


Probing Intermetallic Coupling in Dinuclear N-Heterocyclic Carbene Ruthenium(II) Complexes

Laszlo Mercs,[†] Antonia Neels,[‡] Helen Stoeckli-Evans,[‡] and Martin Albrecht^{*,†,§}

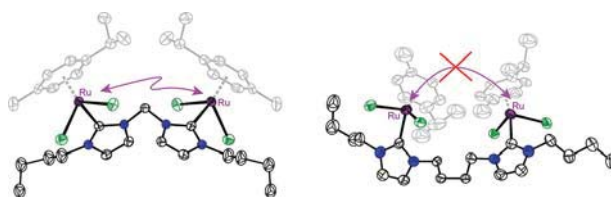
[†]Department of Chemistry, University of Fribourg, Chemin du Musée 9, CH-1700 Fribourg, Switzerland

[‡]XRD Application Lab, Centre Suisse d'Electronique et de Microtechnique (CSEM), Rue Jaquet-Droz 1, CH-2002 Neuchâtel, Switzerland

[§]School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland

 Supporting Information

ABSTRACT: A series of bimetallic N-heterocyclic carbene (NHC) ruthenium(II) complexes were synthesized, which comprise two $[\text{RuCl}_2(\text{cymene})(\text{NHC})]$ units that are interlinked via the NHC nitrogens by alkyl chains of different length. Electrochemical characterization revealed two mutually dependent oxidation processes for the complex with a methylene linker, indicating moderate intramolecular electronic coupling of the two metal centers (class II system). The degree of coupling decreases rapidly upon increasing the number of CH_2 units in the linker and provides essentially decoupled class I species when propylene or butylene linkers are used. Electrochemical analyses combined with structural investigations suggest a through-bond electronic coupling. Replacement of the alkyl linker with a *p*-phenylene group afforded cyclometalated complexes, which were considerably less stable. The electronic coupling in the methylene-linked complex and the relatively robust NHC–ruthenium bond may provide access to species that are switchable on the molecular scale.



■ INTRODUCTION

N-heterocyclic carbenes (NHCs) have had and continue to have an enormous influence on the development of new and highly powerful catalysts based on transition metals.^{1,2} The success of NHCs as ligands has been largely associated with their unique donor properties paired with the strong bond they typically form with transition metals.³ Despite the rapid evolution of these ligands from niche compounds to some of the most relevant scaffolds for transition metal chemistry, the application of NHC ligands in domains other than catalysis has remained scarce.⁴ Perhaps most impressive achievements in noncatalytic domains encompass the exploitation of anticarcinogenic⁵ and antimicrobial activities⁶ of some NHC metal complexes. Applications in other domains such as molecular electronics have been very limited thus far. This seems remarkable, especially when considering the potential of the metal–NHC synthon in such areas, imparted in particular by the significant π character of the $\text{M}–\text{C}$ bond established for various metal NHC complexes.^{7,8} This bonding situation is expected to enhance the electronic coupling between a redox-active metal center and the ligand,⁹ for example, for catalyst (de)activation,¹⁰ and constitutes a pivotal prerequisite for the construction of transition metal-based molecular diodes.¹¹ Specifically, electronic communication between metal and ligand provides access to metal–metal interactions in bimetallic systems, which is essential for generating mixed-valent species,¹² and which offers advantages for the fabrication of electronically active devices such as switches or junctions in molecular wires.¹³ The most successful linkers used today are bi- and terpyridines,¹⁴ and

(poly)acetylenes.¹⁵ Because of their synthetic flexibility and the covalent $\text{M}–\text{C}$ bond, NHCs have great potential for combining the benefits of both types of linkers.

Only recently ditopic NHC ligands have emerged as potentially conjugated spacers for interlinking two metal centers.¹⁶ The dicarbene spacer A (Figure 1), pioneered by Bielawski and co-workers,¹⁷ provides a versatile platform for the formation of bimetallic complexes. Despite the apparent conjugation between the two carbene sites, only very weak intermetallic interactions were observed with different metals (Fe, Ru, Ir).¹⁸ Such weak coupling has been attributed tentatively to a small orbital overlap between the NCN amidylidene fragment and the central benzene ring, resulting in an insulating effect of this spacer unit.^{18a} With heavy transition metals such as iridium, an energy mismatch between the metal 5d orbitals and the carbene 2p orbitals constitutes an additional barrier to electronic metal–metal coupling.^{18b,19} Consistent with these considerations, related ditopic ligands such as the dicarbene B are less efficient spacers.²⁰ In contrast, interconnection of the two ligating carbene sites via the nitrogen atom as in C and D may alleviate the insulating effects encountered with spacer A and may thus stimulate metal–metal interactions. Because of the intrinsic attenuation factor of a CH_2 unit ($\beta = 0.88$) for electron tunneling,²¹ the number of methylene units in the spacer in C should provide a methodology for modulating the intermetallic communication, whereas a phenylene linker as in D is expected to enhance electronic

interactions due to π -conjugation. Here we have explored both approaches and report on a series of bimetallic complexes featuring ruthenium(II) centers interlinked by methylene-bridged dicarbene ligands of type C. Variation of the alkyl unit allows for tailoring the degree of communication between the metal centers, while reversible cycloruthenation renders phenylene spacers of type D inappropriate for such electronic applications.

RESULTS AND DISCUSSION

Synthesis of Dinuclear Ruthenium(II)–NHC Complexes.

The bimetallic ruthenium(II) complexes **2** comprising bridging NHC ligands were synthesized from the corresponding diimidazolium salts **1**²² by transmetalation according to modified procedures (Scheme 1).²³ Notably, the preparation of the Ag-carbene intermediates proceeded much cleaner in warm MeCN than from CH₂Cl₂ solution. Subsequent carbene transfer to [Ru(η^6 -*p*-cymene)Cl₂]₂ was performed in the case of short linkers ($n = 1, 2$) by gradual warming of a frozen CH₂Cl₂ suspension of the silver-carbene complex in the presence of a solution containing the ruthenium(II) precursor. Under these conditions, chelation of the dicarbene ligand²⁴ was successfully prevented.

Formation of the bimetallic complexes **2a–d** was indicated by the expected 1:1 cymene/imidazolylidene ratio in the ¹H NMR spectra. Typically, the cymene protons appear as two pairs of doublets, suggesting a locked conformation of the arene rings in solution. Furthermore, the NCH₂ protons of the *n*Bu wingtip group are magnetically inequivalent and gave two distinct sets of multiplets as a direct consequence of the restricted rotation about the Ru–C_{carbene} bonds. Similar behavior was observed for the monometallic model complex **3** comprising a monotopic NHC ligand,^{18a} and also for related dinuclear rhodium(I) complexes^{23a} containing the same type of ditopic carbene ligands.

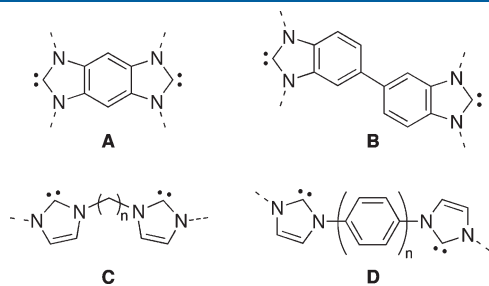
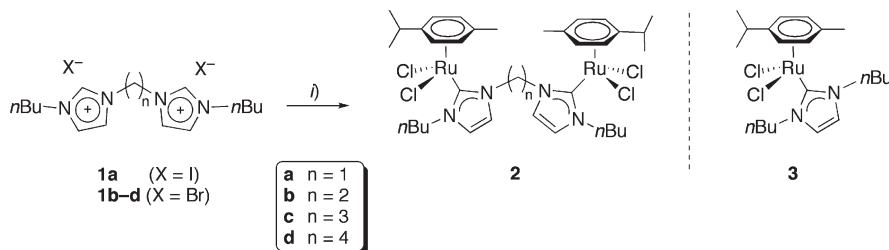


Figure 1. Generic forms of ditopic dicarbene ligands as potential spacers for interconnecting two redox-active sites.

Scheme 1. Synthesis of Bimetallic Ruthenium(II) Carbene Complexes **2** and the Corresponding Monometallic Model Compound **3**^a



^a Reagents and conditions: (i) Ag₂O, MeCN, +40 °C, 16 h, then [RuCl₂(cymene)]₂, CH₂Cl₂, –196 °C to RT or RT, 16 h.

The room temperature ¹H NMR spectrum of **2c** revealed broad signals. Fluxional behavior was evidenced by variable temperature experiments. At –20 °C, three doublets (1:1:2 integral ratio) were observed for the cymene protons, which merged into two doublets (1:1 ratio) upon heating the solution to +55 °C. From the coalescence temperature, $T_c = 300(\pm 2)$ K, an approximate activation energy $\Delta G^\ddagger = 63.6(\pm 0.4)$ kJ mol^{–1} was calculated for this process, tentatively attributed to rotation about the Ru–C_{carbene} bond. Similar behavior and an essentially identical activation energy was also noted for **2d** ($T_c = 311(\pm 2)$ K, $\Delta G^\ddagger = 63.0(\pm 0.4)$ kJ mol^{–1}). The barrier is slightly lower in the related mononuclear complex **3** ($\Delta G^\ddagger = 58.6(\pm 0.6)$ kJ mol^{–1}, $T_c = 311(\pm 3)$ K),^{18a} thus reflecting a larger rigidity in bimetallic as opposed to monometallic species. In addition, two full sets of signals were observed for **2d** at the slow exchange limit (–20 °C), which suggests the presence of two diastereomers (approximately 1:1 integral ratio) originating from chirality at ruthenium upon locking the relative cymene/carbene orientation. Consistent with this model, two distinct carbene resonances were observed at room temperature (δ_C 173.2, 172.9). Similar diastereomeric mixtures were observed in bimetallic Rh₂–(NHC)₂ complexes.^{23a,c} Upon warming, the two sets coalesce ($T_c = 290(\pm 2)$ K for the cymene signals, $\Delta G^\ddagger = 59.8(\pm 0.4)$ kJ mol^{–1}), thus suggesting epimerization of the complexes.

Solid-State Structures. Suitable crystals of **2a** and **2d** were analyzed by X-ray diffraction. The molecular structure of **2a** (Figure 2) confirms the bridging coordination mode of the ditopic carbene ligand as presumed from solution measurements. The unit cell contains two crystallographically independent molecules of **2a**, which differ in their distinct orientation of the arene substituents.²⁵ Moreover, the Ru···Ru distances in the two molecules vary considerably (7.0244(5) Å and 7.2614(6) Å, respectively). Bond lengths and angles around the ruthenium centers are unexceptional.^{18a,23,26} Short intramolecular contacts between all chlorides and NCH₂ hydrogens were observed. For example, the two hydrogen atoms of the CH₂ bridge engage in a C–H···Cl interaction with chlorides bound to different ruthenium centers (average H···Cl distance 2.60 Å).

Remarkably, the intramolecular Ru···Ru distance in the molecular structure of complex **2d** (Figure 3a) is 6.4268(12) Å and hence shorter than in the methylene-bridged analogue **2a** (>7.0 Å). This shorter metal–metal separation illustrates the increased flexibility of the alkyl linker between the heterocycles in **2d**. While the molecular parameters (bond lengths and angles, and also the short intramolecular C–H···Cl–Ru contacts) are similar to those in **2a**, the packing diagram of **2d** is different and shows a lamellar structure consisting of layers of molecules in the *ab* plane (Figure 3b). Four molecules form a channel, which is

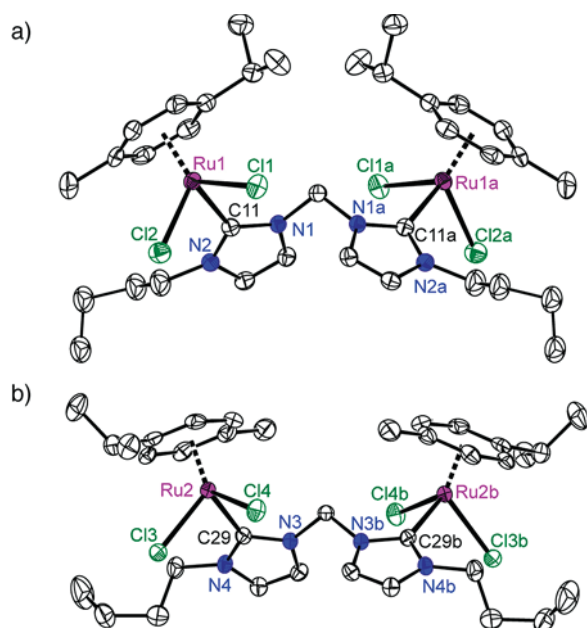


Figure 2. ORTEP representation of the two independent molecules in the unit cell of complex **2a** (50% probability ellipsoids, H atoms omitted for clarity; only one of the two disordered positions of the CH_2CH_3 moiety of the *n*Bu group is shown in a).

Table 1. Selected Bond Lengths (Å) and Angles (deg) of Complexes **2a** and **2d**^a

	2a		2d	
	molecule 1	molecule 2	east part	west part
Ru—C	2.084(4)	2.071(3)	2.070(9)	2.106(9)
Ru—Cl	2.4234(10)	2.4105(10)	2.421(2)	2.414(3)
Ru—Cl	2.4287(10)	2.4317(10)	2.442(3)	2.445(2)
Ru—C _{centroid}	1.7054(16)	1.6789(16)	1.696(5)	1.699(5)
Ru...Ru	7.2614(6)	7.0244(5)	6.4268(12)	

^a Molecule 1 and molecule 2 refer to the two crystallographically independent molecules in the asymmetric unit of **2a**, east and west parts refer to the Ru1 and Ru2 fragments, respectively, of complex **2d**.

filled by molecules from adjacent layers. The intermolecular metal—metal distance is 7.368 Å and thus slightly longer than the intramolecular metal separation. The specific organization of the molecules may suggest some degree of self-assembly. However, we have not succeeded in identifying any specific intermolecular contacts that may point to secondary interactions such as van der Waals or π — π interaction.

(Spectro)Electrochemistry. The electronic properties of these bimetallic complexes were evaluated by electrochemical analysis in CH_2Cl_2 as noncoordinating solvent to avoid ligand exchange between the halide ligands and the solvent molecules. Cyclic voltammetry (CV) showed two partially reversible oxidations for **2a** with an $i_{\text{pc}}/i_{\text{pa}}$ ratio considerably lower than 1 (vide infra). The two distinct anodic peaks are located at $E_{\text{pa}}^1 = 1.20$ V and $E_{\text{pa}}^2 = 1.48$ V vs SCE (Figure 4a) and insinuate electronic coupling of the metal centers. The first oxidation potential compares well with the anodic peak potential of the monometallic analogue **3** ($E_{\text{pa}} = 1.09$ V vs SCE) and points to a similar

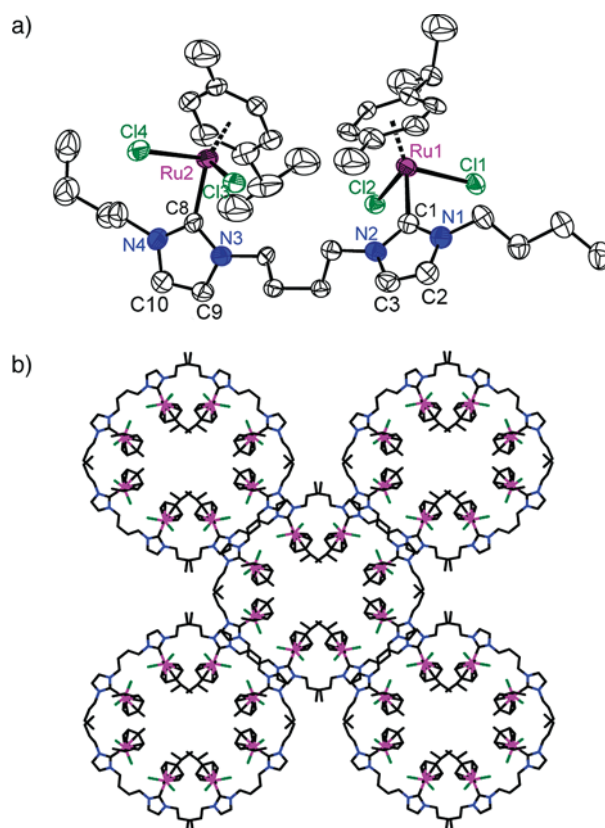


Figure 3. (a) ORTEP representation of **2d** (30% probability ellipsoids; H atoms and cocrystallized Et_2O molecule omitted for clarity) and (b) packing diagram showing the channel-type ordering of the molecules.

redox step in both complexes. For the complexes **2b–d**, the separation of the two oxidation potentials was less evident by CV, and differential pulse voltammetry (DPV) measurements were used to better distinguish the two processes (Figure 4b, Table 2). The separation of the two oxidation potentials gradually decreases as the number of methylene units between the carbene moieties is increased.

While complexes **2c** and **2d** revealed almost symmetric signals, the redox processes of **2a** and **2b** are more complicated as indicated by the asymmetric shape of the DPV signals. Deconvolution using the monometallic complex **3** as a reference indeed revealed an appropriate fit if the first unusually broad redox process of **2a** is surmised to consist of two one-electron processes centered at +1.15 V and +1.24 V, respectively.²⁵ The subsequent oxidation at +1.41 V then corresponds to a two-electron process. Analogous deconvolution of the signal due to **2b** suggests an initial two-electron oxidation at +1.13 V, followed by two one-electron oxidations at +1.21 and +1.31 V, respectively. Accordingly, the two well-resolved signals for **2c** and **2d** presumably reflect two two-electron processes. Tentatively, these processes have been assigned to a stepwise oxidation of Ru^{II} to Ru^{IV} , which is essentially decoupled in **2c** and **2d**, yet weakly coupled in **2a** and **2b**. In such a superexchange model, the first one-electron step produces in **2a** a mixed-valent $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ species, and a mixed-valent $\text{Ru}^{\text{III}}/\text{Ru}^{\text{IV}}$ species when starting from **2b**. Our data do not allow for rationalizing the different behavior of **2a** and **2b**. We speculate that coupling of the Ru^{III} centers in **2b** ensues because of the flexibility of the ethylene linker, which allows the two ruthenium centers to be bridged by halides. Such a conformation is inhibited by the

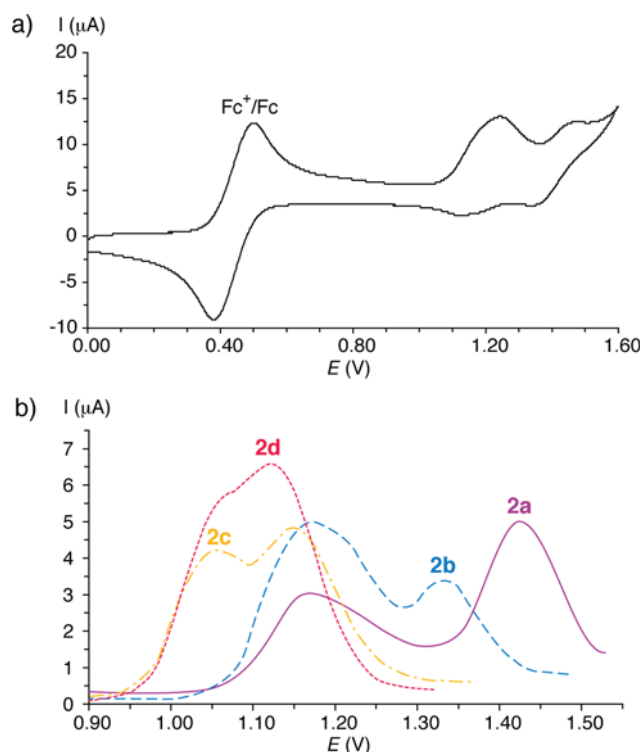


Figure 4. (a) Cyclic voltammogram of complex **2a** (Fc^+/Fc as internal reference) and (b) differential pulse voltammograms of **2a–d**.

Table 2. Electrochemical Data and Comproportionation Constants of Ru^{II} Complexes^a

entry	complex	E_{pa}/V^a	e^- ratio	$\Delta E_{1/2}/\text{mV}^b$	$\log K_c^c$
1	2a	1.15, 1.24, 1.41	1:1:2	88	1.49
2	2b	1.13, 1.21, 1.31	2:1:1	108	1.83
3	2c	1.06, 1.15	1:1		
4	2d	1.06, 1.12	1:1		
6	3^d	1.09			

^a Measured in CH_2Cl_2 , 0.1 M $[\text{Bu}_4\text{N}]\text{PF}_6$ electrolyte, sweep rate 20 mV s^{-1} , calibrated to Fc^+/Fc ($E_{1/2} = 0.46 \text{ V}$ vs SCE), potentials determined by DPV and signal deconvolution (ΔE not resolved apart from the $2e^-$ oxidation of **2a** at 1.41 V ($\Delta E = 145 \text{ mV}$)). ^b Determined for the one-electron processes only, i.e. the first two oxidations in **2a** and the second two oxidations in **2b**. ^c Calculated according to eq 1. ^d From ref 18a.

methylene linker in **2a**. This model insinuates that metal–metal coupling through the NHC-linker-NHC scaffold only occurs in **2a**, while in **2b**, the coupling is imparted by the bridging halide.

The comproportionation constant K_c for complexes for the one-electron processes in **2a** and **2b** was determined using eq 1

$$K_c = 10^{\Delta E_{1/2}/59 \text{ mV}} \quad (1)$$

where $\Delta E_{1/2}$ is the potential difference between the two oxidations. Accordingly, complexes **2a** and **2b** are classified as typical class II systems featuring a charge-localized mixed-valent state.²⁷ These results suggest that one or perhaps two sp^3 -hybridized methylene units between the NHC ligands enable the electron transfer between the two redox-active metal centers. Similar conclusions have been drawn from studies on alkyl-containing molecular rectifiers.²⁸ Recalling the large electron-tunnelling attenuation factor

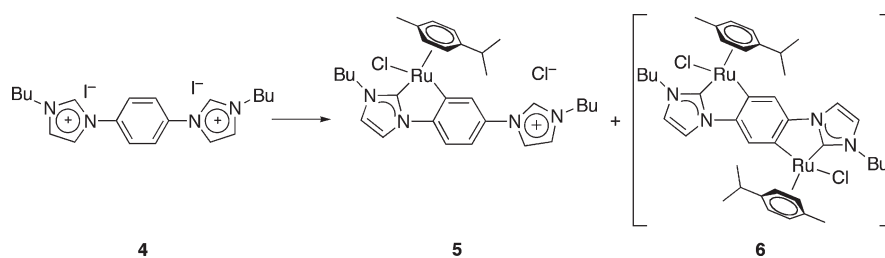
for alkane junctions ($\beta \sim 0.85–1.0$),²¹ the resistance in complexes **2** is indeed expected to increase significantly upon insertion of additional CH_2 groups.²⁹ In an alternative model featuring through-space electron transfer, an optimum rather than a minimum number of methylene linker units would be expected to maximize inter-metallic interactions, since the increased flexibility would bring the redox-active centers in closer proximity than they are in the short-linked system **2a** (cf. X-ray data).

Spectroelectrochemical analyses of complex **2a** using an optically transparent thin-layer electrochemical (OTTLE) cell³⁰ were performed to characterize the putative mixed-valent species. A small bathochromic shift of the charge-transfer (CT) band was noted upon oxidation ($\lambda_{\text{max}} = 403 \text{ nm}$). When reducing the potential back to 0 V, a characteristic NIR absorbance³¹ appeared around $\lambda_{\text{max}} = 950 \text{ nm}$. The band was considerably broader than calculated ($\Delta\nu_{1/2(\text{obs})} = 26,000 \text{ cm}^{-1}$ vs $\Delta\nu_{1/2(\text{calcd})} = 5,100 \text{ cm}^{-1}$), thus supporting a charge-localized mixed-valent state (class II).²⁷ Of note, prolonged oxidation (25 min at 1.2 V) induced the gradual formation of a new species characterized by a $\lambda_{\text{max}} = 412 \text{ nm}$, indicative for a slow chemical reaction following the electron-transfer (EC mechanism). The second process was more pronounced when the oxidation potential was raised to 1.5 V. These observations are consistent with an EC mechanism³² and suggest that the fully oxidized $\text{Ru}^{\text{IV}}/\text{Ru}^{\text{IV}}$ species **2a⁴⁺** has only a limited stability, thus corroborating the incomplete reversibility observed in CV measurements.

To elucidate the stability of the oxidized Ru-carbene system, electrochemical investigations were performed on the monometallic complex **3**. Pertinent CV indicate a single quasi-reversible oxidation with a cathodic/anodic current ratio $i_{\text{pc}}/i_{\text{pa}} = 0.6$. The relative cathodic current diminished further when the system was kept at the switching potential $E = 1.3 \text{ V}$ (vs SCE) for prolonged time. After 25 min, the $i_{\text{pc}}/i_{\text{pa}}$ ratio decreased to 0.4, and became as low as 0.2 after 60 min. Obviously, electrochemically generated **3⁺** undergoes an irreversible chemical reaction. This conclusion is further supported by spectroelectrochemical studies on **3**.²⁵ It is in good agreement with the results obtained for **2a** and may provide a rationale for the nonsymmetric intensity of the observed DPV signals (see above). Accordingly, the oxidized carbene complexes, either Ru^{III} or Ru^{IV} , are unstable and thus difficult to access by synthetic methods. Indeed, our preliminary attempts to prepare **2a⁴⁺** by oxidation using $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ gave ill-defined products. Their spectroscopic properties suggest the presence of species similar to those of the product obtained upon prolonged oxidation of **2a** ($\lambda_{\text{max}} = 412 \text{ nm}$).

Modification of the Bridging Ligand. We sought to further increase the metal–metal interaction by exchanging the methylene linker in complex **2a** by a potentially conjugated phenylene unit. Moreover, the introduction of substituents at the arene may allow for incorporating functional groups and perhaps even for rectifying the electronic process. Therefore, the bisimidazolium salt **4**, synthesized by alkylation of the corresponding bisimidazole, was metalated by a procedure identical to that used for the preparation of **2a–d**. The crude reaction mixture revealed two major products which both appeared to originate from cyclometalation. Attempts to separate the product by column chromatography using SiO_2 as stationary phase gave the products only in low yields and generated significant amounts of decomposition products. Higher yields and purer fractions were obtained from column chromatography over Al_2O_3 and subsequent precipitation, thus affording the monometallic species **5** and the bis-cyclometalated complex **6** rather than the anticipated phenylene-linked dicarbene

Scheme 2. Synthesis of Phenylene-Bridged Ru^{II}–NHC Complexes^a



^a Reagents and conditions: Ag₂O, CH₂Cl₂, 40 °C, 16 h, then [RuCl₂(cymene)]₂, CH₂Cl₂, 40 °C, 16 h.

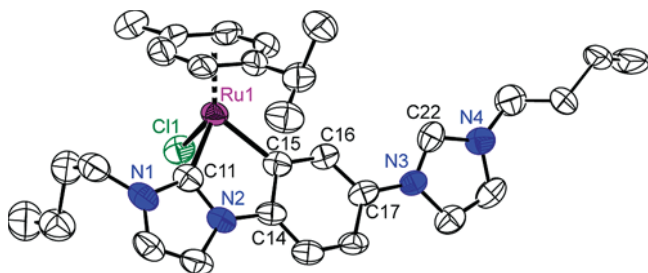


Figure 5. ORTEP representation of **5** (only one of the two independent molecules shown; 30% probability ellipsoids; H atoms and Cl[−] counterion omitted for clarity). Selected bond lengths (Å): Ru1–C11 1.989(12), Ru1–C15 2.072(11), Ru1–C_{centroid} 1.715(6), Ru1–Cl1 2.444(3), C11–N1 1.376(15), C11–N2 1.376(16), C22–N3 1.291(14), C22–N4 1.389(15); bond angles (deg): N1–C11–N2 102.8(10), C11–Ru1–C15 78.0(4), N3–C22–N4 109.2(10).

complex (Scheme 2). Similar cyclometalation of Ru–NHC complexes comprising aryl wingtip groups was observed previously.³³ Apparently, this reactivity pattern is quite general when ruthenium(II) is used as the metal center.

Complex **5** undergoes an immediate color change from orange to green when dissolved in reagent-grade CHCl₃ (EtOH stabilized) or in CDCl₃ (unstabilized). Filtration of the solvent through basic Al₂O₃ suppressed this color change and increased the stability of **5**. The sensitivity of **5** toward CHCl₃ and SiO₂, both slightly acidic, points to a facile acidolysis of the Ru–C_{aryl} bond.³⁴ All NMR spectra of **5** were thus recorded in CDCl₃ that was freshly filtered through a short pad of Al₂O₃. The ¹H NMR spectrum revealed a diagnostic resonance at 11.03 ppm, attributed to the imidazolium NCHN proton. Additionally, two sets of signals for the imidazole-type rings and for the Bu wingtip groups, and four distinct doublets for the cymene aromatic protons were observed. In the ¹³C NMR spectrum, the metal-bound carbons appeared at 188.5 ppm (Ru–C_{NHC}) and at 168.1 ppm (Ru–C_{phenylene}), respectively.³³

Single crystals of **5** were subjected to an X-ray diffraction analysis. The molecular structure comprises a five-membered C,C-ruthenacycle, thus confirming the solution-deduced cyclometalation (Figure 5). The bite angle of the C,C-bidentate ligand is rather acute, C11–Ru1–C15 78.0(4)°. In agreement with other cyclometalated carbene ruthenium complexes,³² the Ru–C_{carbene} bond is shorter (Ru1–C11 1.989(12) Å) than in monodentate systems (cf. **2a** and **2d**). The Ru–C_{Ph} bond is longer (Ru1–C15 2.072(11) Å) and compares well with related systems (2.01–2.14 Å).³² The torsion angle between the carbene and the phenyl ring is 0.2(12)° and illustrates the coplanar arrangement of these rings. In contrast, the imidazolium heterocycle is twisted out of the phenylene plane by 23.0(14)°. Interestingly, the *i*Pr group of the cymene ligand is

located above the phenyl ring. This orientation may also persist in solution as the shielding effect due to the aromatic ring current may explain the unusual upfield shift of the *i*Pr methyl groups observed in solution (δ_{H} 0.6–0.8).

The formation of complex **6** was supported by ¹H NMR spectroscopy, which exhibited a single phenylene resonance (δ_{H} 7.84) in 1:2 Ph/imidazolylidene integral ratio. Additionally, three C_{Ph} resonances were observed in the ¹³C NMR spectrum, indicating ligand desymmetrization because of metalacycle formation. The ruthenium-bound phenylene carbon resonates at δ_{C} 159.1. Solutions of **6** in CDCl₃ were unstable. A gradual transformation to a structurally strongly related complex was noted (*t*_{1/2} = 20 h) and eventual decomposition (within ca. 40 h), as deduced from the accumulation of free cymene. The ¹H NMR spectrum of the intermediate species featured two well-resolved doublets of doublets for the cymene protons, and a low-field shift of one of the imidazolylidene protons.²⁵ Moreover, the α -CH₂ protons of the butyl wingtip group desymmetrize to give two multiplets in the 4.7–4.3 ppm region. Notably, measurements in acetone-*d*₆ do not suggest the formation of a similar intermediate in detectable quantities prior to decomposition (complete within 48 h). The observed solvent-dependence of the transformation suggests that traces of protons may play a critical role in the formation of the intermediate species. On the basis of the above observations and taking into account the planar chirality of the complex, formation of an intermediate from **6** may tentatively be assigned to an acid-catalyzed epimerization process. For example, if the kinetic product is the *rac* isomer, comprising the cymene ligands on the same side of the plane defined by the phenylene spacer unit, steric congestion may constitute a driving force for acid-mediated reversible Ru–C_{phenylene} bond cleavage and for the rearrangement into the thermodynamically presumably more favored *meso* isomer.²⁵ Irrespective of the exact mechanism, however, the limited stability of the phenylene-bridged dinuclear Ru^{II}–NHC renders complexes such as **6** unsuitable for electronic applications.

CONCLUSIONS

Bimetallic ruthenium(II)–NHC complexes with alkyl linkers of various length were synthesized. Electrochemical analyses revealed a strong dependence of the intramolecular metal–metal interaction on the length of the alkyl linker. On the basis of the pertinent comproportionation constants *K*_c, a through-bond model has been deduced for the methylene-linked system. Accordingly, increasing the alkyl linker length rapidly reduces the intermetallic coupling from charge-localized class II systems comprising a charge-localized mixed-valent state to decoupled class I complexes. Detailed investigations of the stability of the oxidized bimetallic Ru–NHC complexes indicated that the

electrochemical oxidation is followed by a relatively fast chemical reaction, rendering the oxidation quasi-reversible only.

The degree of intermetallic electronic coupling in complex **2a** is comparable to the results obtained from studies using dicarbene linkers that are connected by an annelated benzene ring at the remote carbon atoms (cf. **A**, **B**, Figure 1). A weak $d_{\text{ruthenium}}-\pi_{\text{carbene}}$ orbital overlap may thus account for the limited electronic coupling.¹³ This interaction might be improved, perhaps, by locking the orientation of the carbene heterocycle with respect to the metal coordination system, or by moving to 3d metal systems with better orbital overlap potential with the $2p_{\pi}$ orbital of the carbene ligand. These perspectives underline the potential of metal–NHC systems as active sites in molecular electronics.

EXPERIMENTAL SECTION

General Comments. All ruthenation reactions were performed using standard Schlenk techniques under an argon atmosphere. CH_2Cl_2 was dried by passage through solvent purification columns, all other reagents were used without further purification. Silica was purchased from Fisher Scientific, Alox from Sigma-Aldrich. Chloroform (Aldrich, puriss.) was stabilized with 1% EtOH. The syntheses of the diimidazolium salts **1a–d** and the 1,1'-(1,4-phenylene)bis-*N*-imidazole are described elsewhere.²² Unless stated otherwise, all ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at 25 °C on Bruker spectrometers operating at 360 or 400 (^1H NMR) and at 90 or 100 MHz (^{13}C NMR), respectively. Resonance frequencies were referenced to residual solvent ^1H or ^{13}C resonances. Chemical shifts (δ) are given in parts per million (ppm), coupling constants (J) in hertz (Hz). Assignments are based either on distortionless enhancement of polarization transfer (DEPT) experiments or on homo- and heteronuclear shift correlation spectroscopy. Elemental analyses were performed by the Microanalytical Laboratory of Ilse Beetz (Kronach, Germany) and by the Microanalytical Laboratory of the ETH Zürich (Switzerland).

Electrochemical Measurements. Electrochemical studies were carried out using an EG&G Princeton Applied Research Potentiostat Model 273A employing a gastight three-electrode cell under an argon atmosphere. A Pt disk with a 3.80 mm^2 surface area was used as the working electrode and was polished before each measurement. The reference electrode was a Ag/AgCl electrode; the counter electrode was a Pt wire. Bu_4NPF_6 (0.1 M) in dry CH_2Cl_2 was used as a base electrolyte with analyte concentrations of approximately 1×10^{-3} M. The redox potentials were measured against the ferrocenium/ferrocene (Fc^+/Fc) redox couple, which was used as an internal standard ($E_{1/2} = 0.46\text{ V}$ vs SCE).³⁶

UV–vis spectroelectrochemical experiments were carried out in an airtight optically transparent thin-layer electrochemical (OTTLE) cell³⁰ at room temperature, equipped with a Pt minigrid working electrode (32 wires cm^{-1}), a Pt auxiliary electrode, a Ag wire pseudoreference electrode, and a quartz window. The cell was controlled by an EG&G PAR Potentiostat Model 273A. Absorption spectra were measured on a Perkin-Elmer Lambda 900 spectrophotometer.

General Procedure for the Preparation of Dicarbene Complexes **2a–d, **6** and Monocarbene Complex **5**.** A suspension of diimidazolium salt (1.0 mol equiv) in MeCN (15 mL) containing Ag_2O (1.0 mol equiv) was stirred at 40 °C for 16 h in the dark. After solvent evaporation, a solid residue was obtained, which was suspended in dry CH_2Cl_2 (15 mL) and $[\text{RuCl}_2(\eta^6\text{-p-cymene})]_2$ (1.0 mol equiv) was added either at room temperature (RT) or at low temperature. After stirring at RT for 16 h, the solvent was evaporated, and the crude product was purified by gradient column chromatography (SiO_2 ; CH_2Cl_2 /acetone) and by subsequent precipitation from CH_2Cl_2 /pentane. The product was recrystallized by slow diffusion of Et_2O into a CH_2Cl_2 solution to give an analytically pure sample.

Synthesis of **2a.** This complex was prepared according to the general procedure from **1a** (0.52 g, 1.0 mmol) and Ag_2O (0.23 g, 1.0 mmol). $[\text{RuCl}_2(\text{cymene})]_2$ (0.61 g, 1.0 mmol) was added to a frozen CH_2Cl_2 suspension of the Ag-carbene complex. The product was obtained as an orange solid (0.47 g, 54%). ^1H NMR (CDCl_3 , 400 MHz): δ 7.34 (s, 2H, NCH_2N), 7.27, 6.94 ($2 \times \text{d}$, $^3J_{\text{HH}} = 2.2\text{ Hz}$, 4H, H_{NHC}), 5.43, 5.42, 5.10, 5.06 ($4 \times \text{d}$, $^3J_{\text{HH}} = 5.8\text{ Hz}$, 8H, H_{Cym}), 4.54, 4.00 ($2 \times \text{m}$, 4H, NCH_2), 2.95 (septet, $^3J_{\text{HH}} = 6.9\text{ Hz}$, 2H, CHMe_2), 2.06 (s, 6H, $\text{C}_{\text{Cym}}-\text{CH}_3$), 1.99–1.85, 1.73–1.6 ($2 \times \text{m}$, 4H, NCH_2CH_2), 1.52–1.3 (m, 4H, CH_2CH_3), 1.32, 1.31 ($2 \times \text{d}$, $^3J_{\text{HH}} = 6.9\text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 0.96 (t, $^3J_{\text{HH}} = 7.4\text{ Hz}$, 6H, CH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 172.3 ($\text{C}_{\text{NHC}}-\text{Ru}$), 123.7, 121.9 ($2 \times \text{C}_{\text{NHC}}-\text{H}$), 109.0 ($\text{C}_{\text{Cym}}-\text{IPr}$), 99.1 ($\text{C}_{\text{Cym}}-\text{Me}$), 86.3, 85.9, 83.3, 82.4 ($4 \times \text{C}_{\text{Cym}}-\text{H}$), 62.9 (NCH_2N), 51.5 (NCH_2), 33.9 (NCH_2CH_2), 31.0 (CHMe_2), 23.1, 22.3 ($2 \times \text{CH}(\text{CH}_3)_2$), 20.3 (CH_2CH_3), 19.0 ($\text{C}_{\text{Cym}}-\text{CH}_3$), 14.1 (CH_2CH_3). Anal. Calcd. for $\text{C}_{35}\text{H}_{52}\text{Cl}_4\text{N}_4\text{Ru}_2$ (872.77): C 48.17, H 6.01, N 6.42. Found: C 48.04, H 6.03, N 6.34.

Synthesis of **2b.** This complex was prepared according to the general procedure from **1b** (0.234 g, 0.54 mmol) and Ag_2O (0.124 g, 0.54 mmol). $[\text{RuCl}_2(\text{cymene})]_2$ (0.329 g, 0.54 mmol) was added to a frozen CH_2Cl_2 suspension of the Ag-carbene. A mixture of CH_2Cl_2 /MeOH (100:0 to 92:8) was used as eluent for column chromatography. The product was obtained as an orange solid (0.37 g, 77%). ^1H NMR (CDCl_3 , 400 MHz): δ 8.11, 7.05 ($2 \times \text{d}$, $^3J_{\text{HH}} = 1.8\text{ Hz}$, 4H, H_{NHC}), 5.37, 5.33 ($2 \times \text{d}$, $^3J_{\text{HH}} = 5.8\text{ Hz}$, 4H, H_{Cym}), 5.16–5.10 (m, 2H, $\text{NCH}_2\text{CH}_2\text{N}$), 5.08, 5.02 ($2 \times \text{d}$, $^3J_{\text{HH}} = 5.8\text{ Hz}$, 4H, H_{Cym}), 4.56 (m, 2H, NCH_2), 4.41–4.35 (m, 2H, $\text{NCH}_2\text{CH}_2\text{N}$), 3.96 (m, 2H, NCH_2), 2.86 (septet, $^3J_{\text{HH}} = 6.9\text{ Hz}$, 2H, CHMe_2), 2.0–1.86 (m, 2H, NCH_2CH_2), 1.99 (s, 6H, $\text{C}_{\text{Cym}}-\text{CH}_3$), 1.75–1.57 (m, 2H, NCH_2CH_2), 1.55–1.31 (m, 4H, CH_2CH_3), 1.24, 1.19 ($2 \times \text{d}$, $^3J_{\text{HH}} = 6.9\text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 0.98 (t, $^3J_{\text{HH}} = 7.4\text{ Hz}$, 6H, CH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 172.9 ($\text{C}_{\text{NHC}}-\text{Ru}$), 123.9, 122.0 ($2 \times \text{C}_{\text{NHC}}-\text{H}$), 108.6 ($\text{C}_{\text{Cym}}-\text{IPr}$), 99.8 ($\text{C}_{\text{Cym}}-\text{Me}$), 85.4, 84.8, 83.9, 82.4 ($4 \times \text{C}_{\text{Cym}}-\text{H}$), 51.8 ($\text{NCH}_2\text{CH}_2\text{N}$), 51.4 (NCH_2), 34.0 (NCH_2CH_2), 30.8 (CHMe_2), 23.5, 21.9 ($2 \times \text{CH}(\text{CH}_3)_2$), 20.3 (CH_2CH_3), 18.7 ($\text{C}_{\text{Cym}}-\text{CH}_3$), 14.1 (CH_2CH_3). Anal. Calcd. for $\text{C}_{36}\text{H}_{54}\text{Cl}_4\text{N}_4\text{Ru}_2$ (886.79): C 48.76, H 6.14, N 6.32. Found: C 48.77, H 6.03, N 6.30.

Synthesis of **2c.** This complex was prepared according to the general procedure from **1c** (0.225 g, 0.50 mmol) and Ag_2O (0.116 g, 0.50 mmol). $[\text{RuCl}_2(\text{cymene})]_2$ (0.306 g, 0.50 mmol) was added to a CH_2Cl_2 suspension of the Ag-carbene at RT. The product was obtained as a dark brown solid (0.35 g, 78%). ^1H NMR (CDCl_3 , 400 MHz, 253 K): δ 7.10, 7.00 ($2 \times \text{d}$, $^3J_{\text{HH}} = 2.0\text{ Hz}$, 4H, H_{NHC}), 5.39 (d, $^3J_{\text{HH}} = 6.0\text{ Hz}$, 2H, H_{Cym}), 5.35–5.31 (br, 2H, H_{Cym}), 5.09 (d, $^3J_{\text{HH}} = 6.0\text{ Hz}$, 4H, H_{Cym}), 4.79–4.65 (br, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 4.54–4.44 (m, 2H, NCH_2), 3.91–3.77 (br, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$ and NCH_2), 2.88 (sept, $^3J_{\text{HH}} = 6.8\text{ Hz}$, 2H, CHMe_2), 2.39–2.25 (br, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 2.01 (s, 6H, $\text{C}_{\text{Cym}}-\text{CH}_3$), 2.0–1.8 (br, 2H, NCH_2CH_2), 1.68–1.52 (m, 2H, NCH_2CH_2), 1.48–1.10 (m, 16H, CH_2CH_3 and $\text{CH}(\text{CH}_3)_2$), 0.91 (t, $^3J_{\text{HH}} = 7.3\text{ Hz}$, 6H, CH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 172.3 ($\text{C}_{\text{NHC}}-\text{Ru}$), 122.8, 122.0 ($2 \times \text{C}_{\text{NHC}}-\text{H}$), 108.9 ($\text{C}_{\text{Cym}}-\text{IPr}$), 99.7 ($\text{C}_{\text{Cym}}-\text{Me}$), 85.9, 85.4, 82.6, 82.1 ($4 \times \text{C}_{\text{Cym}}-\text{H}$), 51.3 (NCH_2), 48.4 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 35.5 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 33.9 (NCH_2CH_2), 30.8 (CHMe_2), 23.1, 22.2 ($2 \times \text{CH}(\text{CH}_3)_2$), 20.3 (CH_2CH_3), 18.7 ($\text{C}_{\text{Cym}}-\text{CH}_3$), 14.1 (CH_2CH_3). Anal. Calcd. for $\text{C}_{37}\text{H}_{56}\text{Cl}_4\text{N}_4\text{Ru}_2$ (900.82) $\times 1/2\text{ CH}_2\text{Cl}_2$: C 47.75, H 6.09, N 5.94. Found: C 47.31, H 5.93, N 5.84.

Synthesis of **2d.** This complex was prepared according to the general procedure from **1d** (0.232 g, 0.50 mmol) and Ag_2O (0.116 g, 0.50 mmol). $[\text{RuCl}_2(\text{cymene})]_2$ (0.306 g, 0.50 mmol) was added to a CH_2Cl_2 suspension of the Ag-carbene at RT. The product was obtained as a dark brown solid (0.31 g, 70%). ^1H NMR (CDCl_3 , 400 MHz, 253 K; a mixture of diastereoisomers was present in a ratio of 53:47; isomer A: δ 7.15, 7.07 ($2 \times \text{d}$, $^3J_{\text{HH}} = 1.9\text{ Hz}$, 4H, H_{NHC}), 5.4–5.3, 5.16–5.10 ($2 \times \text{br}$, 6H, H_{Cym}),

5.07 (d, $^3J_{\text{HH}} = 5.5$ Hz, 2H, H_{Cym}), 4.76–4.62 (br, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 4.56–4.39, 4.00–3.86 (2 × m, 4H, NCH_2), 3.73–3.53 (br, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 2.81 (m, 2H, CHMe_2), 2.03 (s, 6H, $\text{C}_{\text{cym}}-\text{CH}_3$), 2.00–1.73 (br, 6H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$ and NCH_2CH_2), 1.70–1.54 (br, 2H, NCH_2CH_2), 1.51–1.2 (2 × br, 4H, CH_2CH_3), 1.3–1.10 (m, 12H, $\text{CH}(\text{CH}_3)_2$), 0.98–0.89 (m, 6H, CH_2CH_3); isomer B: δ 7.06 (s, 4H, H_{NHC}), 5.63, 5.57, 5.51, (3 × d, $^3J_{\text{HH}} = 5.8$ Hz, 6H, H_{Cym}), 5.30–5.18 (br, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 5.16–5.10 (br, 2H, H_{Cym}), 4.56–4.39, 4.00–3.86 (2 × m, 4H, NCH_2), 3.73–3.53 (br, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 3.04 (m, 2H, CHMe_2), 2.05 (s, 6H, $\text{C}_{\text{cym}}-\text{CH}_3$), 2.00–1.73 (br, 6H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$ and NCH_2CH_2), 1.70–1.54 (br, 2H, NCH_2CH_2), 1.51–1.2 (2 × br, 4H, CH_2CH_3), 1.3–1.10 (m, 12H, $\text{CH}(\text{CH}_3)_2$), 0.98–0.89 (m, 6H, CH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz): δ 173.2, 172.9 (2 × $\text{C}_{\text{NHC}}-\text{Ru}$), 122.1, 121.7 (2 × $\text{C}_{\text{NHC}}-\text{H}$), 109.4, 107.9 (2 × $\text{C}_{\text{cym}}-\text{Pr}$), 100.1, 99.5 (2 × $\text{C}_{\text{cym}}-\text{Me}$), 85.6, 85.4, 85.0, 84.3, 82.8, 82.6, 81.4 (7 × $\text{C}_{\text{cym}}-\text{H}$), 51.2 (NCH_2), 50.9 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 33.8 (NCH_2CH_2), 30.6 (CHMe_2), 29.1, 28.3 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 23.7, 22.8, 22.3, 21.5 (4 × $\text{CH}(\text{CH}_3)_2$), 20.2 (CH_2CH_3), 18.6 ($\text{C}_{\text{cym}}-\text{CH}_3$), 14.0 (CH_2CH_3). Anal. Calcd. for $\text{C}_{38}\text{H}_{58}\text{Cl}_4\text{N}_4\text{Ru}_2$ (914.85): C 49.89, H 6.39, N 6.12. Found: C 49.77, H 6.34, N 6.07.

Synthesis of 4. Butyl iodide (1.47 g, 8.0 mmol) and 1,1'-(1,4-phenylene)bis-*N*-imidazole (0.42 g, 2.0 mmol) were dissolved in MeCN (6 mL) and stirred at 100 °C in a thick-walled vessel for 16 h. Compound **4** precipitated as a white solid, which was isolated by filtration, washed with tetrahydrofuran (THF), and dried in vacuo (1.05 g, 91%). Recrystallization from MeOH/Et₂O gave analytically pure material. ^1H NMR ($\text{DMSO}-d_6$, 360 MHz): δ 9.95 (s, 2H, NCHN), 8.44 (s, 2H, H_{imi}), 8.12 (s, 4H, Ph), 8.11 (s, 2H, H_{imi}), 4.28 (t, $^3J_{\text{HH}} = 7.3$ Hz, 4H, NCH_2), 1.90 (quint, $^3J_{\text{HH}} = 7.3$ Hz, 4H, NCH_2CH_2), 1.36 (sext, $^3J_{\text{HH}} = 7.3$ Hz, 4H, CH_2CH_3), 0.95 (t, $^3J_{\text{HH}} = 7.3$ Hz, 6H, CH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{DMSO}-d_6$, 100 MHz): δ 135.7 (NCHN), 135.2 (C_{Ph}), 123.5 ($\text{C}_{\text{imi}}-\text{H}$), 123.3 ($\text{C}_{\text{Ph}}-\text{H}$), 121.1 ($\text{C}_{\text{imi}}-\text{H}$), 49.3 (NCH_2), 31.1 (NCH_2CH_2), 18.7 (CH_2CH_3), 13.4 (CH_2CH_3). Anal. Calcd. for $\text{C}_{20}\text{H}_{28}\text{I}_2\text{N}_4$ (578.27): C 41.54, H 4.88, N 9.69. Found: C 41.59, H 4.90, N 9.72.

Synthesis of 5. This complex was prepared according to the general procedure from **4** (0.289 g, 0.50 mmol) and Ag_2O (0.116 g, 0.50 mmol) in CH_2Cl_2 under Ar. $[\text{RuCl}_2(\text{cymene})]_2$ (0.306 g, 0.50 mmol) was added to a CH_2Cl_2 suspension of the Ag-carbene complex at 40 °C. The crude product was purified by gradient column chromatography (Al_2O_3 ; $\text{CH}_2\text{Cl}_2/\text{EtOH}$). The product was obtained as an orange solid (92 mg, 29%). Because of the instability of complex **5** in solution (see text), crystallization attempts failed to provide analytically pure material. ^1H NMR (CDCl_3 , 400 MHz): δ 11.03 (s, 1H, H_{imi}), 8.55 (d, $^4J_{\text{HH}} = 1.9$ Hz, 1H, H_{Ph}), 7.90 (s, 1H, H_{imi}), 7.52 (s, 1H, H_{imi}), 7.45 (d, $^3J_{\text{HH}} = 1.8$ Hz, 1H, H_{NHC}), 7.12 (d, $^3J_{\text{HH}} = 8.3$ Hz, 1H, H_{Ph}), 7.03 (d, $^3J_{\text{HH}} = 1.8$ Hz, 1H, H_{NHC}), 7.01 (d, $^3J_{\text{HH}} = 8.3$ Hz, 1H, H_{Ph}), 6.15, 5.92, 5.81, 5.44 (4 × d, $^3J_{\text{HH}} = 5.9$ Hz, 4H, H_{Cym}), 4.54–4.43, 4.43–4.31, 4.27–4.15, 4.15–4.02 (4 × m, 4H, NCH_2), 2.12 (m, 1H, CHMe_2), 2.03 (s, 3H, $\text{C}_{\text{cym}}-\text{CH}_3$), 2.0–1.8, 1.76–1.63 (2 × br, 4H, CH_2CH_2), 1.49 (sext, $^3J_{\text{HH}} = 7.4$ Hz, 2H, CH_2CH_3), 1.29–1.13 (m, 2H, CH_2CH_3), 1.02 (t, $^3J_{\text{HH}} = 7.4$ Hz, 3H, CH_2CH_3), 0.86–0.77 (m, 6H, $\text{CH}(\text{CH}_3)_2$ and CH_2CH_3), 0.66 (d, $^3J_{\text{HH}} = 6.9$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 188.5 ($\text{C}_{\text{NHC}}-\text{Ru}$), 168.1 ($\text{C}_{\text{Ph}}-\text{Ru}$), 147.1 (C_{Ph}), 135.3 (NCHN), 134.0 ($\text{C}_{\text{Ph}}-\text{H}$), 129.5 (C_{Ph}), 122.9 ($\text{C}_{\text{imi}}-\text{H}$), 121.3 ($\text{C}_{\text{NHC}}-\text{H}$), 120.7 ($\text{C}_{\text{imi}}-\text{H}$), 114.9 ($\text{C}_{\text{NHC}}-\text{H}$), 114.8 ($\text{C}_{\text{Ph}}-\text{H}$), 111.3 ($\text{C}_{\text{Ph}}-\text{H}$), 106.1 ($\text{C}_{\text{cym}}-\text{Me}$), 99.6 ($\text{C}_{\text{cym}}-\text{Pr}$), 93.9, 91.4, 88.3, 85.2 (4 × $\text{C}_{\text{cym}}-\text{H}$), 50.8, 49.4 (2 × NCH_2), 33.3, 32.4 (2 × NCH_2CH_2), 31.1 (CHMe_2), 22.9, 22.1 (2 × $\text{CH}(\text{CH}_3)_2$), 20.3, 19.4 (2 × CH_2CH_3), 19.1 ($\text{C}_{\text{cym}}-\text{CH}_3$), 13.9, 13.5 (2 × CH_2CH_3).

Synthesis of 6. This complex was prepared according to the general procedure from **4** (0.28 g, 0.5 mmol) and Ag_2O (0.11 g, 0.5 mmol). $[\text{RuCl}_2(\text{cymene})]_2$ (0.31 g, 0.5 mmol) was added to a CH_2Cl_2 suspension of the Ag-carbene complex at RT. The precipitation was carried out

from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$. The product was obtained as a green solid (0.23 g, 53%). ^1H NMR (CDCl_3 , 400 MHz): δ 7.84 (s, 2H, H_{Ph}), 7.49, 6.99 (2 × s, 4H, H_{NHC}), 5.68, 5.64, 5.25, 5.03 (4 × d, $^3J_{\text{HH}} = 5.8$ Hz, 8H, H_{Cym}), 4.46 (m, 4H, NCH_2), 2.14–1.87 (2 × m, 6H, CHMe_2 and NCH_2CH_2), 2.06 (s, 6H, $\text{C}_{\text{cym}}-\text{CH}_3$), 1.62–1.48 (m, 4H, CH_2CH_3), 1.07 (t, $^3J_{\text{HH}} = 7.4$ Hz, 6H, CH_2CH_3), 0.87, 0.64 (2 × d, $^3J_{\text{HH}} = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 186.5 ($\text{C}_{\text{NHC}}-\text{Ru}$), 159.1, 154.5 ($\text{C}_{\text{Ph}}-\text{Ru}$ and C_{Ph}), 123.7 ($\text{C}_{\text{Ph}}-\text{H}$), 119.7, 114.9 (2 × $\text{C}_{\text{NHC}}-\text{H}$), 105.6 ($\text{C}_{\text{cym}}-\text{Pr}$), 96.5 ($\text{C}_{\text{cym}}-\text{Me}$), 94.2, 90.5, 86.5, 80.8 (4 × $\text{C}_{\text{cym}}-\text{H}$), 50.6 (NCH_2), 33.8 (NCH_2CH_2), 30.9 (CHMe_2), 23.1, 21.6 (2 × $\text{CH}(\text{CH}_3)_2$), 20.5 (CH_2CH_3), 18.9 ($\text{C}_{\text{cym}}-\text{CH}_3$), 14.1 (CH_2CH_3). Anal. Calcd. for $\text{C}_{40}\text{H}_{52}\text{Cl}_2\text{N}_4\text{Ru}_2$ (861.91) × 1.5 CH_2Cl_2 : C 50.38, H 5.60, N 5.66. Found: C 50.36, H 5.46, N 5.93.

Crystal Structure Determinations. Suitable single crystals were mounted on a Stoe Mark II-Imaging Plate Diffractometer System (Stoe & Cie, 2002) equipped with a graphite-monochromator. Data collections were performed at –100 °C using Mo–K α radiation ($\lambda = 0.71073$ Å) with a nominal crystal to detector distance of 135 mm (for **2a** and **5**) and 130 mm (for **2d**). All structures were solved by direct methods using the program SHELXS-97 and refined by full matrix least-squares on F^2 with SHELXL-97.³⁷ The hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically. Semiempirical absorption corrections were applied using MULscanABS as implemented in PLATON.³⁸ Further crystallographic details are compiled in the Supporting Information. CCDC No. 771526 (**2a**), 771527 (**2d**), and 771528 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

S Supporting Information. Crystallographic data for **2a**, **2d**, and **5**, spectroelectrochemical investigations, comproportionation constant analysis, temperature-dependent NMR spectra of **2c** and **2d** as well as NMR spectra of **6** and its putative isomer. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: martin.albrecht@ucd.ie. Fax: +353-1716-2501.

■ ACKNOWLEDGMENT

We thank the Swiss National Science Foundation for financial support. M.A. gratefully acknowledges an Assistant Professorship of the Alfred Werner Foundation.

■ REFERENCES

- (1) (a) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (b) César, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Chem. Soc. Rev.* **2004**, *33*, 619. (c) *N-heterocyclic carbenes in synthesis*; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, Germany, 2006. (d) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2768. (e) Normand, A. T.; Cavell, K. J. *Eur. J. Inorg. Chem.* **2008**, 2781. (f) Diez-Gonzalez, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612. (g) Poyatos, M.; Mata, J. A.; Peris, E. *Chem. Rev.* **2009**, *109*, 3677.
- (2) For catalysis with carbenes in the absence of transition metals, see: (a) Breslow, R. *J. Am. Chem. Soc.* **1958**, *80*, 3719. (b) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5606. (c) Kamber, N. E.; Jeong, W.; Waymouth, R. M.; Pratt, R. C.; Lohmeijer, B. G.; Hedrick, J. L. *Chem. Rev.*

2007, 107, 5813. (d) Marion, N.; Diez-Gonzalez, S.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2007**, 46, 2988.

(3) (a) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, 100, 39. (b) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, 47, 3122.

(4) Mercks, L.; Albrecht, M. *Chem. Soc. Rev.* **2010**, 39, 1903.

(5) For a review, see: Teyssot, M.-L.; Jarrousse, A.-S.; Manin, M.; Chevy, A.; Roche, S.; Norre, F.; Beaudoin, C.; Morel, L.; Boyer, D.; Mahiou, R.; Gautier, A. *Dalton Trans.* **2009**, 6894.

(6) For reviews, see: (a) Kascatan-Nebioglu, A.; Panzner, M. J.; Tessier, C. A.; Cannon, C. L.; Youngs, W. J. *Coord. Chem. Rev.* **2007**, 251, 884. (b) Hindi, K. M.; Panzner, M. J.; Tessier, C. A.; Cannon, C. L.; Youngs, W. J. *Chem. Rev.* **2009**, 109, 3859.

(7) For representative theoretical studies, see: (a) McGuinness, D. S.; Saendig, N.; Yates, B. F.; Cavell, K. J. *J. Am. Chem. Soc.* **2001**, 123, 4029. (b) Nemcsok, D.; Wichmann, K.; Frenking, G. *Organometallics* **2004**, 23, 3640. (c) Fantasia, S.; Petersen, J. L.; Jacobsen, H.; Cavallo, L.; Nolan, S. P. *Organometallics* **2007**, 26, 5880. (d) Gagliardi, L.; Cramer, C. J. *Inorg. Chem.* **2006**, 45, 9442. (e) Penka, E. F.; Schläpfer, C. W.; Atanasov, M.; Albrecht, M.; Daul, C. J. *Organomet. Chem.* **2007**, 692, 5709. (f) Radius, U.; Bickelhaupt, F. M. *Organometallics* **2008**, 27, 3410. (g) Jacobsen, H.; Correa, A.; Poater, A.; Costabile, C.; Cavallo, L. *Coord. Chem. Rev.* **2009**, 253, 687.

(8) For experimental studies, see: (a) Tulloch, A. D. D.; Danopoulos, A. A.; Kleinhenz, S.; Light, M. E.; Hursthouse, M. B.; Eastham, G. *Organometallics* **2001**, 20, 2027. (b) Hu, X. L.; Castro-Rodriguez, I.; Olsen, K.; Meyer, K. *Organometallics* **2004**, 23, 755. (c) Saravankumar, S.; Oprea, A. I.; Kindermann, M. K.; Jones, P. G.; Heinicke, J. *Chem.—Eur. J.* **2006**, 12, 3143. (d) Herrmann, W. A.; Schütz, J.; Frey, G. D.; Herdtweck, E. *Organometallics* **2006**, 25, 2437. (e) Mercks, L.; Labat, G.; Neels, A.; Ehlers, A.; Albrecht, M. *Organometallics* **2006**, 25, 5648. (f) Khranov, D. M.; Lynch, V. M.; Bielawski, C. W. *Organometallics* **2007**, 26, 6042.

(9) (a) Zhou, Y.; Seyler, J. W.; Weng, W.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, 115, 8509. (b) Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998**, 178–180, 431. (c) Bruce, M. I.; Low, P. J. *Adv. Organomet. Chem.* **2004**, 50, 179.

(10) (a) Khranov, D. M.; Rosen, E. L.; Er, J. A. V.; Vu, P. D.; Lynch, V. M.; Bielawski, C. W. *Tetrahedron* **2008**, 64, 6853. (b) Tennyson, A. G.; Lynch, V. M.; Bielawski, C. W. *J. Am. Chem. Soc.* **2010**, 132, 9420.

(11) (a) Aviram, A.; Ratner, M. *Chem. Phys. Lett.* **1974**, 29, 277. (b) Joachim, C.; Gimzewski, J. K.; Aviram, A. *Nature* **2000**, 408, 541. (c) Lindsay, S. M.; Ratner, M. A. *Adv. Mater.* **2007**, 19, 23.

(12) (a) Hush, N. S. *Prog. Inorg. Chem.* **1967**, 8, 391. (b) Taube, H. *Angew. Chem., Int. Ed. Engl.* **1984**, 23, 329. (c) Hush, N. S. *Coord. Chem. Rev.* **1985**, 64, 135. (d) Creutz, C.; Newton, M. D.; Sutin, N. *J. Photochem. Photobiol. A* **1994**, 82, 47. (e) Brunswig, B. S.; Creutz, C.; Sutin, N. *Chem. Soc. Rev.* **2002**, 31, 168.

(13) (a) Ward, M. D. *Chem. Soc. Rev.* **1995**, 24, 121. (b) Ward, M. D. *Chem. Ind.* **1996**, 568. (c) Astruc, D. *Acc. Chem. Res.* **1997**, 30, 383. (d) McCleverty, J. A.; Ward, M. D. *Acc. Chem. Res.* **1998**, 31, 842. (e) Patoux, C.; Launay, J.-P.; Beley, M.; Chodorowski-Kimmes, S.; Collin, J.-P.; James, S.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1998**, 120, 3717. (f) Steenwinkel, P.; Grove, D. M.; Veldman, N.; Spek, A. L.; van Koten, G. *Organometallics* **1998**, 17, 5647. (g) Launay, J.-P. *Chem. Soc. Rev.* **2001**, 30, 386. (h) Ward, M. D. *J. Chem. Educ.* **2001**, 78, 321. (i) Frayse, S.; Coudret, C.; Launay, J.-P. *J. Am. Chem. Soc.* **2003**, 125, 5880. (j) Cola, L., Ed.; *Topics in Current Chemistry*; Springer: Berlin, Germany, 2005; p 257. (k) Nitzan, A.; Ratner, M. A. *Science* **2007**, 300, 1384. (l) Wenger, O. S. *Coord. Chem. Rev.* **2009**, 253, 1439.

(14) Sauvage, J.-P.; Collin, J.-P.; Chambron, J.-C.; Guillerez, S.; Coudret, C. *Chem. Rev.* **1994**, 94, 993.

(15) Szafert, S.; Gladysz, J. A. *Chem. Rev.* **2003**, 103, 4175.

(16) (a) Guerret, O.; Sole, S.; Gornitzka, H.; Teichert, M.; Trinquier, G.; Bertrand, G. *J. Am. Chem. Soc.* **1997**, 119, 6668. (b) Mas-Marza, E.; Mata, J. A.; Peris, E. *Angew. Chem., Int. Ed.* **2007**, 46, 3729.

(17) (a) Boydston, A. J.; Williams, K. A.; Bielawski, C. W. *J. Am. Chem. Soc.* **2005**, 127, 12496. (b) Boydston, A. J.; Rice, J. D.; Sanderson,

M. D.; Dykhno, O. L.; Bielawski, C. W. *Organometallics* **2006**, 25, 6087. (c) Boydston, A. J.; Bielawski, C. W. *Dalton Trans.* **2006**, 4073. (d) Williams, K. A.; Boydston, A. J.; Bielawski, C. W. *J. R. Soc. Interface* **2007**, 4, 359. (e) Varnado, C. D.; Lynch, V. M.; Bielawski, C. W. *Dalton Trans.* **2009**, 7253. (f) Tennyson, A. G.; Khranov, D. M.; Varnado, C. D.; Creswell, P. T.; Kamplain, J. W.; Lynch, V. M.; Bielawski, C. W. *Organometallics* **2009**, 28, 5142.

(18) (a) Mercks, L.; Neels, A.; Albrecht, M. *Dalton Trans.* **2008**, 5570. (b) Tennyson, A. G.; Rosen, E. L.; Collins, M. S.; Lynch, V. M.; Bielawski, C. W. *Inorg. Chem.* **2009**, 48, 6924.

(19) (a) Fürstner, A.; Davies, P. W. *Angew. Chem., Int. Ed.* **2007**, 46, 3410. (b) Benitez, D.; Shapiro, N. D.; Tkatchouk, E.; Wang, Y.; Goddard, W. A., III; Toste, F. D. *Nat. Chem.* **2009**, 1, 482.

(20) Er, J. A. V.; Tennyson, A. G.; Kamplain, J. W.; Lynch, V. M.; Bielawski, C. W. *Eur. J. Inorg. Chem.* **2009**, 1729.

(21) (a) Sachs, S. B.; Dudek, S. P.; Hsung, R. P.; Sita, L. R.; Smalley, J. F.; Newton, M. D.; Feldberg, S. W.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1997**, 119, 10563. (b) Weber, K.; Hockett, L.; Creager, S. J. *Phys. Chem. B* **1997**, 101, 8286. (c) Liu, H.; Wang, N.; Zhao, J.; Guo, Y.; Yin, X.; Boey, F. Y. C.; Zhang, H. *ChemPhysChem* **2008**, 9, 1416.

(22) (a) Albrecht, M.; Miecznikowski, J. R.; Samuel, A.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2002**, 21, 3596. (b) Cristau, H.-J.; Cellier, P. P.; Spindler, J.-F.; Taillefer, M. *Chem.—Eur. J.* **2004**, 10, 5607.

(23) (a) Mata, J.; Chianese, A. R.; Miecznikowski, J. R.; Poyatos, M.; Peris, E.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2004**, 23, 1253. (b) Viciano, M.; Poyatos, M.; Sanau, M.; Peris, E.; Rossin, A.; Ujaque, G.; Lledos, A. *Organometallics* **2006**, 25, 1120. (c) Leung, C. H.; Incarvito, C. D.; Crabtree, R. H. *Organometallics* **2006**, 25, 6099. (d) Wang, X.; Liu, S.; Weng, L.-H.; Jin, G.-X. *Chem.—Eur. J.* **2007**, 13, 188. (e) Mercks, L.; Neels, A.; Stoeckli-Evans, H.; Albrecht, M. *Dalton Trans.* **2009**, 7168.

(24) Poyatos, M.; Mas-Marza, E.; Sanau, M.; Peris, E. *Inorg. Chem.* **2004**, 43, 1793.

(25) See the Supporting Information for details.

(26) (a) Moret, M.-E.; Chaplin, A. B.; Lawrence, A. K.; Scopelleti, R.; Dyson, P. J. *Organometallics* **2005**, 24, 4039 and references cited. (b) Gandolfi, C.; Heckenroth, M.; Laurency, G.; Neels, A.; Albrecht, M. *Organometallics* **2009**, 28, 5112.

(27) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, 10, 247.

(28) (a) Mann, B.; Kuhn, H. J. *Appl. Phys.* **1971**, 42, 4398. (b) Metzger, R. M.; Chen, B.; Hopfner, U.; Lakshmikantham, M. V.; Vuillaume, D.; Kawai, T.; Wu, X.; Tachibana, H.; Hughes, T. V.; Sakurai, H.; Baldwin, J. W.; Hosch, C.; Cava, M. P.; Brehmer, L.; Ashwell, G. J. *J. Am. Chem. Soc.* **1997**, 119, 10455. (c) Schlicke, B.; De Cola, L.; Belser, P.; Balzani, V. *Coord. Chem. Rev.* **2000**, 208, 267.

(29) (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, 15, 155. (b) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, 811, 265.

(30) Krejci, M.; Danek, M.; Hartl, F. J. *Electroanal. Chem.* **1991**, 317, 179.

(31) Demadis, K. D.; Hartshorn, C. M.; Meyer, T. J. *Chem. Rev.* **2001**, 101, 2655.

(32) Heinze, J. *Angew. Chem., Int. Ed. Engl.* **1984**, 23, 831.

(33) (a) Hitchcock, P. B.; Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Chem. Commun.* **1977**, 196. (b) Hitchcock, P. B.; Lappert, M. F.; Pye, P. L.; Thomas, S. J. *Chem. Soc., Dalton Trans.* **1979**, 1929. (c) Enders, D.; Gielen, H.; Raabe, G.; Runsink, J.; Teles, J. H. *Chem. Ber.* **1997**, 130, 1253. (d) Jazzar, R. F. R.; Macgregor, S. A.; Mahon, M. F.; Richards, S. P.; Whittlesey, M. K. *J. Am. Chem. Soc.* **2002**, 124, 4944. (e) Giunta, D.; Hölscher, M.; Lehmann, C. W.; Mynott, R.; Wirtz, C.; Leitner, W. *Adv. Synth. Catal.* **2003**, 345, 1139. (f) Hong, S. H.; Chlenov, A.; Day, M. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2007**, 46, 5148. (g) Diggle, R. A.; Kennedy, A. A.; Macgregor, S. A.; Whittlesey, M. K. *Organometallics* **2008**, 27, 938. (h) Armstrong, R.; Ecott, C.; Mas-Marza, E.; Page, M. J.; Mahon, M. F.; Whittlesey, M. K. *Organometallics* **2010**, 29, 991.

(34) (a) Ryabov, A. D. *Chem. Rev.* **1990**, 90, 403. (b) Albrecht, M. *Chem. Rev.* **2010**, 110, 576.

- (35) Fan, J.; Hanson, B. E. *Inorg. Chem.* **2005**, *44*, 6998.
(36) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.
(37) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112.
(38) Spek, A. L. *Acta Crystallogr., Sect. D: Biol. Crystallogr.* **2009**, *65*, 148.