

Reactivity of Cationic Triruthenium Carbonyl Clusters: From Pyrimidinium Ligands to N-Heterocyclic Carbenes

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The reaction of $[Ru_3(CO)_{12}]$ with pyrimidine (Hpym) leads to the isomeric cyclometalated derivatives $[Ru_3(\mu-H)(\mu-\kappa^2N^1,C^6-pym)(CO)_{10}]$ (1) and $[Ru_3(\mu-H)(\mu-\kappa^2N^1,C^2-pym)(CO)_{10}]$ (2), which have been treated with $[Me_3O][BF_4]$ to give the corresponding *N*-methylpyrimidinium derivatives $[Ru_3(\mu-H)(\mu-\kappa^2N^1,C^6-pymMe)(CO)_{10}][BF_4]$ (3[BF4]) and $[Ru_3(\mu-H)(\mu-\kappa^2N^1,C^2-pymMe)(CO)_{10}]$ -[BF4] (4[BF4]). The reaction of 4[BF4] with K-Selectride renders a separable mixture of two neutral trinuclear products, $[Ru_3(\mu-H)\{\mu-\kappa^2N^1,C^2-(6-HpymMe)\}(CO)_9]$ (5) and $[Ru_3(\mu-H)\{\mu-\kappa^2N^1,C^2-(4-HpymMe)\}(CO)_9]$ (6), which arise from the nucleophilic attack of a hydride at the ligand C⁶ and C⁴ carbon atoms of 4⁺. This cationic complex can be reduced to the short-lived radical species 4[•], which spontaneously dimerizes by forming an intermolecular C–C bond between the ligands of two such radicals. Three hexanuclear derivatives, $[Ru_6(\mu-H)_2\{\mu_6-\kappa^4N^1,N^{1\prime},C^2,C^{2\prime}-(4,6\prime-bipymMe_2)\}(CO)_{18}]$ (isomers 7 and 8) and $[Ru_6(\mu-H)_2\{\mu_6-\kappa^4N^1,N^{1\prime},C^2,C^{2\prime}-(4,4\prime-bipymMe_2)\}(CO)_{18}]$ (isomer 9), have been isolated by reducing 4[BF4] with cobaltocene. Molecular orbital calculations (at the DFT level) and electrochemical studies have helped rationalize the experimental results. The ligand-based character of the LUMO of 4⁺ and its atomic orbital composition account for the regiochemistry observed in the reactions of this cationic complex. The N-heterocyclic ligands of 5–9, which have two N atoms in a six-membered ring and a doubly metalated N atom, constitute novel types of N-heterocyclic carbones.

Introduction

Among the large and fast-growing family of N-heterocyclic carbene (NHC) ligands known to date, those having the carbene C atom in a five-membered ring (NHC_{R5}) are far more common than those having the carbene C atom in a sixmembered ring (NHC_{R6}).¹ This is mainly due to the fact that many NHC_{R5} carbones are isolable as pure compounds or can be prepared in situ by simple synthetic procedures.

Pyridylidenes (also named pyridinylidenes) and some benzo-annulated relatives (derived from quinoline, isoquinoline, acridine, etc.) are NHC_{R6} carbenes that contain only one N atom in the carbenic ring (NHC_{R6-1N}).² Although their isolation as free carbenes has been elusive, a few reports describing indirect routes to various types of transitionmetal complexes containing NHC_{R6-1N} ligands have been published.^{2–7} In this context, we have recently communicated

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⁽¹⁾ For an excellent review on cyclic carbenes and related species that cites all review articles and books on NHCs published since 2007, see: Melaimi, M.; Soleihavoup, M.; Bertrand, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 8810.

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that pyrid-2-ylidenes, generated in situ by deprotonation of pyridinium cations, can be trapped by $[Ru_3(CO)_{12}]$,⁷ but the great basicity of these ligands and the polynuclear character of the ruthenium cluster trigger the roomtemperature ortho metalation of the initial $\kappa^1 C^2$ -pyrid-2ylidene ligands to give face-capping μ_3 - $\kappa^2 C^2$, C^3 -pyrid-3yl-2-ylidene ligands (Scheme1).

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Scheme 1



Considering that N-heterocyclic carbenes containing two nitrogen atoms in a six-membered carbenic ring (NHC_{R6-2N}) are restricted to 1,3-dialkyl- and 1,3-diaryl-3,4,5,6-tetrahydropyrimidin-2-ylidenes,⁸ the results shown in Scheme 1 led us to attempt the synthesis of ruthenium cluster complexes containing NHC_{R6-2N} ligands derived from quinoxaline, pyrazine, and pyrimidine, following an analogous synthetic procedure. However, N-methylquinoxalinium,⁹ N-methylpyrazinium,⁹ and N-methylpyrimidinium¹⁰ cations could not be satisfactorily deprotonated with strong bases in the presence of $[Ru_3(CO)_{12}]$. We then reasoned that previous coordination of these cations would enhance their acidity, but they failed to react with $[Ru_3(CO)_{12}]$ even at tempera-tures higher than 100 °C.^{9,10} Finally, we decided to attempt the preparation of the desired cationic clusters by stepwise treatment of $[Ru_3(CO)_{12}]$ with the neutral heterocycles (this would lead to heterocycle-derived neutral clusters) and then with an electrophilic methylating reagent, such as methyl triflate (this would lead to cationic derivatives if N-methylation of the free N atom was achieved). A subsequent deprotonation of these cationic clusters would lead to the desired products: i.e., compounds containing NHC_{R6-2N} ligands.

In a previous paper,⁹ we have reported that, although we have succeeded in preparing triruthenium clusters containing cationic pyrazinium- and quinoxalinium-derived ligands by quaternization of neutral pyrazine- and quinoxaline-derived clusters, the subsequent treatment of these cationic clusters with some bases does not lead to isolable deprotonation products but to clusters with neutral ligands that have no significant carbene character and that arise from the nucleophilic addition of the corresponding base to a ligand ring carbon atom (see, for example, Scheme 2).

We now report the synthesis of cationic triruthenium clusters having pyrimidinium-derived ligands and show that their reactions with K-Selectride and cobaltocene lead to neutral products that contain novel types of $\rm NHC_{R6-2N}$ ligands.

While we were preparing this paper, a report describing the synthesis of rhodium(I) and iridium(I) complexes containing monodentate phthalaz-2-ylidene ligands (Scheme 3) has been published.¹¹

Results and Discussion

Synthesis of the Isomeric Cationic Clusters $[Ru_3(\mu-H)(\mu-\kappa^2N^1, C^6-pymMe)(CO)_{10}]^+$ (3⁺) and $[Ru_3(\mu-H)(\mu-\kappa^2N^1, C^2-pymMe)-(CO)_{10}]^+$ (4⁺). These compounds were prepared following a two-step synthetic protocol related to that reported previously for the synthesis of the related complexes $[Ru_3(\mu-H)(\mu-\kappa^2N^1, C^2-\mu)]^+$

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 C^{2} -LMe)(CO)₁₀]⁺ (HLMe = N-methylpyrazinium, N-methylquinoxalinium): that is, treatment of $[Ru_3(CO)_{12}]$ with the N-heterocycle and subsequent methylation of the product with methyl triflate.⁹ However, the reaction of $[Ru_3(CO)_{12}]$ with 1 equiv of pyrimidine (Hpym), in THF solution at reflux temperature, did not lead to a single product but to a mixture of the neutral cyclometalated hydrido derivatives [Ru₃- $(\mu-H)(\mu-\kappa^2 N^1, C^6-\text{pym})(\text{CO})_{10}]$ (1) and $[\text{Ru}_3(\mu-H)(\mu-\kappa^2 N^1, \mu-\kappa^2)]$ C^2 -pym)(CO)₁₀] (2) (Scheme 4), which were satisfactorily separated by thin-layer chromatography (TLC).¹² The subsequent methylation of 1 and 2 with methyl triflate was unsuccessful, because an equilibrium between the reactants and the methylated products was established and this prevented the isolation of the latter as pure compounds. Fortunately, the use of trimethyloxonium tetrafluoroborate as methylating reagent led to the desired cationic complexes, $[Ru_3(\mu-H)(\mu-\kappa^2 N^1, C^6-pymMe)(CO)_{10}]^+$ (3⁺) and $[Ru_3(\mu-H)-K^6-pymMe)(CO)_{10}]^+$ (3⁺) $(\mu - \kappa^2 N^1, C^2 - \text{pymMe})(\text{CO})_{10}]^+$ (4⁺) (Scheme 4).

The composition of $3[BF_4]$ and $4[BF_4]$ was established by their microanalyses and FAB mass spectra. In addition, the cationic character of the clusters was confirmed by their IR and NMR spectra, since their ν (CO) absorptions are shifted toward wavenumbers higher than those of their neutral precursors 1 and 2 and the ¹H and ¹³C NMR signals of their heterocyclic ligands appear at chemical shifts higher than those of 1 and 2. The high ¹H (δ 4.35 ppm for 3[BF₄] and 4.60 ppm for 4[BF₄]) and ¹³C (δ 44.7 ppm for 3[BF₄] and 50.3 ppm for 4[BF₄]) chemical shifts of their methyl groups corroborate the methylation of the uncoordinated N atoms of 1 and 2. The solid-state structure of 4[BF₄] was verified by X-ray diffraction (Figure 1). A selection of bond lengths is given in Table 1.

Reactions of Compounds 3[BF₄] and 4[BF₄] with Bases. The reactivity of these ionic compounds with potassium *tert*-but-



(**3**[BF₄]) (**4**[BF₄])

oxide, methyllithium, and potassium tris(*sec*-butyl)hydridoborate (K-Selectride) was studied.

Both $3[BF_4]$ and $4[BF_4]$ reacted readily with 1 equiv of potassium *tert*-butoxide and methyllithium to give mixtures of products, from which $[Ru_3(CO)_{12}]$ was the only complex that could be satisfactorily separated by TLC. Similar results were obtained when $3[BF_4]$ was treated with K-Selectride. It seems that the initial products of these reactions are not stable enough to be isolated and that they evolve to thermodynamically driven mixtures that contain $[Ru_3(CO)_{12}]$ and other decomposition products.

However, although a mixture of products was also formed when **4**[BF₄] was treated with K-Selectride at room temperature, a subsequent chromatographic workup allowed the isolation of the yellow isomeric nonacarbonyl products [Ru₃(μ -H){ μ - $\kappa^2 N^1$, C^2 -(6-HpymMe)}(CO)₉] (**5**) and [Ru₃-(μ -H){ μ - $\kappa^2 N^1$, C^2 -(4-HpymMe)}(CO)₉] (**6**) (Scheme 5), which contain novel NHC_{R6-2N} ligands that arise from the nucleophilic attack of the hydride ion at different C atoms of the bridging N-heterocyclic ligand of **4**⁺. In the processes that lead to **5** and **6**, the nucleophilic attack of the hydride ion at **4**⁺ should precede the release of the CO ligand, because the decacarbonyl cation **4**⁺ is stable in solution at room temperature.

The structures of compounds **5** and **6** were determined by X-ray diffraction (Figures 2 and 3, respectively). Table 1 contains a selection of bond lengths that permits a comparison between related interatomic distances of compounds **4**–**6**. Both structures comprise a closed [Ru₃(CO)₉] core that is edge-bridged by a hydride ligand and face-capped by the corresponding pyrimidinium-derived ligand, which bridges the Ru2–Ru3 edge through the N1 atom while it is also attached to the Ru1 atom through the carbene C1 atom. The C1–Ru1 distances, 2.069(5) Å in **5** and 2.04(1) Å in **6**, are comparable to the Ru–C_{carbene} distances reported for tri- and tetraruthenium clusters containing NHC_{R5-N2} ligands.¹³ The main difference between compounds **5** and **6** is that the former results from the addition of the hydride to the C⁶ carbon atom (C2 in Figure 2) of the original

⁽¹²⁾ Compounds 1 and 2 have been previously prepared by treating [Ru₃(CO)₁₀(MeCN)₂] with Hpym: Foulds, G. A.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1985**, *294*, 123.



Figure 1. Structure of the cationic part of **4**[BF₄]. Thermal ellipsoids are drawn at 30% probability level.

 Table 1. Selected Interatomic Distances (Å) in Compounds
 4[BF₄], 5, and 6

-[22 4], 0, 414 0				
	4 [BF ₄]	5	6	
Ru(1)-Ru(2)	2.8784(9)	2.7402(4)	2.747(2)	
Ru(1) - Ru(3)	2.8743(9)	2.7530(4)	2.753(2)	
Ru(2)-Ru(3)	2.8498(9)	2.7797(4)	2.767(2)	
C(1) - Ru(1)	2.090(7)	2.069(4)	2.04(1)	
N(1) - Ru(2)	2.132(6)	2.132(3)	2.19(1)	
N(1) - Ru(3)		2.170(3)	2.14(1)	
C(1) - N(1)	1.339(10)	1.372(5)	1.43(2)	
C(1) - N(2)	1.368(9)	1.345(5)	1.35(2)	
C(2) - N(1)	1.334(10)	1.488(5)	1.39(2)	
C(2) - C(3)	1.383(11)	1.506(6)	1.30(2)	
C(3) - C(4)	1.351(12)	1.313(7)	1.50(2)	
C(4) - N(2)	1.346(10)	1.423(6)	1.47(2)	
C(5) - N(2)	1.492(10)	1.462(6)	1.44(2)	

N-methylpyrimidinium ligand, whereas in complex **6**, such an addition has occurred on the C⁴ carbon atom (C4 in Figure 3). While the C–C and C–N distances of the pymMe ligand of compound **4**⁺ are typical of an aromatic system (they are in the range 1.34-1.38 Å), those of the 6-HpymMe and 4-HpymMe ligands of **5** and **6** respectively indicate that these ligands are no longer aromatic, since a C=C double bond is clearly localized between the C3 and C4 atoms of compound **5** (C3–C4 = 1.313(7) Å) and between the C2 and C3 atoms of compound **6** (C2–C3 = 1.30(2) Å), while the remaining ring interatomic distances are considerably longer, particularly those involving the carbon atom of the corresponding CH₂ group. While all six ring atoms of the 4-HpymMe ligand of compound **6** are nearly coplanar and the plane they define is perpendicular



Figure 2. Molecular structure of compound **5**. Thermal ellipsoids are drawn at the 30% probability level.



to the Ru₃ plane, the C2 carbon atom of the 6-HpymMe ligand of compound **5** is 0.53(1) Å away from the plane defined by the remaining ligand ring atoms, which forms a dihedral angle of $65.0(1)^\circ$ with the Ru₃ plane.

As expected, the IR spectra of **5** and **6** are almost identical but are very different from that of their cationic decacarbonyl precursor **4**⁺. Their ¹H NMR spectra contain a hydride resonance at -14.53 ppm for **5** and -14.07 ppm for **6** (that of **4**⁺ is observed at -14.12 ppm). While the ¹³C NMR signal of the pymMe NCN carbon atom of **4**⁺ is observed at 184.6 ppm, those of the C_{carbene} atoms of **5** and **6** appear at 209.7 and 206.1 ppm, respectively, being in the upper part of the range previously observed for many cyclic diaminocarbene complexes (180–210 ppm).¹⁴

DFT calculations have already demonstrated that, in cationic ligand-bridged triruthenium clusters, the greatest positive atomic charges are located in the carbonyl C atoms.⁹ As no attack at the CO ligands of 4^+ was observed when it was treated with K-Selectride, this reaction should be orbital-controlled. Having this in mind, we performed a molecular orbital study of 4^+ aimed at rationalizing the experimental results. Figure 4 shows (a) that the LUMO of 4^+ is a combination of π -type orbitals of atoms of the bridging ligand, with negligible contributions from orbitals of the remaining atoms of the cluster, (b) that the major contributors

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Figure 3. Molecular structure of compound 6. Thermal ellipsoids are drawn at the 30% probability level.



Figure 4. LUMOs of the cationic complexes 3^+ and 4^+ , shown at an isosurface value of 0.05.

to this molecular orbital are the C^4 and C^6 carbon atoms, and (c) that their contributions are very similar. The composition of the LUMO of 4^+ explains the selective attack of the hydride ion at the ligand ring and accounts for the isolation of the isomeric products **5** and **6** in similar yields. However, it is not yet clear why the behavior of methyllithium is so different from that of K-Selectride in their reactions with 4^+ .

Interestingly, Figure 4 also shows that the LUMO of 3^+ differs from that of 4^+ in that the former has a non-negligible participation of the metal atoms and that its major contributor is the metal-coordinated C² carbon atom. This may account for the very different reactivities observed for these two cationic compounds.

The above-described reaction of K-Selectride with 4^+ seems to follow a reactivity pattern similar to that observed for the cationic compounds $[Ru_3(\mu-H)(\mu-\kappa^2N^1,C^2-LMe)-(CO)_{10}]^+$ (HLMe = *N*-methylpyrazinium, *N*-methylquinoxalinium), which also give nonacarbonyl products resulting from the addition of a hydride to a ligand ring carbon atom (see, for example, Scheme 2).⁹ However, the different positions of the N atoms in the N-heterocyclic ligands of these cationic clusters account for the different natures of the final products of their reactions. While the ligands of **5** and **6** are N-heterocyclic carbenes, the products of the reactions of the related *N*-methylpyrazinium- and



Figure 5. Cyclic voltammograms of $4[BF_4]$ acquired at 20 °C in 0.1 M [NEt₄][BF₄] dichloromethane solutions at different scan rates.

N-methylquinoxalinium-derived triruthenium clusters contain ligands with no carbene character.⁹

It has been previously shown that, on treatment with anionic nucleophiles, hydrido triruthenium carbonyl clusters that have neutral N-heterocyclic ligands either undergo hydride deprotonation (when the starting clusters are neutral¹⁵ or cationic¹⁶) or a nucleophilic attack at a carbonyl C atom (only observed for cationic starting clusters).¹⁶ Therefore, it is clear that the cationic character of 4^+ and of [Ru₃(μ -H)] $(\mu - \kappa^2 N^1, C^2 - LMe)(CO)_{10}]^+$ (HLMe = N-methylpyrazinium, N-methylquinoxalinium) and the fact that they have ligandbased LUMOs account for the enhanced tendency of these clusters to add anionic nucleophiles at the carbon atoms of their bridging N-heterocyclic ligands. It has been reported that coordinatively unsaturated triosmium clusters having neutral N-heterocyclic bridging ligands undergo addition of anionic carbon nucleophiles at a C atom of the bridging ligand,¹⁷ but that chemistry has no parallel in ruthenium cluster chemistry.

Reductive Dimerization of 4⁺. In an earlier report, we have described that the cationic compounds $[\operatorname{Ru}_3(\mu-H)(\mu-\kappa^2N^1, C^2-LMe)(CO)_{10}]^+$ (HLMe = *N*-methylpyrazinium, *N*-methylquinoxalinium) can be reduced by cobaltocene to give dimeric hexanuclear products that arise from the coupling of two ligand-centered trinuclear radical species (Scheme 6).¹⁸ These findings and the different results obtained from the reactions of these two trinuclear cationic clusters and compound 4⁺ with K-Selectride, noted above, prompted us to study the reduction chemistry of 4⁺.

The cyclic voltammograms of **4**[BF₄] in dichloromethane (Figure 5) show a reduction peak at a potential, $E_{\rm red} = -0.70$ at 0.200 V s⁻¹, that is similar to those found for [Ru₃(μ -H) (μ - $\kappa^2 N^1$, C^2 -LMe)(CO)₁₀]⁺: -0.74 V for HLMe = *N*-methylpyrazinium and -0.77 V for HLMe = *N*-methylquinoxalinium, at 0.200 V s⁻¹.¹⁸ Figure 5 also illustrates that the reduction processes are completely irreversible, even at fast

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scan rates, indicating that the molecules of the reduced oddelectron species 4[•] has a very short half-life in solution.

The reaction of **4**[BF₄] with 1 equiv of cobaltocene led to a mixture of products from which three neutral hexanuclear derivatives, namely, [Ru₆(μ -H)₂{ μ_6 - $\kappa^4 N^1$, $N^{1\prime}$, C^2 , $C^{2\prime}$ -(4,6^{\prime}-bipymMe₂)}(CO)₁₈] (isomers **7** and **8**) and [Ru₆(μ -H)₂{ μ_6 - $\kappa^4 N^1$, $N^{1\prime}$, C^2 , $C^{2\prime}$ -(4,4^{\prime}-bipymMe₂)}(CO)₁₈] (isomer **9**), were separated by TLC (Scheme 7). They were all characterized by analytical and spectroscopic techniques and, in the cases of **7** and **8**, also by X-ray diffraction.

The solid-state molecular structures of compounds 7 and 8 (Figures 6 and 7, Table 2) have many features in common. Both molecules comprise two closed trimetallic units, each edge-bridged by a hydride and face-capped by a ligand, 4,6'-bipymMe₂, that arises from the intermolecular formation of a C–C bond between the pymMe ligands of two molecules of the radical **4**°. In 7 and **8**, the new C–C bond involves the heterocyclic C⁴ carbon atom (C4 in Figures 6 and 7) of one



Figure 6. Molecular structure of compound 7. Thermal ellipsoids are drawn at the 30% probability level.



Figure 7. Molecular structure of compound 8. Thermal ellipsoids are drawn at the 30% probability level.

Table 2.	Selected	Interatomic	Distances	(\mathbf{A}) in	Compounds
		$7 \cdot CH_2C$	l ₂ and 8		

	$7 \cdot CH_2Cl_2$	8
Ru(1)-Ru(2)	2.762(1)	2.7498(5)
Ru(1) - Ru(3)	2.747(1)	2.7340(5)
Ru(2)-Ru(3)	2.779(1)	2.7671(5)
Ru(4) - Ru(5)	2.747(1)	2.7325(5)
Ru(4) - Ru(6)	2.930(1)	2.7378(5)
Ru(5) - Ru(6)	2.662(1)	2.7853(5)
C(1) - Ru(1)	2.085(12)	2.077(4)
C(1) - N(1)	1.39(2)	1.373(6)
C(1) - N(2)	1.33(2)	1.324(6)
C(2) - N(1)	1.40(2)	1.428(5)
C(2) - C(3)	1.31(2)	1.296(7)
C(3) - C(4)	1.50(2)	1.494(7)
C(4) - C(7)	1.58(2)	1.571(7)
C(4) - N(2)	1.48(2)	1.494(6)
C(5) - N(2)	1.44(2)	1.463(7)
C(6) - N(3)	1.36(2)	1.372(6)
C(6) - N(4)	1.36(2)	1.342(6)
C(7) - C(8)	1.49(2)	1.484(7)
C(7) - N(3)	1.47(2)	1.477(6)
C(8) - C(9)	1.33(2)	1.313(9)
C(9) - N(4)	1.42(2)	1.396(8)
C(10) - N(4)	1.45(2)	1.470(8)
N(1)-Ru(2)	2.158(11)	2.137(3)
N(1)-Ru(3)	2.158(9)	2.160(4)
N(3) - Ru(5)	2.196(8)	2.146(3)
N(3) - Ru(6)	2.136(10)	2.197(4)

trinuclear unit, $Ru_3H(4-pymMe)(CO)_9$, and the heterocyclic C⁶ carbon atom (C7 in Figures 6 and 7) of the other trinuclear unit, $Ru_3H(6'-pymMe)(CO)_9$. The key difference

between both molecules is that their C7 carbon atoms have opposite stereochemistries, while the stereochemistries of their C4 carbon atoms are the same. The coordination of the bridging ligand to the metal atoms of the Ru₃H-(4-pymMe)(CO)₉ units of 7 and 8 is essentially identical with that found in compound 6 (Figure 3); however, the different stereochemistry of the C7 carbon atom of each molecule induces a different arrangement of the atoms of the corresponding Ru₃H(6'-pymMe)(CO)₉ unit. While that of 7 is analogous to that found in $[Ru_6(\mu-H)_2]{\mu_6-\kappa^4N^1, N^{1\prime}, C^2, C^{2\prime}-(3,3'$ biquinoxMe₂) $(CO)_{18}$ (HquinoxMe = N-methylquinoxaline) (Scheme 6),¹⁸ that of **8** is the same as that found in compound 5 (Figure 2). We believe that the coordination mode found for the bridging ligand 4,6'-bipymMe₂ in the Ru₃H(6'pymMe)(CO)₉ unit of 7 minimizes steric interactions (involving CO ligands and C-H groups) that would be more intense if it had the coordination mode found for the same trinuclear unit in compound 8. In both molecules, the rotation about the C4-C7 bond is sterically impeded. This steric hindrance should also be responsible for the very long C4-C7 interatomic distances: 1.58(2) Å in 7 and 1.571(7) Å in 8.

Although no crystals of compound 9 suitable for X-ray diffraction could be obtained, its atom connectivity (see Scheme 7) was satisfactorily inferred from its spectroscopic data. The ν_{CO} region of its IR spectrum is comparable to those of compounds 7 and 8, which are almost identical despite corresponding to compounds with different, but related, molecular structures. Both the ¹H and ¹³C NMR spectra of compound 9 contain duplicated resonances, indicating that the compound consists of two essentially identical parts that are not symmetry related. The $C^4-C^{4/2}$ coupling was unambiguously confirmed by its 135-DEPT and ¹³C{¹H} NMR spectra, which in addition to the resonances of the HC⁴–HC^{4/} group (δ 59.9 and 57.7 ppm) contain the resonances of the remaining ring CH (δ 147.3, 146.7, 101.5, and 100.0 ppm) and carbene C atoms (\$\delta\$ 210.8 and 210.0 ppm) at chemical shifts very close to those found for 6 and for the Ru₃H(4pymMe)(CO)₉ units of 7 and 8, whose structures have been established by X-ray diffraction. This confirms that the C=C double bond of the heterocyclic ring is located between the C^5 and C^6 carbon atoms.

The fact that both trinuclear units of this compound are not symmetry related implies that the C⁴ and C⁴ carbon atoms have different stereochemistries (R,S or S,R), because otherwise (R,R or S,S) the molecule would have C_2 symmetry. In addition, there should be no free rotation about the C⁴-C⁴ bond, because for 0°-eclipsed or 180°-alternated conformations there would be a mirror plane bisecting the C⁴-C⁴ bond or an inversion center between the C⁴ and C⁴ atoms, respectively, and molecular models have shown that the steric repulsion between the atoms of the two parts of the molecule is stronger at the 0°-eclipsed and 180°-alternated conformations than at any other intermediate conformation.

Upon addition of one electron, the LUMO of 4^+ (Figure 4) is converted to the SOMO of the odd-electron species 4^{\bullet} , which should have an atomic orbital composition analogous to that of the LUMO of 4^+ : i.e., with the ligand C⁴ and C⁶ atoms as the major contributors. In this radical, the endo face of the N-heterocyclic ligand is protected by one of the axial CO ligands of the Ru(CO)₄ moiety and, therefore, its dimerization is expected to occur only through the exo face of its ligand. In addition, as this radical species is asymmetric, it is in fact a racemic mixture (dextro and levo enantiomers). Considering these facts and the structures of compounds 7–9, it can be deduced that each enantiomer of 4° may couple through its C⁴ atom to the C⁶ atom of both enantiomers (thus leading to compounds 7 and 8 as racemic mixtures) and to the C⁴ atom of the opposite enantiomer (thus leading to compound 9 as a racemic mixture). Most probably, steric factors are responsible for the nonoccurrence (at least to an observable extent) of C⁶–C⁶ couplings between molecules of any enantiomer and C⁴–C⁴ couplings between molecules of the same enantiomer.

The cyclic voltammogram of compound **3**[BF₄] also shows an irreversible reduction at any scan rate, but the reduction potential, $E_{\rm red} \approx -0.86$ at 0.200 V s⁻¹, is lower than that of **4**[BF₄] ($E_{\rm red} \approx -0.70$ at 0.200 V s⁻¹), in agreement with the fact that the LUMO of **3**⁺, which has a DFT-calculated energy of -6.841 eV, is more stable than the LUMO of **4**⁺ (-6.371 eV). The reaction of **3**[BF₄] with cobaltocene was also performed, but [Ru₃(CO)₁₂] was the only metal-containing product that could be isolated.

The reductive intermolecular formation of C-C bonds between ligands of transition-metal clusters has only been previously observed for $[Ru_3(\mu-H)(\mu-\kappa^2 N^1, C^2-LMe)(CO)_{10}]^+$ (HLMe = N-methylpyrazinium, N-methylquinoxalinium)but there are a few examples of related couplings in mononuclear chemistry. In general, these metal complexes are cationic and have ligand-based LUMOs. This is the case for the diazoalkane amido complexes $[Mo{4-RC_6H_4C(H)NN}(N'Bu Ar)_{3}$ ⁺ (various R and Ar), which dimerize at the diazoalkane C atom, ¹⁹ the salophen derivatives [M(salophen)]ⁿ⁺ (M = Ni, ²⁰ Ti, 21 V, 21 Mn²²), which undergo a reversible dimerization at a ligand C atom, the 2,2'-bipyridine alkylidyne complex [W] $CC_6H_4NMe_2$)(κ^2N_2 -bipy)(NCMe)(CO)₂]⁺, which dimerizes at a bipy C atom,²³ some propargyl cobalt complexes, which dimerize at a ligand C atom, 24 and the carbene derivative [Cr(= $CNEt_2)(CO)_5]^+$, which dimerizes at the carbene C atom.²⁵ It has been reported that the reaction of the titanium complex *trans*-[TiCl₂($\kappa^2 N_2$ -tmeda)₂] (tmeda = Me₂NCH₂CH₂NMe₂) with acetonitrile leads to the reductive coupling of the latter, affording the dimetallic eneimido derivative trans-[Ti2Cl4-{ μ - $\kappa^2 N_2$ -NC(Me)=(Me)CN}($\kappa^2 N_2$ -tmeda)₂].²⁶ In contrast, the reductive dimerization of complexes with metal-based LUMOs leads to dimers with a new metal-metal bond, as is the case for the trinuclear clusters [Ru₃(μ_3 - $\kappa^2 N_2$ -Hampy)(CO)₁₀]⁺ (H₂ampy = 2-amino-6-methylpyridine)^{$\tilde{2}7$} and [Pd₃(μ_3 - κ^7 -C₇H₇)₂(MeCN)₃]²⁺,²⁸ which give hexanuclear products with seven metal-metal bonds.

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Concluding Remarks

The present work has demonstrated that triruthenium cluster compounds having cationic ligands derived from *N*-methylpyrimidinium (compounds 3^+ and 4^+) can be prepared by methylation with [Me₃O][BF₄] of the uncoordinated N atoms of neutral precursors containing ortho-metalated pyrimidine ligands (compounds 1 and 2). DFT calculations have shown that these cationic complexes have ligand-based LUMOs. The ligand of 4^+ has been transformed into various NHC ligands by treating the complex with K-Selectride (compounds 5 and 6) and cobaltocene (compounds 7-9). The N-heterocyclic ligands of 5-9, which have two N atoms in a six-membered ring and a doubly metalated N atom, constitute novel types of N-heterocyclic carbenes.

Experimental Section

General Data. Solvents were dried over sodium diphenyl ketyl (hydrocarbons, diethyl ether, THF) or CaH₂ (dichloromethane) and distilled under nitrogen before use. The reactions were carried out under nitrogen, using Schlenk-vacuum-line techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region) and/or spot TLC. IR spectra were recorded in solution on a Perkin-Elmer Paragon 1000 FT spectrophotometer. ¹H NMR spectra were run on a Bruker DPX-300 instrument, using the dichloromethane solvent resonance as internal standard (δ 5.30). Microanalyses were obtained from the University of Oviedo Analytical Service. (+)-FAB mass spectra were obtained from the University of Santiago de Compostela Mass Spectrometric Service; data given refer to the most abundant molecular ion isotopomer.

 $[\operatorname{Ru}_{3}(\mu-\mathrm{H})(\mu-\kappa^{2}N^{1},C^{6}-\operatorname{pym})(\mathrm{CO})_{10}](1) \text{ and } [\operatorname{Ru}_{3}(\mu-\mathrm{H})(\mu-\kappa^{2}N^{1},C^{6}-\operatorname{pym})(\mathrm{CO})_{10}](1)$ C^{2} -pym)(CO)₁₀] (2). A solution of [Ru₃(CO)₁₂] (500 mg, 0.782 mmol) and pyrimidine (68 µL, 0.860 mmol) in THF (50 mL) was stirred at reflux temperature for 2.5 h. The solvent was removed under reduced pressure, and the resulting residue was redissolved in dichloromethane (4 mL). This solution was supported on preparative silica gel TLC plates. Hexane/diethyl ether (2/1)eluted three yellow bands. The first one contained a small amount of [Ru₃(CO)₁₂]. The second and third bands contained compounds 1 (190 mg, 37%) and 2 (134 mg, 26%), respectively. Data for 1 are as follows. Anal. Calcd for C₁₄H₄N₂O₁₀Ru₃ (663.40): C, 25.35; H, 0.61; N, 4.22. Found: C, 25.42; H, 0.66; N, 4.18. (+)-FAB MS: m/z 665 $[M]^+$. IR (CH₂Cl₂): ν_{CO} 2101 (w), 2064 (s), 2051 (vs), 2024 (m), 2012 (m), 1983 (sh). ¹H NMR (CD₂Cl₂, 293 K): δ 8.51 (d, J = 1.6 Hz, 1 H, CH), 7.99 (d, J = 5.0 Hz, 1 H, CH), 7.49 (dd, J = 5.0, 1.6 Hz, 1 H, CH), -14.53 (s, 1 H, μ -H). ¹³C{¹H}

NMR (CD₂Cl₂, 293 K): δ 207.4 (CO), 205.9 (CO), 200.7 (CO), 200.4 (CO), 199.2 (2 COs), 195.6 (CO), 195.4 (CO), 191.7 (CO), 190.8 (CO), 189.4 (C), 160.5 (CH), 150.0 (CH), 136.0 (CH). Data for **2** are as follows. Anal. Calcd for C₁₄H₄N₂O₁₀Ru₃

(663.40): C, 25.35; H, 0.61; N, 4.22. Found: C, 25.34; H, 0.61; N, 4.17. (+)-FAB MS: m/z 665 $[M]^+$. IR (CH₂Cl₂): ν_{CO} 2101 (w), 2064 (s), 2051 (vs), 2024 (m), 2012 (m), 1983 (sh). ¹H NMR (CD₂Cl₂, 293 K): δ 8.44 (dd, J = 4.8, 2.4 Hz, 1 H, CH), 8.07 (dd, J = 5.6, 2.4 Hz, 1 H, CH), 6.86 (dd, J = 5.6, 4.8 Hz, 1 H, CH), -14.48 (s, 1 H, μ -H). ¹³C{¹H} NMR (CD₂Cl₂, 293 K): δ 207.9, 205.9, 200.8, 200.6, 195.4, 195.1, 194.5, 192.3, 191.2, 189.6 (10 COs), 185.9 (C), 157.7 (CH), 155.7 (CH), 117.3 (CH). **[Ru₃(\mu-H)(\mu-k^2N^1, C⁶-pymMe)(CO)₁₀][BF₄]** (**3[BF₄]).** Solid

 $[\mathbf{Ru}_3(\boldsymbol{\mu}-\mathbf{H})(\boldsymbol{\mu}-\kappa^2 N^4, \mathbf{C}^6$ -pymMe)(CO)₁₀][BF₄] (3[BF₄]). Solid [Me₃O][BF₄] (200 mg, 1.352 mmol) was added to a solution of compound 1 (190 mg, 0.286 mmol) in dichloromethane (40 mL). After it was stirred at room temperature for 24 h, the solution changed from yellow to orange and contained some orange solid. The solvent was removed under reduced pressure, and the resulting residue was redissolved in acetone (2 × 15 mL). The filtered solution was evaporated to dryness, and the residue was washed with diethyl ether (2 × 10 mL) to give 3[BF₄] as a yellow

solid (178 mg, 81%). Anal. Calcd for $C_{15}H_7BF_4N_2O_{10}Ru_3$ (765.24): C, 23.54; H, 0.92; N, 3.66. Found: C, 23.58; H, 0.97; N, 3.62. (+)-FAB MS: m/z 679 $[M - BF_4]^+$. IR (CH₂Cl₂): ν_{CO} 2108 (w), 2074 (s), 2062 (vs), 2028 (s), 2016 (s). ^TH NMR (acetone- d_6 , 293 K): δ 9.81 (d, J = 1.2 Hz, 1 H, CH), 8.51 (dd, J = 6.3, 1.2 Hz, 1 H, CH), 8.47 (d, J = 6.3 Hz, 1 H, CH), 4.35 (s, 3 H, CH₃), -14.44 (s, 1 H, μ -H). ¹³C{^TH} NMR (acetone- d_6 , 293 K): δ 203.1, 202.9, 200.4, 199.5, 197.2, 194.0, 192.6, 191.6, 190.7, 188.4 (10 COs), 184.2 (C), 154.4 (CH), 140.5 (CH), 135.7 (CH), 44.7 (CH₃). Cyclic voltammetry: E_{red} (scan rate) -0.83 V (0.05 V s⁻¹), -0.84 V (0.10 V s⁻¹), -0.86 V (0.20 V s⁻¹).

[**Ru**₃(*μ*-**H**)(*μ*-*κ*²*N*¹,*C*²-**pymMe**)(**CO**)₁₀][**BF**₄] (4[**BF**₄]). This product was prepared as described above for 3[**B**F₄], using compound **2** (134 mg, 0.202 mmol) and [Me₃O][**B**F₄] (138 mg, 0.933 mmol) as starting materials. It is a yellow-orange solid (101 mg, 65%). Anal. Calcd for C₁₅H₇BF₄N₂O₁₀Ru₃ (765.24): C, 23.54; H, 0.92; N, 3.66. Found: C, 23.55; H, 0.94; N, 3.63. (+)-FAB MS: *m*/*z* 679 [*M* – **B**F₄]⁺. IR (CH₂Cl₂): ν_{CO} 2113 (w), 2079 (s), 2067 (vs), 2044 (w) 2020 (m, br), 2016 (s). ¹H NMR (acetone*d*₆, 293 K): δ 9.32 (dd, *J* = 5.1, 1.5 Hz, 1 H, CH), 9.23 (dd, *J* = 6.6, 1.5 Hz, 1 H, CH), 7.85 (dd, *J*_{H−H} = 6.6, 5.1 Hz, 1 H, CH), 4.60 (s, 3 H, CH₃), −14.12 (s, 1 H, *μ*-H). ¹³C{¹H} NMR (acetone-*d*₆, 293 K): δ 206.8, 205.8, 202.9, 200.1, 199.9, 193.6, 192.3, 190.2, 189.9, 187.6 (10 COs), 184.6 (C), 164.2 (CH), 153.6 (CH), 119.1 (CH), 50.3 (CH₃). Cyclic voltammetry: E_{red} (scan rate) −0.66 V (0.05 V s⁻¹), −0.68 V (0.10 V s⁻¹), −0.70 V (0.20 V s⁻¹).

[Ru₃(μ -H){ μ - $\kappa^2 N^1$, C^2 -(6-HpymMe)}(CO)₉] (5) and [Ru₃(μ -H)-{ μ - $\kappa^2 N^1$, C^2 -(4-HpymMe)}(CO)₉] (6). A THF solution of K-Selectride (78 μ L, 1 M, 0.078 mmol) was added dropwise to a solution of 4[BF₄] (60 mg, 0.078 mmol) in the same solvent. The color changed from yellow to orange. After the mixture was stirred for 1 h, the solvent was removed under reduced pressure and the resulting residue was redissolved in dichloromethane (3 mL) and was supported on preparative silica gel TLC plates. Dichloromethane/ hexane (2/1) eluted four yellow bands. The first and fourth bands contained small amounts of [Ru₃(CO)₁₂] and compound **2**, respectively. The second and third bands contained compounds **5** (8 mg, 16%) and **6** (12 mg, 24%), respectively.

Data for **5** are as follows. Anal. Calcd for $C_{14}H_8N_2O_9Ru_3$ (651.43): C, 25.81; H, 1.24; N, 4.30. Found: C, 25.88; H, 1.30; N, 4.21. (+)-FAB MS: m/z 653 $[M]^+$. IR (CH₂Cl₂): ν_{CO} 2083 (w), 2055 (s), 2029 (vs), 1999 (m, br), 1967 (w, sh), 1950 (w, br). ¹H NMR (CD₂Cl₂, 293 K): δ 6.04 (dt, J = 7.6, 1.6 Hz, 1 H, CH), 5.17 (dt, J = 7.6, 4.0 Hz, 1 H, CH), 3.65 (dd, J = 4.0, 1.6 Hz, 2 H, CH₂), 3.40 (s, 3 H, CH₃), -14.53 (s, 1 H, μ -H). ¹³C{¹H} and DEPT NMR (CD₂Cl₂, 293 K): δ 209.7 (C), 204.2 (br, COs), 195.5 (br, COs), 128.3 (CH), 107.0 (CH), 62.4 (CH₂), 42.7 (CH₃).

Data for **6** are as follows. Anal. Calcd for $C_{14}H_8N_2O_9Ru_3$ (651.43): C, 25.81; H, 1.24; N, 4.30. Found: C, 25.85; H, 1.31; N, 4.24. (+)-FAB MS: m/z 653 $[M]^+$. IR (CH₂Cl₂): ν_{CO} 2082 (w), 2054 (vs), 2020 (vs), 1998 (m, a), 1969 (w, sh), 1948 (w, br). ¹H NMR (CD₂Cl₂, 293 K): δ 5.27 (dt, J = 7.8, 2.0 Hz, 1 H, CH), 4.93 (dt, J = 7.8, 3.2 Hz, 1 H, CH), 4.04 (dd, J = 3.2, 2.0 Hz, 2 H, CH₂), 3.33 (s, 3 H, CH₃), -14.07 (s, 1 H, μ -H). ¹³C{¹H} and DEPT NMR (CD₂Cl₂, 293 K): δ 206.1 (C), 205.0 (br, COs) (COs), 196.0 (br, COs), 144.2 (CH), 103.4 (CH), 46.8 (CH₂), 44.3 (CH₃).

196.0 (br, COs), 144.2 (CH), 103.4 (CH), 46.8 (CH₂), 44.3 (CH₃). **[Ru₆(\mu-H)₂{\mu_6-\kappa^4 N^1,N^1,C^2,C^{2\prime}-(4,6'-bipymMe₂)}(CO)₁₈] (Isomers 7 and 8) and [Ru₆(\mu-H)₂{\mu_6-\kappa^4 N^1,N^1,C^2,C^{2\prime}-(4,4'bipymMe₂)}(CO)₁₈] (Isomer 9**). Solid cobaltocene (20 mg, 0.105 mmol) was added to a solution of 4[BF₄] (80 mg, 0.105 mmol) in THF (30 mL). The color changed immediately from yellow to dark orange. After it was stirred for 10 min, the mixture was concentrated to ca. 3 mL and the resulting solution was supported on silica gel TLC plates. Hexane/dichloromethane (2/1) eluted seven yellow bands. The first one contained a small amount of [Ru₃(CO)₁₂]. The second and third bands contained compounds 7 (6 mg, 8%) and 8 (6 mg, 8%), respectively. The fourth and fifth bands contained small amounts of mixtures of unidentified compounds. The sixth band contained compound 9 (12 mg, 18%). The seventh band contained a small amount of compound 2.

Data for 7 are as follows. Anal. Calcd for C₂₈H₁₄N₄O₁₈Ru₆ (1300.86): C, 25.85; H, 1.08; N, 4.31. Found: C, 25.92; H, 1.15; N, 4.24. (+)-FAB MS: m/z 652 $[M/2]^+$. IR (CH₂Cl₂): ν_{CO} 2083 (w), 2050 (vs), 2034 (s), 2001 (m, br), 1972 (w, sh), 1953 (w, sh). ¹H NMR (CD₂Cl₂, 293 K): δ 6.22 (d, J = 8.0 Hz, 1 H, CH), 5.38 (d, J = 7.5 Hz, 1 H, CH), 4.98 (dd, J = 8.0, 5.1 Hz, 1 H, CH),4.67 (dd, J = 7.5, 4.3 Hz, 1 H, CH), 4.30 (d, J = 4.3 Hz, 1 H, CH), 3.93 (d, J = 5.1 Hz, 1 H, CH), $3.29 (s, 3 H, NCH_3)$, $3.24 (s, 3 H, NCH_3)$, 3.24 (s, 3 H,3 H, NCH₃), -14.06 (s, 1 H, μ -H), -15.45 (s, 1 H, μ -H). $^{13}C{^{1}H}$ and DEPT NMR (CD₂Cl₂, 293 K): 8 210.1 (C), 204.3 (br, COs), 200.3 (br, COs), 193.5 (br, COs), 192.5 (br, COs), 173.5 (C), 145.2 (CH), 131.2 (CH), 103.7 (CH), 103.3 (CH), 75.6 (CHR), 67.9 (CHR), 44.2 (NCH₃), 43.1 (NCH₃).

Data for 8 are as follows. Anal. Calcd for C₂₈H₁₄N₄O₁₈Ru₆ (1300.86): C, 25.85; H, 1.08; N, 4.31. Found: C, 25.94; H, 1.14; N, 4.22. (+)-FAB MS: m/z 652 $[M/2]^+$. IR (CH₂Cl₂): ν_{CO} 2083 (w), 2050 (vs), 2033 (s), 2002 (m, br), 1972 (w, sh), 1953 (w, sh). ¹H NMR (CD_2Cl_2 , 293 K): δ 6.25 (d, J = 7.7 Hz, 1 H, CH), 5.44 (dd, J = 7.9, 1.0 Hz, 1 H, CH), 5.00 (dd, J = 7.7, 5.5 Hz, 1 H, CH), 4.54 (dd, J = 7.9, 4.0 Hz, 1 H, CH), 4.21 (ddd, J = 4.3, 4.0, 1.0 Hz, 1 H,CH), 3.40 (dd, J = 5.5, 4.3 Hz, 1 H, CH), 3.37 (s, 3 H, NCH₃), 3.21 (s, 3 H, NCH₃), -13.96 (s, 1 H, μ -H), -15.07 (s, 1 H, μ -H). ¹³C{¹H} and DEPT NMR (acetone- d_6 , 293 K): δ 208.8 (C), 205.4 (C), 205.1 (br, COs), 204.4 (br, COs), 202.4 (br, COs), 195.2 (br, COs), 193.8 (br, COs), 147.3 (CH), 131.8 (CH), 106.4 (CH), 101.8 (CH), 68.5 (CHR), 66.5 (CHR), 43.6 (NCH₃), 42.9 (NCH₃).

Data for 9 are as follows. Anal. Calcd for C₂₈H₁₄N₄O₁₈Ru₆ (1300.86): C, 25.85; H, 1.08; N, 4.31. Found: C, 25.92; H, 1.13; N, 4.25. (+)-FAB MS: m/z 652 $[M/2]^+$. IR (CH₂Cl₂): ν_{CO} 2083 (w), 2057 (vs), 2032 (s), 2001 (m, br), 1972 (w, sh), 1952 (w, sh). ¹H NMR (CD₂Cl₂, 293 K): δ 5.49 (d, J = 7.3 Hz, 1 H, *CH*), 5.45 (dd, *J* = 7.7, 1.3 Hz, 1 H, *CH*), 4.73 (dd, *J* = 7.7, 3.2 Hz, 1 H, CH), 4.65 (m, 2 H, CH), 4.37 (m, 1 H, CH), 3.45 (s, 3 H, NCH₃), 3.40 (s, 3 H, NCH₃), -14.04 (s, 1 H, μ -H), -14.05 (s, 1 H, μ -H). $^{13}C{}^{1}H{}$ and DEPT NMR (CD₂Cl₂, 293 K): δ 210.6 (C), 209.8 (C), 203.9 (br, COs), 195.3 (br, COs), 195.1 (br, COs), 147.3 (CH), 146.7 (CH), 101.5 (CH), 100.0 (CH), 59.9 (CHR), 57.7 (CHR), 42.9 (NCH₃), 42.5 (NCH₃).

Electrochemical Studies. Cyclic voltammetric measurements were carried out by using an AUTOLAB-III potentiostat connected to a homemade single-compartment micro cell containing a 1 mm platinum disk as working electrode, a platinum wire as auxiliary electrode, and a silver wire as pseudoreference electrode. All measurements were carried out in deoxygenated 0.1 M [NEt₄][BF₄] dichloromethane (freshly distilled from CaH₂) solutions. The concentration of each cluster complex analyte was 0.5×10^{-3} M. To measure potentials, ferrocene was used as internal standard. The [FeCp₂]^{0/+} couple was referenced to $E_{1/2} = 0.59$ V versus SCE. As the reductions of both 3[BF₄] and $4[BF_4]$ were completely irreversible, the given E_{red} values correspond to the reduction peaks at the corresponding scan rate.

Theoretical Calculations. Density functional theory (DFT) calculations were carried out with the Gaussian03 package,²⁹ using Becke's three-parameter hybrid exchange-correlation functional³⁰ and the B3LYP nonlocal gradient correction.³ The LanL2DZ basis set, with relativistic effective core potentials, was used for the Ru atoms.³² The basis set used for the remaining atoms was 6-31G, with addition of (d,p)-polarization.³³ The optimized structures were confirmed as energy minima by analytical calculation of frequencies (all positive eigenvalues). Molecular orbital data were obtained from the natural bond order (NBO) analysis of the data.³⁴ Cartesian atomic coordinates for the optimized structures are given in the Supporting Information.

X-ray Diffraction Analyses. Diffraction data for 4[BF₄] were collected on a Nonius Kappa-CCD diffractometer, using graphite-monochromated Mo Ka radiation. A semiempirical absorption correction was performed with SORTAV.35 Diffraction data for 5, 6, $7 \cdot CH_2Cl_2$, and 8 were collected on a Oxford Diffraction Xcalibur Nova diffractometer, using graphitemonochromated Cu Ka radiation. Empirical absorption corrections were applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED.³⁶ Structures were solved by Patterson interpretation using the program DIRDIF.37 Isotropic and full-matrix anisotropic least-squares refinements were carried out using SHELXL.38 After many crystallization attempts, low-quality crystals of compound 6 were obtained from CH2Cl2/hexane. Its molecular structure could be completely solved from one of these crystals, but anisotropic refinement led to nonpositive-definite ellipsoids for several atoms. Therefore, all nonruthenium atoms were isotropically refined in the final model. All non-H atoms of all the other structures were refined anisotropically. Hydride atom positions were calculated with the program XHYDEX.³⁹ The remaining hydrogen atoms were set in calculated positions and refined riding on their parent atoms. The molecular plots were made with the PLATON program package.⁴⁰ The WINGX program system⁴¹ was used throughout the structure determinations. A selection of crystal, measurement, and refinement data is given as Supporting Information. CCDC deposition numbers: 807868 (4[BF₄]), 807869 (5), 807870 (6), 807871 (7 · CH₂Cl₂), and 807872 (8).

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Supporting Information Available: Atomic coordinates of the structures optimized by DFT calculations (Tables S1 and S2), a selection of crystal, measurement, and refinement data for the compounds studied by X-ray diffraction (Table S3), and CIF files giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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