H, 5.48; N, 3.54. Found: C, 59.14; H, 5.46; N, 3.73%.

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^{1}H NMR (CD_3CN, 300 MHz, 298 K): δ 7.27 (m, 16H, *o*-Ph), 7.03 (m, 4H, 4-Im, and 5-Im), 6.99 (dd, $^3J_{H-H} \approx$ 7.4 Hz, $^3J_{H-H} \approx$ 7.4 Hz, 16H, *m*-Ph), 6.84 (tt, $^3J_{H-H}$ = 7.2 Hz, $^4J_{H-H}$ = 1.3 Hz, 8H, *p*-Ph), 4.56 (m, 2H, CH_2), 4.24 (m, 2H, CH_2), 3.54 (s, $^4J_{H-Pt}$ = 2.9 Hz, 6H, Me), 1.91 (s, 15H, Cp*), 1.88 (s, 15H, Cp*). ^{13}C NMR (CD_3CN, 75 MHz, 298 K): δ 164.7 (q, $^1J_{C-B}$ = 49.4 Hz, *C*-B), 152.0 (2-Im), 136.7 (q, $^2J_{C-B}$ = 1.4 Hz, *o*-Ph), 126.5 (q, $^3J_{C-B}$ = 2.8 Hz, *m*-Ph), 123.7 (s, 4-Im), 123.5 (s, 5-Im), 122.7 (s, *p*-Ph), 103.2 (s, Cp*-ring), 103.1 (s, Cp*-ring), 48.3 (s, $^3J_{C-Pt}$ = 8.4 Hz, CH_2), 39.3 (s, Me), 11.2 (s, Cp*-Me), 11.1 (s, Cp*-Me). ^{1}H NMR (DMSO-d_6, 300 MHz, 298 K): δ 7.39 (d, $^3J_{H-H}$ = 2.0 Hz, 2H, 4-Im), 7.38 (d, $^3J_{H-H}$ = 2.0 Hz, 2H, 5-Im), 7.18 (m, 16H, BPh_4-*o*-Ph), 6.92 (t, $^3J_{H-H}$ = 7.4 Hz, 16H, BPh_4-*m*-Ph), 6.78 (t, $^3J_{H-H}$ = 7.1 Hz, 8H, BPh_4-*p*-Ph), 4.65−4.50 (m, 2H, N−CH_2), 4.45−4.30 (m, 2H, N−CH_2), 3.55 (s, 6H, N-Me), 1.92 (s, 15H, Cp*-Me), 1.89 (s, 15H, Cp*-Me). ^{13}C NMR (DMSO-d_6, 75 MHz, 298 K): δ 163.4 (q, $^1J_{C-B}$ = 49.4 Hz, C−B), 149.8 (2-Im), 135.5 (q, $^2J_{C-B}$ = 1.1 Hz, *o*-Ph), 125.3 (q, $^3J_{C-B}$ = 2.7 Hz, *m*-Ph), 123.1 (4-Im), 122.9 (5-Im), 121.5 (*p*-Ph), 101.9 (d, $^1J_{C-Rh}$ = 7.4 Hz, Cp*-ring), 101.8 (d, $^1J_{C-Rh}$ = 7.1 Hz, Cp*-ring), 47.1 (N-$\underline{C}H_2$), 38.1 (N-Me), 10.54 (Cp*-Me), 10.49 (Cp*-Me).

[(RhCp)$_2${Pt(bisNHC-C3-Me)}(μ_3-S)$_2$](BPh$_4$)$_2$*, ***3-C3-Me***. Complex **3-C3-Me** was prepared analogously to **3-C1-Me**. Addition of diethyl ether into a solution of the crude product in a mixture of dichloromethane and acetonitrile afforded microcrystals of the complex. Yield: 76%. Single crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a solution of the complex in dichloromethane. Anal. Calcd for $C_{79}H_{86}B_2N_4Pt\,Rh_2S_2\cdot H_2O$: C, 59.44; H, 5.56; N, 3.51. Found: C, 59.60; H, 5.49; N, 3.63%. ^{1}H NMR (DMSO-d_6, 300 MHz, 298 K): δ 7.36 (d, $^3J_{H-H}$ = 2.0 Hz, 2H, 4-Im), 7.34 (d, $^3J_{H-H}$ = 1.9 Hz, 2H, 5-Im), 7.18 (m, 16H, BPh_4-*o*-Ph), 6.92 (t, $^3J_{H-H}$ = 7.4 Hz, 16H, BPh_4-*m*-Ph), 6.79 (t, $^3J_{H-H}$ = 7.2 Hz, 8H, BPh_4-*p*-Ph), 4.28−3.70 (m, 4H, N−CH_2), 3.47 (s, 6H, N-Me), 1.92 (s, 15H, Cp*-Me), 1.91 (s, 15H, Cp*-Me), 1.65−1.45 (m, 2H, 2-$(CH_2)_3$). ^{13}C NMR (DMSO-d_6, 75 MHz, 298 K): δ 163.4 (q, $^1J_{C-B}$ = 49.4 Hz, C−B), 151.9 (2-Im), 135.6 (q, $^2J_{C-B}$ = 1.3 Hz, *o*-Ph), 125.3 (q, $^3J_{C-B}$ = 2.7 Hz, *m*-Ph), 123.0 (4-Im), 122.9 (5-Im), 121.6 (*p*-Ph), 101.85 (d, $^1J_{C-Rh}$ = 7.4 Hz, Cp*-ring), 101.79 (d, $^1J_{C-Rh}$ = 7.2 Hz, Cp*-ring), 51.5 (N-$\underline{C}H_2$), 37.9 (N-Me), 10.6 (Cp*-Me), 10.5 (Cp*-Me), 9.3 (2-$(CH_2)_3$).

[(RhCp)$_2${Pt(bisNHC-C1-iPr)}(μ_3-S)$_2$](BPh$_4$)$_2$*, ***3-C1-iPr***. Complex **3-C1-*i*Pr** was prepared analogously to **3-C1-Me**. Addition of diethyl ether into a solution of the crude product in dichloromethane afforded microcrystals of the complex. Yield: 67%. Single crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a solution of the complex in dichloromethane. Anal. Calcd for $C_{81}H_{90}B_2N_4PtRh_2S_2\cdot 3/2CH_2Cl_2$: C, 57.16; H, 5.41; N, 3.23. Found: C, 57.26; H, 5.66; N, 3.38%. ^{1}H NMR (DMSO-d_6, 300 MHz, 298 K): δ 7.64 (d, $^3J_{H-H}$ = 2.1 Hz, 2H, 4-Im), 7.57 (d, $^3J_{H-H}$ = 2.0 Hz, 2H, 5-Im), 7.18 (m, 16H, BPh_4-*o*-Ph), 6.92 (t, $^3J_{H-H}$ = 7.4 Hz, 16H, BPh_4-*m*-Ph), 6.78 (t, $^3J_{H-H}$ = 7.1 Hz, 8H, BPh_4-*p*-Ph), 6.14 (d, $^2J_{H-H}$ = 13.2 Hz, 1H, N−CH_2), 5.30 (d, $^2J_{H-H}$ = 13.1 Hz, 1H, N−CH_2), 4.79 (sep, $^3J_{H-H}$ = 6.6 Hz, 2H, *i*Pr-CH), 1.94 (s, 15H, Cp*-Me), 1.85 (s, 15H, Cp*-Me), 1.68 (d, $^3J_{H-H}$ = 6.7 Hz, 6H, *i*Pr-Me), 1.17 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, *i*Pr-Me). ^{13}C NMR (DMSO-d_6, 75 MHz, 298 K): δ 163.4 (q, $^1J_{C-B}$ = 49.4 Hz, C−B), 151.3 (2-Im), 135.6 (q, $^2J_{C-B}$ = 1.1 Hz, *o*-Ph), 125.4 (q, $^3J_{C-B}$ = 2.6 Hz, *m*-Ph), 122.1 (4-Im), 121.6 (*p*-Ph), 117.8 (5-Im), 102.4 (d, $^1J_{C-Rh}$ = 7.4 Hz, Cp*-ring), 102.0 (d, $^1J_{C-Rh}$ = 7.2 Hz, Cp*-ring), 62.3 (N-$\underline{C}H_2$), 52.6 (*i*Pr-$\underline{C}$H), 23.0 (*i*Pr-Me), 22.8 (*i*Pr-Me), 10.5 (Cp*-Me).

[(RhCp)$_2${Pt(bisNHC-C2-iPr)}(μ_3-S)$_2$](BPh$_4$)$_2$*, ***3-C2-iPr***. Complex **3-C2-*i*Pr** was prepared analogously to **3-C1-Me**. Addition of diethyl ether into a solution of the crude product in a mixture of DMSO and acetonitrile afforded microcrystals of the complex. Yield: 86%. Anal. Calcd for $C_{82}H_{92}B_2N_4PtRh_2S_2\cdot$DMSO$\cdot 1/2CH_3CN$: C, 59.39; H, 5.83; N, 3.67. Found: C, 59.55; H, 5.77; N, 3.63%. ^{1}H NMR (DMSO-d_6, 300 MHz, 298 K): δ 7.60 (d, $^3J_{H-H}$ = 2.1 Hz, 2H, 4-Im), 7.43 (d, $^3J_{H-H}$ = 2.0 Hz, 2H, 5-Im), 7.19 (m, 16H, BPh_4-*o*-Ph), 6.93 (t, $^3J_{H-H}$ = 7.4 Hz, 16H, BPh_4-*m*-Ph), 6.79 (t, $^3J_{H-H}$ = 7.2 Hz, 8H, BPh_4-*p*-Ph), 4.70−4.25 (6H, N−CH_2, *i*Pr-CH), 1.92 (s, 15H, Cp*-Me), 1.89 (s, 15H, Cp*-Me), 1.58 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, *i*Pr-Me), 1.14 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, *i*Pr-Me). ^{13}C NMR (DMSO-d_6, 75 MHz, 298 K): δ 163.4 (q, $^1J_{C-B}$ = 49.4 Hz, C−B), 148.3 (2-Im), 135.6 (q, $^2J_{C-B}$ = 1.3 Hz, *o*-Ph), 125.3 (q, $^3J_{C-B}$ = 2.8 Hz, *m*-Ph), 124.2 (4-Im), 121.6 (*p*-Ph), 118.1 (5-Im), 102.1 (d, $^1J_{C-Rh}$ = 7.4 Hz, Cp*-ring), 101.8 (d, $^1J_{C-Rh}$ = 7.2 Hz, Cp*-ring), 52.5 (*i*Pr-$\underline{C}$H), 47.0 (N-$\underline{C}H_2$), 22.8 (*i*Pr-Me), 22.7 (*i*Pr-Me), 10.6 (Cp*-Me), 10.5 (Cp*-Me).

[(RhCp)$_2${Pt(bisNHC-C3-iPr)}(μ_3-S)$_2$](BPh$_4$)$_2$*, ***3-C3-iPr***. Complex **3-C3-*i*Pr** was prepared analogously to **3-C1-Me**. Addition of diethyl ether into a solution of the crude product in a mixture of dichloromethane and acetonitrile afforded microcrystals of the complex. Yield: 77%. Anal. Calcd for $C_{83}H_{94}B_2N_4PtRh_2S_2\cdot 5/2CH_2Cl_2\cdot 1/2CH_3CN$: C, 55.64; H, 5.43; N, 3.38. Found: C, 55.48; H, 5.56; N, 3.56%. ^{1}H NMR (DMSO-d_6, 300 MHz, 298 K): δ 7.53 (d, $^3J_{H-H}$ = 2.1 Hz, 2H, 4-Im), 7.41 (d, $^3J_{H-H}$ = 2.0 Hz, 2H, 5-Im), 7.18 (m, 16H, BPh_4-*o*-Ph), 6.93 (t, $^3J_{H-H}$ = 7.4 Hz, 16H, BPh_4-*m*-Ph), 6.79 (t, $^3J_{H-H}$ = 7.1 Hz, 8H, BPh_4-*p*-Ph), 4.45−4.05 (m, 4H, N−CH_2, *i*Pr-CH), 4.00−3.95 (m, 2H, N−CH_2), 1.915 (s, 15H, Cp*-Me), 1.910 (s, 15H, Cp*-Me), 1.46 (d, $^3J_{H-H}$ = 6.7 Hz, 6H, *i*Pr-Me), 1.29 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, *i*Pr-Me), 1.6−1.2 (m, 2H, 2-$(CH_2)_3$). ^{13}C NMR (DMSO-d_6, 75 MHz, 298 K): δ 163.4 (q, $^1J_{C-B}$ = 49.4 Hz, C−B), 150.2 (2-Im), 135.6 (q, $^2J_{C-B}$ = 1.3 Hz, *o*-Ph), 125.3 (q, $^3J_{C-B}$ = 2.7 Hz, *m*-Ph), 124.3 (4-Im), 121.5 (*p*-Ph), 117.9 (5-Im), 102.1 (d, $^1J_{C-Rh}$ = 7.1 Hz, Cp*-ring), 102.0 (d, $^1J_{C-Rh}$ = 6.7 Hz, Cp*-ring), 52.1 (*i*Pr-$\underline{C}$H), 51.6 (N-$\underline{C}H_2$), 24.4 (*i*Pr-Me), 21.6 (*i*Pr-Me), 10.7 (Cp*-Me), 10.5 (Cp*-Me), 9.0 (2-$(CH_2)_3$).

[(RhCp)$_2${Pt(bisNHC-C1-Bn)}(μ_3-S)$_2$](BPh$_4$)$_2$*, ***3-C1-Bn***. Complex **3-C1-Bn** was prepared analogously to **3-C1-Me**. Addition of diethyl ether into a solution of the crude product in a mixture of dichloromethane and acetonitrile afforded microcrystals of the complex. Yield: 12%. Single crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a solution of the complex in dichloromethane. Anal. Calcd for $C_{89}H_{90}B_2N_4PtRh_2S_2\cdot CH_2Cl_2\cdot CH_3CN$: C, 60.44; H, 5.24; N, 3.83. Found: C, 60.11; H, 5.28; N, 4.09%. ^{1}H NMR (DMSO-d_6, 300 MHz, 298 K): δ 7.62 (d, $^3J_{H-H}$ = 2.1 Hz, 2H, 4-Im), 7.40−7.30 (m, 8H, Bn-Ph, 5-Im), 7.17 (m, 16H, BPh_4-*o*-Ph), 7.07 (m, 4H, Bn-Ph), 6.92 (t, $^3J_{H-H}$ = 7.4 Hz, 16H, BPh_4-*m*-Ph), 6.78 (t, $^3J_{H-H}$ = 7.1 Hz, 8H, BPh_4-*p*-Ph), 6.31 (d, $^2J_{H-H}$ = 13.5 Hz, 1H, N−CH_2), 5.76 (d, $^2J_{H-H}$ = 15.7 Hz, 2H, Bn-CH_2), 5.46 (d, $^2J_{H-H}$ = 13.3 Hz, 1H, N−CH_2), 5.34 (d, $^2J_{H-H}$ = 15.4 Hz, 2H, Bn-CH_2), 1.87 (s, 15H, Cp*-Me), 1.64 (s, 15H, Cp*-Me). ^{13}C NMR (DMSO-d_6, 75 MHz, 298 K): δ 163.4 (q, $^1J_{C-B}$ = 49.3 Hz, C−B), 159.6 (2-Im), 136.4 (Bn-1-Ph), 135.5 (q, $^2J_{C-B}$ = 1.3 Hz, BPh_4-*o*-Ph), 128.9 (Bn-3-Ph), 128.1 (Bn-4-Ph), 126.6 (Bn-2-Ph), 125.3 (q, $^3J_{C-B}$ = 2.7 Hz, BPh_4-*m*-Ph), 122.42 (4-Im), 122.36 (5-Im), 121.5 (BPh_4-*p*-Ph), 102.5 (d, $^1J_{C-Rh}$ = 7.4 Hz, Cp*-ring), 102.1 (d, $^1J_{C-Rh}$ = 7.2 Hz, Cp*-ring), 62.6 (N-$\underline{C}H_2$), 52.9 (Bn-$\underline{C}H_2$), 40.0 (N-Me), 10.5 (Cp*-Me), 10.2 (Cp*-Me).

[(RhCp)$_2${Pt(bisNHC-C2-Bn)}(μ_3-S)$_2$](BPh$_4$)$_2$*, ***3-C2-Bn***. Complex **3-C2-Bn** was prepared analogously to **3-C1-Me**. Addition of diethyl ether into a solution of the crude product in dichloromethane afforded microcrystals of the complex. Yield: 38%. Anal. Calcd for $C_{90}H_{92}B_2N_4PtRh_2S_2\cdot CH_2Cl_2$: C, 60.68; H, 5.26; N, 3.11. Found: C, 60.67; H, 5.35; N, 3.43%. ^{1}H NMR (DMSO-d_6, 300 MHz, 298 K): δ 7.52 (d, $^3J_{H-H}$ = 2.1 Hz, 2H, 4-Im), 7.42 (m, 6H, Bn-Ph), 7.23 (d, $^3J_{H-H}$ = 2.0 Hz, 2H, 5-Im), 7.18 (m, 16H, BPh_4-*o*-Ph), 7.08 (m, 4H, Bn-Ph), 6.92 (t, $^3J_{H-H}$ = 7.4 Hz, 16H, BPh_4-*m*-Ph), 6.78 (t, $^3J_{H-H}$ = 7.1 Hz, 8H, BPh_4-*p*-Ph), 5.18 (d, $^2J_{H-H}$ = 15.3 Hz, 2H, Bn-CH_2), 5.03 (d, $^2J_{H-H}$ = 15.3 Hz, 2H, Bn-CH_2), 4.75−4.65 (m, 2H, N−CH_2), 4.60−4.47 (m, 2H, N−CH_2), 1.93 (s, 15H, Cp*-Me), 1.62 (s, 15H, Cp*-Me). ^{13}C NMR (DMSO-d_6, 75 MHz, 298 K): δ 163.4 (q, $^1J_{C-B}$ = 49.4 Hz, C−B), 149.7 (2-Im), 135.7 (Bn-1-Ph), 135.5 (q, $^2J_{C-B}$ = 1.3 Hz, BPh_4-*o*-Ph), 128.9 (Bn-3-Ph), 128.3 (Bn-4-Ph), 127.1 (Bn-2-Ph), 125.3 (q, $^3J_{C-B}$ = 2.7 Hz, BPh_4-*m*-Ph), 124.4 (4-Im), 121.6 (5-Im), 121.5 (BPh_4-*p*-Ph), 102.2 (d, $^1J_{C-Rh}$ = 7.4 Hz, Cp*-ring), 101.8 (d, $^1J_{C-Rh}$ = 7.2 Hz, Cp*-ring), 53.2 (Bn-$\underline{C}H_2$), 47.3 (N-$\underline{C}H_2$), 10.6 (Cp*-Me), 10.2 (Cp*-Me).

[(RhCp)$_2${Pt(bisNHC-C3-Bn)}(μ_3-S)$_2$](BPh$_4$)$_2$*, ***3-C3-Bn***. Complex **3-C3-Bn** was prepared analogously to **3-C1-Me**. Addition of diethyl

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ether into a solution of the crude product in dichloromethane afforded microcrystals of the complex. Yield: 58%. Anal. Calcd for $C_{91}H_{94}B_2N_4PtRh_2S_2\cdot 1/2CH_2Cl_2$: C, 61.99; H, 5.40; N, 3.16. Found: C, 61.89; H, 5.43; N, 3.29%. ^{1}H NMR (DMSO-d_6, 300 MHz, 298 K): δ 7.50−7.30 (m, 8H, 4-Im, Bn-Ph), 7.18 (m, 16H, BPh_4-*o*-Ph), 7.14 (d, $^3J_{H-H}$ = 2.1 Hz, 2H, 5-Im), 7.07 (m, 4H, Bn-Ph), 6.92 (t, $^3J_{H-H}$ = 7.4 Hz, 16H, BPh_4-*m*-Ph), 6.78 (t, $^3J_{H-H}$ = 7.2 Hz, 8H, BPh_4-*p*-Ph), 5.17 (d, $^2J_{H-H}$ = 15.2 Hz, 2H, Bn-CH_2), 4.68 (d, $^2J_{H-H}$ = 15.3 Hz, 2H, Bn-CH_2), 4.33 (d, $^2J_{H-H}$ = 14.3 Hz, $^3J_{H-H}$ = 5.4 Hz, 2H, N−CH_2), 4.05 (d, $^2J_{H-H}$ = 15.3 Hz, $^3J_{H-H}$ = 11.5 Hz, 2H, N−CH_2), 1.96 (s, 15H, Cp*-Me), 1.53 (s, 15H, Cp*-Me), 1.50 (m, 1H, 2-$(CH_2)_3$), 1.43 (m, 1H, 2-$(CH_2)_3$). ^{13}C NMR (DMSO-d_6, 75 MHz, 298 K): δ 163.4 (q, $^1J_{C-B}$ = 49.3 Hz, C−B), 152.6 (2-Im), 135.7 (Bn-1-Ph), 135.6 (q, $^2J_{C-B}$ = 1.3 Hz, BPh_4-*o*-Ph), 129.0 (Bn-3-Ph), 128.3 (Bn-4-Ph), 126.9 (Bn-2-Ph), 125.3 (q, $^3J_{C-B}$ = 2.7 Hz, BPh_4-*m*-Ph), 124.2 (4-Im, 5-Im), 121.5 (BPh_4-*p*-Ph), 102.2 (d, $^1J_{C-Rh}$ = 7.1 Hz, Cp*-ring), 101.8 (d, $^1J_{C-Rh}$ = 7.1 Hz, Cp*-ring), 52.8 (Bn-$\underline{C}H_2$), 51.6 (N-$\underline{C}H_2$), 10.7 (Cp*-Me), 10.0 (Cp*-Me), 8.8 (2-$(CH_2)_3$).

[(IrCp)$_2${Pt(bisNHC-C1-Me)}(μ_3-S)$_2$](BPh$_4$)$_2$*, **4-C1-Me**. Complex **4-C1-Me** was prepared analogously to **3-C1-Me**. Addition of diethyl ether into a solution of the crude product in dichloromethane afforded microcrystals of the complex. Yield: 66%. Single crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a solution of the complex in dichloromethane. Anal. Calcd for $C_{77}H_{82}B_2Ir_2N_4PtS_2\cdot 0.8CH_2Cl_2$: C, 52.01; H, 4.69; N, 3.12. Found: C, 51.96; H, 4.77; N, 3.40%. ^{1}H NMR (DMSO-d_6, 300 MHz, 298 K): δ 7.53 (d, $^3J_{H-H}$ = 2.0 Hz, 2H, 4-Im), 7.40 (d, $^3J_{H-H}$ = 2.0 Hz, 2H, 5-Im), 7.19 (m, 16H, BPh_4-*o*-Ph), 6.93 (t, $^3J_{H-H}$ = 7.3 Hz, 16H, BPh_4-*m*-Ph), 6.79 (t, $^3J_{H-H}$ = 7.1 Hz, 8H, BPh_4-*p*-Ph), 6.18 (d, $^2J_{H-H}$ = 13.1 Hz, 1H, N−CH_2), 5.37 (d, $^2J_{H-H}$ = 13.1 Hz, 1H, N−CH_2), 3.72 (s, 6H, N-Me), 2.08 (s, 15H, Cp*-Me), 1.98 (s, 15H, Cp*-Me). ^{13}C NMR (DMSO-d_6, 75 MHz, 298 K): δ 163.4 (q, $^1J_{C-B}$ = 49.3 Hz, C−B), 149.7 (2-Im), 135.6 (q, $^2J_{C-B}$ = 1.0 Hz, *o*-Ph), 125.3 (q, $^3J_{C-B}$ = 2.7 Hz, *m*-Ph), 122.8 (4-Im), 121.6 (*p*-Ph), 121.1 (5-Im), 96.20 (Cp*-ring), 96.17 (Cp*-ring), 62.2 (N-$\underline{C}H_2$), 38.1 (N-Me), 10.5 (Cp*-Me), 10.3 (Cp*-Me).

[(IrCp)$_2${Pt(bisNHC-C2-Me)}(μ_3-S)$_2$](BPh$_4$)$_2$*, **4-C2-Me**. Complex **4-C2-Me** was prepared analogously to **3-C1-Me**. Addition of diethyl ether into a solution of the crude product in a mixture of dichloromethane and acetonitrile afforded microcrystals of the complex. Yield: 31%. Single crystals suitable for X-ray analysis were obtained from a solution of the complex in dichloromethane by slow diffusion of diethyl ether. Anal. Calcd for $C_{78}H_{84}B_2Ir_2N_4PtS_2\cdot H_2O$: C, 53.20; H, 4.92; N, 3.18. Found: C, 53.21; H, 5.00; N, 3.22%. ^{1}H NMR (CD_3CN, 300 MHz, 298 K): δ 7.27 (m, 16H, *o*-Ph), 7.05 (d, $^3J_{H-H}$ = 2.0 Hz, 2H, 4-Im), 7.04 (d, $^3J_{H-H}$ = 2.0 Hz, 2H, 5-Im), 6.99 (dd, $^3J_{H-H}$ ≈ 7.4 Hz, $^3J_{H-H}$ ≈ 7.4 Hz, 16H, *m*-Ph), 6.84 (tt, $^3J_{H-H}$ = 7.2 Hz, $^4J_{H-H}$ = 1.3 Hz, 8H, *p*-Ph), 4.57(m, 2H, CH_2), 4.27 (m, 2H, CH_2), 3.53 (m, $^4J_{H-Pt}$ = 2.9 Hz, 6H, Me), 2.05 (s, 15H, Cp*), 2.02 (s, 15H, Cp*). ^{13}C NMR (CD_3CN, 75 MHz, 298 K): δ 164.7 (q, $^1J_{C-B}$ = 49.4 Hz, *C*-B), 148.9 (2-Im), 136.7 (q, $^2J_{C-B}$ = 1.4 Hz, *o*-Ph), 126.5 (q, $^3J_{C-B}$ = 2.8 Hz, *m*-Ph), 123.7 (s, 4-Im), 123.6 (s, 5-Im), 122.7 (s, *p*-Ph), 97.2 (s, Cp*-ring), 97.1 (s, Cp*-ring), 48.4 (s, $^3J_{C-Pt}$ = 8.4 Hz, CH_2), 39.7 (s, Me), 11.05 (s, Cp*-Me), 10.99 (s, Cp*-Me). ^{1}H NMR (DMSO-d_6, 300 MHz, 298 K): δ 7.29 (m, 4H, 4-Im, 5-Im), 7.18 (m, 16H, BPh_4-*o*-Ph), 6.92 (t, $^3J_{H-H}$ = 7.4 Hz, 16H, BPh_4-*m*-Ph), 6.79 (t, $^3J_{H-H}$ = 7.2 Hz, 8H, BPh_4-*p*-Ph), 4.70−4.30 (m, 4H, N−CH_2), 3.54 (s, 6H, N-Me), 2.06 (s, 15H, Cp*-Me), 2.03 (s, 15H, Cp*-Me). ^{13}C NMR (DMSO-d_6, 75 MHz, 298 K): δ 163.4 (q, $^1J_{C-B}$ = 49.4 Hz, C−B), 146.6 (2-Im), 135.5 (q, $^2J_{C-B}$ = 1.3 Hz, *o*-Ph), 125.3 (q, $^3J_{C-B}$ = 2.7 Hz, *m*-Ph), 123.2 (4-Im), 123.0 (5-Im), 121.5 (*p*-Ph), 95.84 (Cp*-ring), 95.81 (Cp*-ring), 47.3 (N-$\underline{C}H_2$), 38.5 (N-Me), 10.40 (Cp*-Me), 10.38 (Cp*-Me).

[(IrCp)$_2${Pt(bisNHC-C3-Me)}(μ_3-S)$_2$](BPh$_4$)$_2$*, **4-C3-Me**. Complex **4-C3-Me** was prepared analogously to **3-C1-Me**. Addition of diethyl ether into a solution of the crude product in a mixture of dichloromethane and acetonitrile afforded microcrystals of the complex. Yield: 70%. Anal. Calcd for $C_{79}H_{86}B_2Ir_2N_4PtS_2\cdot H_2O$: C, 53.46; H, 5.00; N, 3.16. Found: C, 53.67; H, 4.96; N, 3.27%. ^{1}H NMR (DMSO-d_6, 300 MHz, 298 K): δ 7.39 (d, $^3J_{H-H}$ = 1.9 Hz, 2H, 4-Im), 7.37 (d, $^3J_{H-H}$ = 1.9 Hz, 2H, 5-Im), 7.18 (m, 16H, BPh_4-*o*-Ph), 6.92 (t, $^3J_{H-H}$ = 7.4 Hz, 16H, BPh_4-*m*-Ph), 6.79 (t, $^3J_{H-H}$ = 7.2 Hz, 8H, BPh_4-*p*-Ph), 4.45−3.60 (m, 4H, N−CH_2), 3.47 (s, 6H, N-Me), 2.07 (s, 15H, Cp*-Me), 2.05 (s, 15H, Cp*-Me), 1.7−1.3 (m, 2H, 2-$(CH_2)_3$). ^{13}C NMR (DMSO-d_6, 75 MHz, 298 K): δ 163.4 (q, $^1J_{C-B}$ = 49.3 Hz, C−B), 148.6 (2-Im), 135.5 (q, $^2J_{C-B}$ = 1.1 Hz, *o*-Ph), 125.3 (q, $^3J_{C-B}$ = 2.7 Hz, *m*-Ph), 123.0 (4,5-Im), 121.5 (*p*-Ph), 95.73 (Cp*-ring), 95.71 (Cp*-ring), 51.6 (N-$\underline{C}H_2$), 38.1 (N-Me), 10.5 (Cp*-Me), 10.3 (Cp*-Me), 8.9 (2-$(CH_2)_3$).

[(IrCp)$_2${Pt(bisNHC-C1-iPr)}(μ_3-S)$_2$](BPh$_4$)$_2$*, **4-C1-iPr**. Complex **4-C1-*i*Pr** was prepared analogously to **3-C1-Me**. Addition of diethyl ether into a solution of the crude product in a mixture of DMSO and acetonitrile afforded microcrystals of the complex. Yield: 67%. Single crystals suitable for X-ray analysis were obtained from a solution of the complex in dichloromethane by slow diffusion of diethyl ether. Anal. Calcd for $C_{81}H_{90}B_2Ir_2N_4PtS_2\cdot$DMSO: C, 53.51; H, 5.19; N, 3.01. Found: C, 53.71; H, 5.15; N, 3.15%. ^{1}H NMR (DMSO-d_6, 300 MHz, 298 K): δ 7.66 (d, $^3J_{H-H}$ = 2.0 Hz, 2H, 4-Im), 7.59 (d, $^3J_{H-H}$ = 1.9 Hz, 2H, 5-Im), 7.19 (m, 16H, BPh_4-*o*-Ph), 6.93 (t, $^3J_{H-H}$ = 7.4 Hz, 16H, BPh_4-*m*-Ph), 6.79 (t, $^3J_{H-H}$ = 7.1 Hz, 8H, BPh_4-*p*-Ph), 6.16 (d, $^2J_{H-H}$ = 13.3 Hz, 1H, N−CH_2), 5.32 (d, $^2J_{H-H}$ = 13.2 Hz, 1H, N−CH_2), 4.63 (sep, $^3J_{H-H}$ = 6.6 Hz, 2H, *i*Pr-CH), 2.07 (s, 15H, Cp*-Me), 1.99 (s, 15H, Cp*-Me), 1.69 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, *i*Pr-Me), 1.19 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, *i*Pr-Me). ^{13}C NMR (DMSO-d_6, 75 MHz, 298 K): δ 163.4 (q, $^1J_{C-B}$ = 49.3 Hz, C−B), 148.4 (2-Im), 135.5 (q, $^2J_{C-B}$ = 1.3 Hz, *o*-Ph), 125.3 (q, $^3J_{C-B}$ = 2.8 Hz, *m*-Ph), 122.3 (4-Im), 121.5 (*p*-Ph), 117.8 (5-Im), 96.4 (Cp*-ring), 96.0 (Cp*-ring), 62.3 (N-$\underline{C}H_2$), 53.1 (*i*Pr-$\underline{C}$H), 23.0 (*i*Pr-Me), 22.8 (*i*Pr-Me), 10.32 (Cp*-Me), 10.30 (Cp*-Me).

[(IrCp)$_2${Pt(bisNHC-C2-iPr)}(μ_3-S)$_2$](BPh$_4$)$_2$*, **4-C2-iPr**. Complex **4-C2-*i*Pr** was prepared analogously to **3-C1-Me**. Addition of diethyl ether into a solution of the crude product in a mixture of chloroform and acetonitrile afforded microcrystals of the complex. Yield: 74%. Anal. Calcd for $C_{82}H_{92}B_2Ir_2N_4PtS_2\cdot 2.5CHCl_3\cdot 2CH_3CN$: C, 48.77; H, 4.65; N, 3.86. Found: C, 48.58; H, 4.89; N, 3.85%. ^{1}H NMR (DMSO-d_6, 300 MHz, 298 K): δ 7.64 (d, $^3J_{H-H}$ = 2.1 Hz, 2H, 4-Im), 7.46 (d, $^3J_{H-H}$ = 2.0 Hz, 2H, 5-Im), 7.18 (m, 16H, BPh_4-*o*-Ph), 6.92 (t, $^3J_{H-H}$ = 7.4 Hz, 16H, BPh_4-*m*-Ph), 6.79 (t, $^3J_{H-H}$ = 7.2 Hz, 8H, BPh_4-*p*-Ph), 4.65−4.30 (6H, N−CH_2, *i*Pr-CH), 2.06 (s, 15H, Cp*-Me), 2.04 (s, 15H, Cp*-Me), 1.57 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, *i*Pr-Me), 1.15 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, *i*Pr-Me). ^{13}C NMR (DMSO-d_6, 75 MHz, 298 K): δ 163.4 (q, $^1J_{C-B}$ = 49.3 Hz, C−B), 145.1 (2-Im), 135.5 (q, $^2J_{C-B}$ = 1.3 Hz, *o*-Ph), 125.3 (q, $^3J_{C-B}$ = 2.7 Hz, *m*-Ph), 124.3 (4-Im), 121.5 (*p*-Ph), 118.1 (5-Im), 96.0 (Cp*-ring), 95.8 (Cp*-ring), 52.9 (*i*Pr-$\underline{C}$H), 47.1 (N-$\underline{C}H_2$), 22.73 (*i*Pr-Me), 22.70 (*i*Pr-Me), 10.42 (Cp*-Me), 10.36 (Cp*-Me).

[(IrCp)$_2${Pt(bisNHC-C3-iPr)}(μ_3-S)$_2$](BPh$_4$)$_2$*, **4-C3-iPr**. Complex **4-C3-*i*Pr** was prepared analogously to **3-C1-Me**. Addition of diethyl ether into a solution of the crude product in a mixture of dichloromethane and acetonitrile afforded microcrystals of the complex. Yield: 74%. Anal. Calcd for $C_{83}H_{94}B_2Ir_2N_4PtS_2\cdot CH_2Cl_2\cdot 1/2CH_3CN$: C, 53.22; H, 5.12; N, 3.29. Found: C, 53.27; H, 5.21; N, 3.22%. ^{1}H NMR (DMSO-d_6, 300 MHz, 298 K): δ 7.56 (d, $^3J_{H-H}$ = 2.0 Hz, 2H, 4-Im), 7.43 (d, $^3J_{H-H}$ = 2.0 Hz, 2H, 5-Im), 7.19 (m, 16H, BPh_4-*o*-Ph), 6.93 (t, $^3J_{H-H}$ = 7.4 Hz, 16H, BPh_4-*m*-Ph), 6.79 (t, $^3J_{H-H}$ = 7.1 Hz, 8H, BPh_4-*p*-Ph), 4.32−4.14 (m, 4H, N−CH_2, *i*Pr-CH), 3.95−3.80 (m, 2H, N−CH_2), 2.054 (s, 15H, Cp*-Me), 2.047 (s, 15H, Cp*-Me), 1.44 (d, $^3J_{H-H}$ = 6.4 Hz, 6H, *i*Pr-Me), 1.31 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, *i*Pr-Me), 1.6−1.3 (m, 2H, 2-$(CH_2)_3$). ^{13}C NMR (DMSO-d_6, 75 MHz, 298 K): δ 163.4 (q, $^1J_{C-B}$ = 49.4 Hz, C−B), 146.9 (2-Im), 135.5 (q, $^2J_{C-B}$ = 1.1 Hz, *o*-Ph), 125.3 (q, $^3J_{C-B}$ = 2.8 Hz, *m*-Ph), 124.4 (4-Im), 121.5 (*p*-Ph), 118.0 (5-Im), 96.0 (Cp*-ring), 52.4 (*i*Pr-$\underline{C}$H), 51.8 (N-$\underline{C}H_2$), 24.3 (*i*Pr-Me), 21.6 (*i*Pr-Me), 10.5 (Cp*-Me), 10.4 (Cp*-Me), 8.5 (2-$(CH_2)_3$).

[(IrCp)$_2${Pt(bisNHC-C1-Bn)}(μ_3-S)$_2$](BPh$_4$)$_2$*, **4-C1-Bn**. Complex **4-C1-Bn** was prepared analogously to **3-C1-Me**. Addition of diethyl ether into a solution of the crude product in a mixture of dichloromethane and acetonitrile afforded microcrystals of the complex. Yield: 35%. Anal. Calcd for $C_{89}H_{90}B_2Ir_2N_4PtS_2\cdot 3/2CH_2Cl_2\cdot 2CH_3CN$: C, 54.29; H, 4.77; N, 4.02. Found: C, 54.21; H, 4.68; N, 4.12%. ^{1}H NMR (DMSO-d_6, 300 MHz, 298 K): δ 7.65 (d, $^3J_{H-H}$ = 2.0

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Hz, 2H, 4-Im), 7.39 (d, $^3J_{H-H}$ = 2.0 Hz, 2H, 5-Im), 7.17 (m, 16H, BPh_4-*o*-Ph), 7.07 (m, 4H, Bn-Ph), 6.92 (t, $^3J_{H-H}$ = 7.4 Hz, 16H, BPh_4-*m*-Ph), 6.78 (t, $^3J_{H-H}$ = 7.2 Hz, 8H, BPh_4-*p*-Ph), 6.33 (d, $^2J_{H-H}$ = 13.3 Hz, 1H, N−CH_2), 5.61 (d, $^2J_{H-H}$ = 15.3 Hz, 2H, Bn-CH_2), 5.47 (d, $^2J_{H-H}$ = 13.1 Hz, 1H, N−CH_2), 5.32 (d, $^2J_{H-H}$ = 15.6 Hz, 2H, Bn-CH_2), 2.01 (s, 15H, Cp*-Me), 1.80 (s, 15H, Cp*-Me). ^{13}C NMR (DMSO-d_6, 75 MHz, 298 K): δ 163.4 (q, $^1J_{C-B}$ = 49.2 Hz, C−B), 150.3 (2-Im), 136.3 (Bn-1-Ph), 135.5 (q, $^2J_{C-B}$ = 1.3 Hz, BPh_4-*o*-Ph), 128.9 (Bn-3-Ph), 128.2 (Bn-4-Ph), 126.7 (Bn-2-Ph), 125.3 (q, $^3J_{C-B}$ = 2.8 Hz, BPh_4-*m*-Ph), 122.6 (4-Im, 5-Im), 121.5 (BPh_4-*p*-Ph), 96.4 (Cp*-ring), 96.1 (Cp*-ring), 62.1 (N-$\underline{C}H_2$), 53.3 (Bn-$\underline{C}H_2$), 10.3 (Cp*-Me), 10.1 (Cp*-Me).

[(IrCp)$_2${Pt(bisNHC-C2-Bn)}(μ_3-S)$_2$](BPh$_4$)$_2$*, **4-C2-Bn**. Complex **4-C2-Bn** was prepared analogously to **3-C1-Me**. Addition of diethyl ether into a solution of the crude product in dichloromethane afforded microcrystals of the complex. Yield: 47%. Anal. Calcd for $C_{90}H_{92}B_2Ir_2N_4PtS_2{\cdot}CH_2Cl_2$: C, 55.20; H, 4.79; N, 2.83. Found: C, 55.17; H, 4.86; N, 2.98%. ^{1}H NMR (DMSO-d_6, 300 MHz, 298 K): δ 7.55 (d, $^3J_{H-H}$ = 2.1 Hz, 2H, 4-Im), 7.37 (m, 6H, Bn-Ph), 7.27 (d, $^3J_{H-H}$ = 2.1 Hz, 2H, 5-Im), 7.17 (m, 16H, BPh_4-*o*-Ph), 7.07 (m, 4H, Bn-Ph), 6.92 (t, $^3J_{H-H}$ = 7.4 Hz, 16H, BPh_4-*m*-Ph), 6.78 (t, $^3J_{H-H}$ = 7.1 Hz, 8H, BPh_4-*p*-Ph), 5.12 (d, $^2J_{H-H}$ = 15.0 Hz, 2H, Bn-CH_2), 4.99 (d, $^2J_{H-H}$ = 15.2 Hz, 2H, Bn-CH_2), 4.80−4.63 (m, 2H, N−CH_2), 4.63−4.45 (m, 2H, N−CH_2), 2.07 (s, 15H, Cp*-Me), 1.75 (s, 15H, Cp*-Me). ^{13}C NMR (DMSO-d_6, 75 MHz, 298 K): δ 163.4 (q, $^1J_{C-B}$ = 49.3 Hz, C−B), 147.5 (2-Im), 135.7 (Bn-1-Ph), 135.5 (q, $^2J_{C-B}$ = 1.3 Hz, BPh_4-*o*-Ph), 129.0 (Bn-3-Ph), 128.3 (Bn-4-Ph), 127.1 (Bn-2-Ph), 125.3 (q, $^3J_{C-B}$ = 2.8 Hz, BPh_4-*m*-Ph), 124.5 (4-Im), 121.7 (5-Im), 121.5 (BPh_4-*p*-Ph), 96.2 (Cp*-ring), 95.8 (Cp*-ring), 53.5 (Bn-$\underline{C}H_2$), 47.5 (N-$\underline{C}H_2$), 10.4 (Cp*-Me), 10.0 (Cp*-Me).

[(IrCp)$_2${Pt(bisNHC-C3-Bn)}(μ_3-S)$_2$](BPh$_4$)$_2$*, **4-C3-Bn**. Complex **4-C3-Bn** was prepared analogously to **3-C1-Me**. Addition of diethyl ether into a solution of the crude product in a mixture of dichloromethane and acetonitrile afforded microcrystals of the complex. Yield: 56%. Anal. Calcd for $C_{91}H_{94}B_2Ir_2N_4PtS_2{\cdot}2/3CH_2Cl_2{\cdot}1/3CH_3CN$: C, 56.03; H, 4.91; N, 3.07. Found: C, 56.02; H, 4.94; N, 3.26%. ^{1}H NMR (DMSO-d_6, 300 MHz, 298 K): δ 7.52 (d, $^3J_{H-H}$ = 2.0 Hz, 2H, 4-Im), 7.51−7.32 (m, 6H, Bn-Ph), 7.22−7.13 (m, 18H, BPh_4-*o*-Ph, 5-Im), 7.02 (m, 4H, Bn-Ph), 6.92 (t, $^3J_{H-H}$ = 7.4 Hz, 16H, BPh_4-*m*-Ph), 6.78 (t, $^3J_{H-H}$ = 7.1 Hz, 8H, BPh_4-*p*-Ph), 5.13 (d, $^2J_{H-H}$ = 15.2 Hz, 2H, Bn-CH_2), 4.71 (d, $^2J_{H-H}$ = 15.2 Hz, 2H, Bn-CH_2), 4.35 (d, $^2J_{H-H}$ = 13.9 Hz, $^3J_{H-H}$ = 4.9 Hz, 2H, N−CH_2), 4.05 (d, $^2J_{H-H}$ = 13.9 Hz, $^3J_{H-H}$ = 11.7 Hz, 2H, N−CH_2), 2.11 (s, 15H, Cp*-Me), 1.67 (s, 15H, Cp*-Me), 1.50 (m, 2H, 2-$(CH_2)_3$). ^{13}C NMR (DMSO-d_6, 75 MHz, 298 K): δ 163.4 (q, $^1J_{C-B}$ = 49.4 Hz, C−B), 149.5 (2-Im), 135.7 (Bn-1-Ph), 135.6 (q, $^2J_{C-B}$ = 1.3 Hz, BPh_4-*o*-Ph), 129.1 (Bn-3-Ph), 128.4 (Bn-4-Ph), 126.9 (Bn-2-Ph), 125.3 (q, $^3J_{C-B}$ = 2.7 Hz, BPh_4-*m*-Ph), 124.3 (4-Im), 121.6 (5-Im), 121.5 (BPh_4-*p*-Ph), 96.1 (Cp*-ring), 95.7 (Cp*-ring), 53.0 (Bn-$\underline{C}H_2$), 51.8 (N-$\underline{C}H_2$), 10.5 (Cp*-Me), 9.8 (Cp*-Me), 8.4 (2-$(CH_2)_3$).

[(RhCp)$_2${Pd(bisNHC-C1-Me)}(μ_3-S)$_2$](BPh$_4$)$_2$*, **5-C1-Me**. A solution of [Pd(bisNHC-C1-Me)Cl_2] **2-C1-Me** (88.4 mg, 0.25 mmol) in DMSO (2 mL) was added to a green solution of NaSH (30.8 mg, 0.55 mmol) in 4 mL of DMSO. The solution was stirred for 20 min. The solution was added to a solution of [$(RhCp^*)_2(\mu\text{-}OH)_3$]$BPh_4$ (211.6 mg, 0.25 mmol) in 30 mL of methanol. The suspension was stirred for 30 min. A solution of $NaBPh_4$ (855.5 mg, 2.50 mmol) in 30 mL of methanol was slowly added to the suspension. The solid was collected by filtration and washed with methanol. Addition of diethyl ether into a solution of the crude product in a mixture of chloroform and acetonitrile afforded microcrystals of the complex. Yield: 12%. Single crystals suitable for X-ray analysis were obtained from a solution of the complex in chloroform by slow diffusion of diethyl ether. Anal. Calcd for $C_{77}H_{82}B_2N_4PdRh_2S_2{\cdot}3/2CHCl_3{\cdot}1/2CH_3CN$: C, 57.48; H, 5.16; N, 3.79. Found: C, 57.34; H, 5.18; N, 3.72%. ^{1}H NMR (DMSO-d_6, 300 MHz, 293 K): δ 7.54 (d, $^3J_{H-H}$ = 1.9 Hz, 2H, 4-Im), 7.38 (d, $^3J_{H-H}$ = 1.9 Hz, 2H, 5-Im), 7.18 (m, 16H, BPh_4-*o*-Ph), 6.92 (t, $^3J_{H-H}$ = 7.3 Hz, 16H, BPh_4-*m*-Ph), 6.78 (t, $^3J_{H-H}$ = 7.1 Hz, 8H, BPh_4-*p*-Ph), 6.23 (d, $^2J_{H-H}$ = 13.6 Hz, 2H, N−CH_2), 5.46 (d, $^2J_{H-H}$ = 13.2 Hz, 2H, N−CH_2), 3.8 (s, 3H, N-Me), 1.93 (s, 15H, Cp*-Me), 1.83 (s, 15H, Cp*-Me). ^{13}C NMR (DMSO-d_6, 75 MHz, 293 K): δ 163.4 (q, $^1J_{C-B}$ = 49.3 Hz, C−B), 163.6 (2-Im), 135.5 (q, $^2J_{C-B}$ = 1.4 Hz, *o*-Ph), 125.3 (q, $^3J_{C-B}$ = 2.7 Hz, *m*-Ph), 123.3 (4-Im), 121.9 (5-Im), 121.5 (*p*-Ph), 102.4 (d, $^1J_{C-Rh}$ = 5.6 Hz, Cp*-ring), 102.3 (d, $^1J_{C-Rh}$ = 6.1 Hz, Cp*-ring), 62.5 (N−CH_2), 38 (N-Me), 10.59 (Cp*-Me), 10.57 (Cp*-Me).

[(RhCp)$_2${Pd(bisNHC-C2-Me)}(μ_3-S)$_2$](BPh$_4$)$_2$*, **5-C2-Me**. Complex **5-C2-Me** was prepared analogously to **5-C1-Me**. Addition of diethyl ether into a solution of the crude product in dichloromethane afforded microcrystals of the complex. Yield: 13%. Single crystals suitable for X-ray analysis were obtained from a solution of the complex in dichloromethane by slow diffusion of diethyl ether. Anal. Calcd for $C_{78}H_{84}B_2N_4PdRh_2S_2$: C, 63.49; H, 5.74; N, 3.80. Found: C, 63.23; H, 5.79; N, 4.05%. ^{1}H NMR (DMSO-d_6, 300 MHz, 293 K): δ 7.42 (d, $^3J_{H-H}$ = 2 Hz, 2H, 4-Im), 7.41 (d, $^3J_{H-H}$ = 2 Hz, 2H, 5-Im), 7.17 (m, 16H, BPh_4-*o*-Ph), 6.92 (t, $^3J_{H-H}$ = 7.4 Hz, 16H, BPh_4-*m*-Ph), 6.78 (t, $^3J_{H-H}$ = 7.1 Hz, 8H, BPh_4-*p*-Ph), 4.58−4.48 (m, 1H, N−CH_2), 4.43−4.34 (m, 1H, N−CH_2), 3.61 (s, 3H, N-Me), 1.91 (s, 15H, Cp*-Me), 1.87 (s, 15H, Cp*-Me). ^{13}C NMR (DMSO-d_6, 75 MHz, 293 K): δ 163.4 (q, $^1J_{C-B}$ = 49.4 Hz, C−B), 159.8 (2-Im), 135.5 (q, $^2J_{C-B}$ = 1.3 Hz, *o*-Ph), 125.3 (q, $^3J_{C-B}$ = 2.7 Hz, *m*-Ph), 124 (4-Im), 123.5 (5-Im), 121.5 (*p*-Ph), 102.2 (d, $^1J_{C-Rh}$ = 7.1 Hz, Cp*-ring), 102.1 (d, $^1J_{C-Rh}$ = 7.2 Hz, Cp*-ring), 47.1 (N−CH_2), 38.2 (N-Me), 10.7 (Cp*-Me), 10.5 (Cp*-Me).

[(RhCp)$_2${Pd(bisNHC-C3-Me)}(μ_3-S)$_2$](BPh$_4$)$_2$*, **5-C3-Me**. Complex **5-C3-Me** was prepared analogously to **5-C1-Me**. Addition of diethyl ether into a solution of the crude product in dichloromethane afforded microcrystals of the complex. Yield: 14%. Anal. Calcd for $C_{79}H_{86}B_2N_4PdRh_2S_2{\cdot}1/2CH_2Cl_2{\cdot}1/2Et_2O$: C, 62.39; H, 5.91; N, 3.57. Found: C, 62.06; H, 6.06; N, 3.72%. ^{1}H NMR (DMSO-d_6, 300 MHz, 293 K): δ 7.38 (d, $^3J_{H-H}$ = 1.9 Hz, 2H, 4-Im), 7.34 (d, $^3J_{H-H}$ = 1.9 Hz, 2H, 5-Im), 7.17 (m, 16H, BPh_4-*o*-Ph), 6.92 (t, $^3J_{H-H}$ = 7.4 Hz, 16H, BPh_4-*m*-Ph), 6.78 (t, $^3J_{H-H}$ = 7.1 Hz, 8H, BPh_4-*p*-Ph), 4.28 (dd, $^2J_{H-H}$ = 14.2 Hz, $^3J_{H-H}$ = 5.4 Hz, 2H, N−CH_2), 3.87 (dd, $^2J_{H-H}$ = 14 Hz, $^3J_{H-H}$ = 11.2 Hz, 2H, N−CH_2), 3.52 (s, 3H, N-Me), 2.29−2.17 (m, 1H, 2-$(CH_2)_3$), 1.91 (s, 15H, Cp*-Me), 1.9 (s, 15H, Cp*-Me), 1.76−1.55 (m, 1H, 2-$(CH_2)_3$). ^{13}C NMR (DMSO-d_6, 75 MHz, 293 K): δ 163.4 (q, $^1J_{C-B}$ = 49.4 Hz, C−B), 161.9 (2-Im), 135.5 (q, $^2J_{C-B}$ = 1.1 Hz, *o*-Ph), 125.3 (q, $^3J_{C-B}$ = 2.7 Hz, *m*-Ph), 123.8 (4-Im), 123.75 (5-Im), 121.5 (*p*-Ph), 102.2 (d, $^1J_{C-Rh}$ = 5.8 Hz, Cp*-ring), 102.1 (d, $^1J_{C-Rh}$ = 6.9 Hz, Cp*-ring), 64.9 (N−CH_2), 37.9 (N-Me), 15.2 (2-$(CH_2)_3$), 10.7 (Cp*-Me), 10.6 (Cp*-Me).

[(IrCp)$_2${Pd(bisNHC-C1-Me)}(μ_3-S)$_2$](BPh$_4$)$_2$*, **6-C1-Me**. Complex **6-C1-Me** was prepared analogously to **5-C1-Me**. Addition of diethyl ether into a solution of the crude product in a mixture of chloroform, dichloromethane, and acetonitrile afforded microcrystals of the complex. Yield: 26%. Single crystals suitable for X-ray analysis were obtained from a solution of the complex in chloroform and dichloromethane by slow diffusion of diethyl ether. Anal. Calcd for $C_{77}H_{82}B_2Ir_2N_4PdS_2{\cdot}CHCl_3{\cdot}CH_2Cl_2{\cdot}1/2\ CH_3CN$: C, 51.52; H, 4.68; N, 3.38. Found: C, 51.26; H, 4.63; N, 3.37%. ^{1}H NMR (DMSO-d_6, 300 MHz, 293 K): δ 7.58 (d, $^3J_{H-H}$ = 1.8 Hz, 2H, 4-Im), 7.43 (d, $^3J_{H-H}$ = 1.8 Hz, 2H, 5-Im), 7.18 (m, 16H, BPh_4-*o*-Ph), 6.92 (t, $^3J_{H-H}$ = 7.4 Hz, 16H, BPh_4-*m*-Ph), 6.78 (t, $^3J_{H-H}$ = 7.2 Hz, 8H, BPh_4-*p*-Ph), 6.26 (d, $^2J_{H-H}$ = 13.2 Hz, 2H, N−CH_2), 5.49 (d, $^2J_{H-H}$ = 12.7 Hz, 2H, N−CH_2), 3.79 (s, 3H, N-Me), 2.09 (s, 15H, Cp*-Me), 1.99 (s, 15H, Cp*-Me). ^{13}C NMR (DMSO-d_6, 75 MHz, 293 K): δ 163.4 (q, $^1J_{C-B}$ = 49.4 Hz, C−B), 162.7 (2-Im), 135.5 (q, $^2J_{C-B}$ = 1.3 Hz, *o*-Ph), 125.3 (q, $^3J_{C-B}$ = 2.7 Hz, *m*-Ph), 123.4 (4-Im), 122.2 (5-Im), 121.5 (*p*-Ph), 96.4 (Cp*-ring), 96.4 (Cp*-ring), 62.5 (N−CH_2), 38.4 (N-Me), 10.4 (Cp*-Me).

[(IrCp)$_2${Pd(bisNHC-C2-Me)}(μ_3-S)$_2$](BPh$_4$)$_2$*, **6-C2-Me**. Complex **6-C2-Me** was prepared analogously to **5-C1-Me**. Addition of diethyl ether into a solution of the crude product in dichloromethane afforded microcrystals of the complex. Yield: 41%. Anal. Calcd for $C_{78}H_{84}B_2Ir_2N_4PdS_2$: C, 56.64; H, 5.12; N, 3.39. Found: C, 56.44; H, 5.16; N, 3.45%. ^{1}H NMR (DMSO-d_6, 300 MHz, 293 K): δ 7.45 (d, $^3J_{H-H}$ = 2.1 Hz, 2H, 4-Im), 7.44 (d, $^3J_{H-H}$ = 2.1 Hz, 2H, 5-Im), 7.18 (m, 16H, BPh_4-*o*-Ph), 6.92 (t, $^3J_{H-H}$ = 7.4 Hz, 16H, BPh_4-*m*-Ph), 6.78

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(t, $^3J_{H-H}$ = 7.1 Hz, 8H, BPh_4-*p*-Ph), 4.58−4.49 (m, 1H, N−CH_2), 4.46−4.36 (m, 1H, N−CH_2), 3.6 (s, 3H, N-Me), 2.05 (s, 15H, Cp*-Me), 2.03 (s, 15H, Cp*-Me). ^{13}C NMR (DMSO-d_6, 75 MHz, 293 K): δ 163.4 (q, $^1J_{C-B}$ = 49.4 Hz, C−B), 158.5 (2-Im), 135.5 (q, $^2J_{C-B}$ = 1.3 Hz, *o*-Ph), 125.3 (q, $^3J_{C-B}$ = 2.7 Hz, *m*-Ph), 124.1 (4-Im), 123.7 (5-Im), 121.5 (*p*-Ph), 96.1 (Cp*-ring), 47.1 (N−CH_2), 38.5 (N-Me), 10.5 (Cp*-Me), 10.4 (Cp*-Me).

[(IrCp)$_2${Pd(bisNHC-C3-Me)}(μ_3-S)$_2$](BPh$_4$)$_2$,* ***6-C3-Me.*** Complex **6-C3-Me** was prepared analogously to **5-C1-Me**. Addition of diethyl ether into a solution of the crude product in dichloromethane afforded microcrystals of the complex. Yield: 21%. Anal. Calcd for $C_{79}H_{86}B_2Ir_2N_4PdS_2 \cdot 1/2CH_2Cl_2$: C, 55.82; H, 5.13; N, 3.28. Found: C, 55.93; H, 5.18; N, 3.51%. ^{1}H NMR (DMSO-d_6, 300 MHz, 293 K): δ 7.42 (d, $^3J_{H-H}$ = 1.9 Hz, 2H, 4-Im), 7.38 (d, $^3J_{H-H}$ = 1.9 Hz, 2H, 5-Im), 7.17 (m, 16H, BPh_4-*o*-Ph), 6.92 (t, $^3J_{H-H}$ = 7.4 Hz, 16H, BPh_4-*m*-Ph), 6.78 (t, $^3J_{H-H}$ = 7.2 Hz, 8H, BPh_4-*p*-Ph), 4.3 (dd, $^2J_{H-H}$ = 14.1 Hz, $^3J_{H-H}$ = 6.2 Hz, 2H, N−CH_2), 3.87 (dd, $^2J_{H-H}$ = 14 Hz, $^3J_{H-H}$ = 11.4 Hz, 2H, N−CH_2), 3.53 (s, 3H, N-Me), 2.28−2.19 (m, 1H, 2-$(CH_2)_3$), 2.07 (s, 15H, Cp*-Me), 2.06 (s, 15H, Cp*-Me), 1.74−1.61 (m, 1H, 2-$(CH_2)_3$). ^{13}C NMR (DMSO-d_6, 75 MHz, 293 K): δ 163.4 (q, $^1J_{C-B}$ = 49.3 Hz, C−B), 160.5 (2-Im), 135.5 (q, $^2J_{C-B}$ = 1.2 Hz, *o*-Ph), 125.3 (q, $^3J_{C-B}$ = 2.7 Hz, *m*-Ph), 124 (4,5-Im), 121.5 (*p*-Ph), 96.1 (Cp*-ring), 96.1 (Cp*-ring), 51.7 (N−CH_2), 38 (N-Me), 30.9 (2-$(CH_2)_3$), 10.6 (Cp*-Me), 10.4 (Cp*-Me).

Preparation of Samples for ESI-MS and ^{1}H NMR Spectroscopy to Study the Reaction of [Pt(bisNHC-C2-Me)(SH)$_2$] (1-C2-Me) and [(IrCp)$_2$(μ-OH)$_3$](BPh$_4$) in Acetonitrile.* A solution of **1-C2-Me** (4.5 mg, 10.0 mmol) in 1 mL of acetonitrile was added to a solution of [(IrCp*)$_2$(μ-OH)$_3$](BPh$_4$) (10.1 mg, 9.9 mmol) in 1 mL of acetonitrile. A solution of $NaBPh_4$ (17 mg, 50 mmol) in acetonitrile (5 mL) was added to the solution. The solvent of the reaction mixture was evaporated under reduced pressure to afford a green solid, which was collected by filtration and washed with methanol.

Preparation of Samples for ESI-MS and ^{1}H NMR Spectroscopy to Study the Reaction of 1-C2-Me and [(RhCp)$_2$(μ-OH)$_3$](BPh$_4$) in Acetonitrile.* A procedure similar to that for the Ir complex was applied for the preparation of the Rh complex using **1-C2-Me** (4.5 mg, 10.0 mmol) in 1 mL of MeCN, [(RhCp*)$_2$(μ-OH)$_3$](BPh$_4$) (8.5 mg, 10.0 mmol) in 1 mL of acetonitrile and $NaBPh_4$ (17 mg, 50 mmol) in acetonitrile (5 mL) to give a yellowish green solid.

Preparation of Samples for ESI-MS and ^{1}H NMR Spectroscopy to Study the Reaction of 1-C2-Me with a Mixture of [(IrCp)$_2$(μ-OH)$_3$](BPh$_4$) and [(RhCp*)$_2$(μ-OH)$_3$](BPh$_4$) in Methanol.* A mixture of [(IrCp*)$_2$(μ-OH)$_3$](BPh$_4$) (10.3 mg, 10.0 mmol) and [(RhCp*)$_2$(μ-OH)$_3$](BPh$_4$) (8.5 mg, 10.0 mmol) in 2 mL of methanol was added to a solution of **1-C2-Me** (9.0 mg, 20.0 mmol) in 2 mL of methanol. After the reaction mixture was stirred for 5 min, a solution of $NaBPh_4$ (23.3 mg, 68.1 mmol) in 2 mL of methanol was added. The mixture was stirred for additional 30 min to afford a dark brown precipitate, which was collected by using filtration.

Preparation of Samples for ESI-MS and ^{1}H NMR Spectroscopy to Study the Reaction of 1-C2-Me with a Mixture of [(IrCp)$_2$(μ-OH)$_3$](BPh$_4$) and [(RhCp*)$_2$(μ-OH)$_3$](BPh$_4$) in Acetonitrile.* A mixture of [(IrCp*)$_2$(μ-OH)$_3$](BPh$_4$) (10.3 mg, 10.0 mmol) and [(RhCp*)$_2$(μ-OH)$_3$](BPh$_4$) (8.5 mg, 10.0 mmol) in 2 mL of acetonitrile was stirred for 4 h. The mixture was added to a solution of **1-C2-Me** (9.0 mg, 20.0 mmol) in 2 mL of acetonitrile and stirred for 1h. The resulting solution was diluted with acetonitrile and then used for mass measurements.

Preparation of a Sample for ESI-MS to Study the Reaction of [(IrCp)$_2$(μ-OH)$_3$](BPh$_4$) and [(RhCp*)$_2$(μ-OH)$_3$](BPh$_4$) in Methanol.* A solution of [(IrCp*)$_2$(μ-OH)$_3$](BPh$_4$) (10.3 mg, 10.0 mmol) in 1 mL of methanol was added to a solution of [(RhCp*)$_2$(μ-OH)$_3$](BPh$_4$) (8.5 mg, 10.0 mmol) in 1 mL of MeOH. The reaction mixture was diluted with methanol and then used for mass spectrometric measurements.

Preparation of Sample for ESI-MS to Study the Reaction of [(IrCp)$_2$(μ-OH)$_3$](BPh$_4$) and [(RhCp*)$_2$(μ-OH)$_3$](BPh$_4$) in Acetonitrile.* The same procedures were performed for the above-mentioned reaction in methanol using acetonitrile.

Cyclic Voltammetry. Cyclic voltammetry was performed on an ALS Model 600C electrochemical analyzer using glassy carbon (ϕ3 mm), platinum wire, and Ag/Ag^+ electrodes as working, counter, and reference electrodes, respectively. nBu$_4$NPF$_6$ was used as the supporting electrolyte (0.10 mol/L in acetonitrile) and recrystallized three times from ethanol solutions before use. The ferrocene/ferrocenium couple (0.380 V vs SCE) was used as an external standard. The redox potentials are expressed versus saturated calomel electrode. Concentrations of the trinuclear complexes were 1.0 mmol/L or 0.2 mmol/L. Scan rate was 100 mV/s.

Variable-Temperature ^{1}H NMR Spectroscopy and Lineshape Analyses. ^{1}H NMR spectra for the complexes in DMSO-d_6 at variable temperatures were obtained using a Bruker AVANCE 300 FT-NMR spectrometer. For line-shape analyses, ^{1}H NMR signals with various kinetic constants were simulated using a NMR simulation program in the NMRV4 program pakage.[22] Activation parameters for the complexes were calculated using the obtained kinetic constants for various temperatures using the Microsoft Excel software.

X-ray Crystallography. Crystallographic analyses were performed for a series of the heterometallic trinuclear complexes, **3-C*n*-Me** (n = 1−3), **4-C*n*-Me** (n = 1, 2), **3-C*n*-*i*Pr** (n = 1, 2), **4-C1-*i*Pr**, **3-C1-Bn**, **5-C*n*-Me** (n = 1, 2), and **6-C1-Me**. Single crystals were mounted on glass fibers. Diffraction data were collected at 193(1) K on an AFC7/CCD Mercury or VariMax Saturn diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å) using a rotation method. The data were integrated, scaled, sorted, and averaged using the CrystalClear[23] software. Absorption corrections were applied using the multiscan method. The structures were solved using SIR97[24] or SHELX97,[25] expanded using Fourier techniques, and refined by using full matrix least-squares against F^2 with CRYSTALS[26] or SHELXL97 equipped in a CrystalStructure[27] software. Crystallographic data are summarized in the Supporting Information. The Cp* ligands in **3-C1-Me**, **4-C1-Me**, and **3-C1-Bn**, one of the phenyl groups of the NHC ligands in **3-C1-Bn**, and some solvent molecules were treated as disordered. All hydrogen atoms except for some of those attached to the disordered atoms were located at calculated positions and refined as riding models.

DFT Calculations. DFT calculations were carried out on a series of the heterometallic trinuclear complex dications with the methyl N-substituents, **3-C*n*-Me** and **4-C*n*-Me**, and their 1e$^-$- and 2e$^-$-reduced complexes using Gaussian03.[28] Atomic coordinates were optimized at the level of RB3LYP or UB3LYP/LanL2DZ for the Pt, Ir, and Rh atoms and 6-31G(d,p) for the others. Structural optimizations were started from the structures obtained from crystallographic analyses when they were available or constructed by replacement of the substituents of available crystal structures for the dicationic complexes and the optimized structures of the oxidized forms of the corresponding complexes for the 1e$^-$-reduced monocationic and 2e$^-$-reduced molecular complexes. Vibrational frequencies were calculated for all converged structures, and no imaginary frequencies were determined showing that these structures lie on minima.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of line-shape analyses, cyclic voltammetry, absorption spectra, DFT calculations, structures and coordinates, and CIF files of all crystallographic data. 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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