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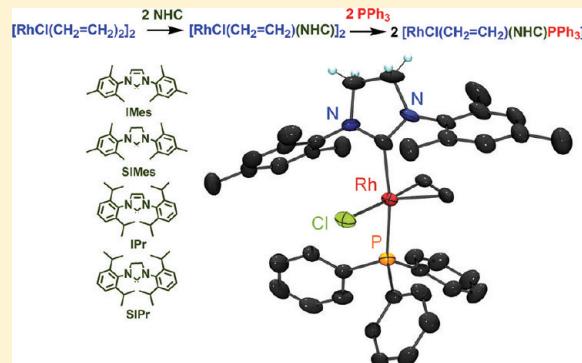
Dimeric Rhodium–Ethylene NHC Complexes As Reactive Intermediates for the Preparation of Tetra-heteroleptic NHC Complexes

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Supporting Information

ABSTRACT: Dimeric rhodium complexes with various N-heterocyclic carbene (NHC) ligands have been synthesized and fully characterized. X-ray analysis unambiguously confirms the bimetallic nature of these complexes, and in all cases one molecule of ethylene is coordinated to each metal center in an η^2 -fashion. The Rh atoms are also coordinated to one NHC ligand and are interconnected by two μ -chlorine bridges. The dimeric nature of the complexes is most likely stabilized due to the significant steric bulk around the metal centers provided by the carbene ligands. Consistent with this, modulating the steric properties and backbone saturation of the ligands was shown to have a significant effect on the stability and geometry of the complexes. Treatment of the carbene dimers with ligands such as PPh_3 results in cleavage of the dimers and a unique synthesis of tetra-heteroleptic complexes of the general formula $[\text{ClRh}(\text{NHC})(\text{PR}_3)(\text{CH}_2=\text{CH}_2)]$. The stabilities of these compounds have been assessed, and although decomposition to Wilkinson's complex is observed upon treatment with an excess of phosphine for prolonged times, the presence of the ethylene ligand provides greatly increased stability compared with the bis-phosphine analogues $[\text{ClRh}(\text{NHC})(\text{PPh}_3)_2]$.



INTRODUCTION

Since pioneering studies by Wanzlick,¹ Öfele,² and Bertrand,³ and after their eventual isolation by Arduengo,⁴ N-heterocyclic carbenes (NHCs) have been studied extensively as ligands in homogeneous catalysis.^{5–21} Due largely to their strong σ -donation, large steric bulk, and the relatively good stability of their complexes toward air and moisture, NHCs have emerged as promising ligands for a variety of organic transformations. In particular, much success has been demonstrated for the stabilization of reactive metal complexes, as well as the general enhancement of catalytic activity of metal complexes relative to those modified by more traditional phosphine ligands. Research efforts in recent years have focused primarily on the synthesis of new NHCs,^{8,10,20,22–31} as well as the development of highly active metal catalysts based on these ligands.^{5,6}

Heteroleptic transition metal NHC complexes in particular have significant potential as catalysts, since the NHC ligand can be employed to add stability, while other, more labile ligands can be used to generate active sites on the metal. Organ and co-workers have demonstrated this elegantly in their series of palladium NHC pyridine complexes that have proven to be versatile catalysts in a variety of C–C bond forming reactions.^{32–35} Although there have been reports of heteroleptic phosphine NHC complexes of ruthenium,^{36–39} there are far fewer examples of similar compounds of rhodium.^{13,40–42} Typically, mixed NHC–phosphine complexes are based on chelating NHC–phosphine ligands, which can be difficult to synthesize and often do not address the key issue of providing a

labile ligand for coordination of substrates. Although examples of unchelated NHC phosphine complexes have been reported, these are far less common.^{13,43,44} A reliable and general procedure for the synthesis of heteroleptic Rh-NHC complexes would be a significant addition to the literature. We focused on dimeric complexes of rhodium with the general structure of $[\text{Rh}(\text{NHC})(\text{olefin})\text{Cl}]_2$ as the starting point for addressing this deficiency.

Remarkably, dimeric NHC olefin complexes have been investigated by only a handful of groups, starting with Nolan, who demonstrated that the reaction of $[\text{Rh}(\text{COE})_2\text{Cl}]_2$ with the very sterically bulky tBu ligand resulted in a Rh(I) complex where each rhodium was coordinated to one molecule of an NHC and to one molecule of COE.^{45,46} These structures proved to be very unstable, as cyclometalation of the NHC occurred rapidly in solution. Further studies by James illustrated that NHCs with less steric bulk were more resistant toward cyclometalation, and complexes of the type $[\text{Rh}(\text{NHC})(\text{COE})\text{Cl}]_2$ could be isolated, although no crystal structures have been reported to date.⁴⁷ Recently, we described a novel dimeric rhodium complex in which each rhodium was coordinated to one molecule of the saturated NHC *N,N'*-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene (SiPr) and one molecule of ethylene.⁴⁸ This complex was isolated and unambiguously characterized by X-ray crystallography, clearly

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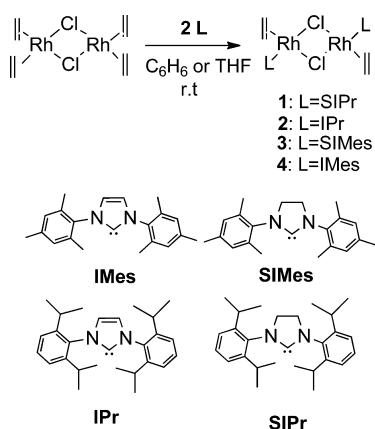
displaying its dimeric character. Although nonsymmetrical dimeric complexes of ruthenium coordinated both to an NHC and to ethylene have been reported,⁴⁹ to the best of our knowledge this was the first example of a fully characterized dimeric rhodium NHC ethylene complex.

As dimeric NHC complexes may have great potential in catalysis, we set out to design a reliable and general method for the synthesis of Rh NHC dimers and investigated their reactivity toward phosphine ligands. These dimeric complexes appear to be kinetically accessible regardless of the nature of the carbene used. As we will demonstrate herein, these complexes not only provide potential starting materials for the generation of coordinatively unsaturated catalysts but may also act as valuable precursors for the synthesis of bis(NHC) complexes⁴⁸ and heteroleptic complexes of the general type [ClRh(CH₂=CH₂)(NHC)(L)], where L is, for example, a phosphine ligand.

Synthesis and Structure of Dimeric Rh NHC Complexes.

The reaction of [Rh(C₂H₄)₂Cl]₂ with 2 equiv of the corresponding NHC (SIPr, IPr, SIMes, IMes) in an organic solvent (e.g., benzene, THF) at room temperature results in the quantitative formation of dimeric complexes **1–4** (Scheme 1).⁴⁸

Scheme 1. Formation of Dimeric Rhodium NHC Ethylene Complexes **1–4**



η^2 -Coordination of ethylene to each metal center is evident from the ¹H and ¹³C{¹H} spectra, which exhibit characteristic signals typical for such interactions (see Table 1).^{45,48,50,51} The values of the observed coupling constants are consistent with the structurally related complex reported by Nolan.⁴⁵ Complexes **2–4** were isolated and characterized by a combination of ¹H and ¹³C{¹H} NMR spectroscopy and elemental analysis. Complexes **2** and **3** were also characterized by high-resolution mass spectrometry. Complex **1** was previously reported by us.⁴⁸ The molecular structures of complexes **1–3** were unambiguously

verified by single-crystal X-ray analysis. Selected geometrical parameters of these complexes are reported in Table S1. All attempts to crystallize complex **4** led to disordered crystals.⁵² Upon detailed inspection of the X-ray structures of complexes **1–3**, it appears that both complexes **2** and **3** contain multiple weak noncovalent interactions that influence the crystal organization (*vide infra*). However, these interactions are not present in complex **1**. The solid-state molecular structures of complexes **2** and **3** are depicted in Figures 1 and 2. In complexes **1–3**, the two metal centers are both coordinated to one ethylene in an η^2 -fashion and to one NHC ligand. The metal centers are interconnected by two μ -chlorine bridges. In addition, the carbene ligands are oriented *anti* to each other, likely due to steric constraints (Figures 1A, 2A). In solution, complex **3** appears to be a mixture of both *syn* and *anti* complexes, as evidenced by ¹H and ¹³C NMR spectroscopy (see Table 1). However this is the only complex that appears to be comprised of such a mixture.

Unlike complex **1**, which exhibits a nearly planar geometry around the two metal centers with both the rhodium and chlorine atoms sitting within one plane, complexes **2** and **3** both contain significant distortion in this rhodium–chlorine plane with angles of 37.33° and 43.06°, respectively (see Figure 3). This is likely due to the weak noncovalent C–H···Cl interactions (*vide infra*) that appear to have a significant effect on the solid-state structures of complexes **2** and **3**, but not **1**. It is likely that the increased steric constraints imposed by the bulkier SIPr ligand prevent such interactions.

The heterocyclic rings of the carbene ligands in complexes **1** and **2** are not planar, as the C3 and C2 atoms are distorted out of the plane containing the N1C1N2 atoms. The deviation from planarity of the heterocyclic ring of the carbene ligand is represented by the torsion angle (N1C2C3N2) and is highly dependent on the carbene ligand in question. In the case of SIPr, the torsion angle is quite large (25.61°), whereas for SIMes, it is significantly smaller (6.79°) and is negligible for IPr (0.58°). The distances between the two Rh centers correlate well to the relative steric bulk of the corresponding carbene ligands, decreasing in the order SIPr (3.613 Å) > IPr (3.452 Å) > SIMes (3.399 Å). The coordination of ethylene to the rhodium centers induces significant lengthening of the C=C bonds in all complexes: 1.383(4) Å (**1**, SIPr), 1.389(3) Å (**2**, IPr), and 1.399(5) Å (**3**, SIMes), in comparison with those of uncomplexed ethylene, 1.3391(13) Å.^{51,53} The Rh–C=C bond lengths are very similar for all complexes and lie in the range 2.091–2.098 Å.⁵⁴

Since complex **2** was crystallized from a CH₂Cl₂–THF mixture, we observed CH₂Cl₂ incorporated into the crystal lattice. Interestingly, multiple weak noncovalent interactions were observed between this molecule and Rh complex **2**, likely playing an important role in the crystal organization.^{55,56} Three

Table 1. Characteristic NMR Features of Complexes **1–4**

compound	¹ H		¹³ C{ ¹ H}		NCN–Rh	
	Rh (η^2 -CH ₂ =CH ₂)	δ , ppm	Rh (η^2 -CH ₂ =CH ₂)	δ , ppm	J_{RhC} , Hz	δ , ppm
[Rh(SIPr)(C ₂ H ₄)Cl] ₂ (1)	2.58; 2.27		46.7	16.7		205.89
[Rh(IPr)(C ₂ H ₄)Cl] ₂ (2)	2.23; 1.96		43.7	16.5		179.05
[Rh(SIMes)(C ₂ H ₄)Cl] ₂ (3a(b)) ^a	2.56; 2.07 (2.43; 2.22)		45.93 (45.14)	16.1 (16.8)		207.02 (204.02)
[Rh(IMes)(C ₂ H ₄)Cl] ₂ (4)	2.25; 2.14		43.3	16.5		176.03
^a Mixture of <i>syn</i> and <i>anti</i> isomers, see text.						

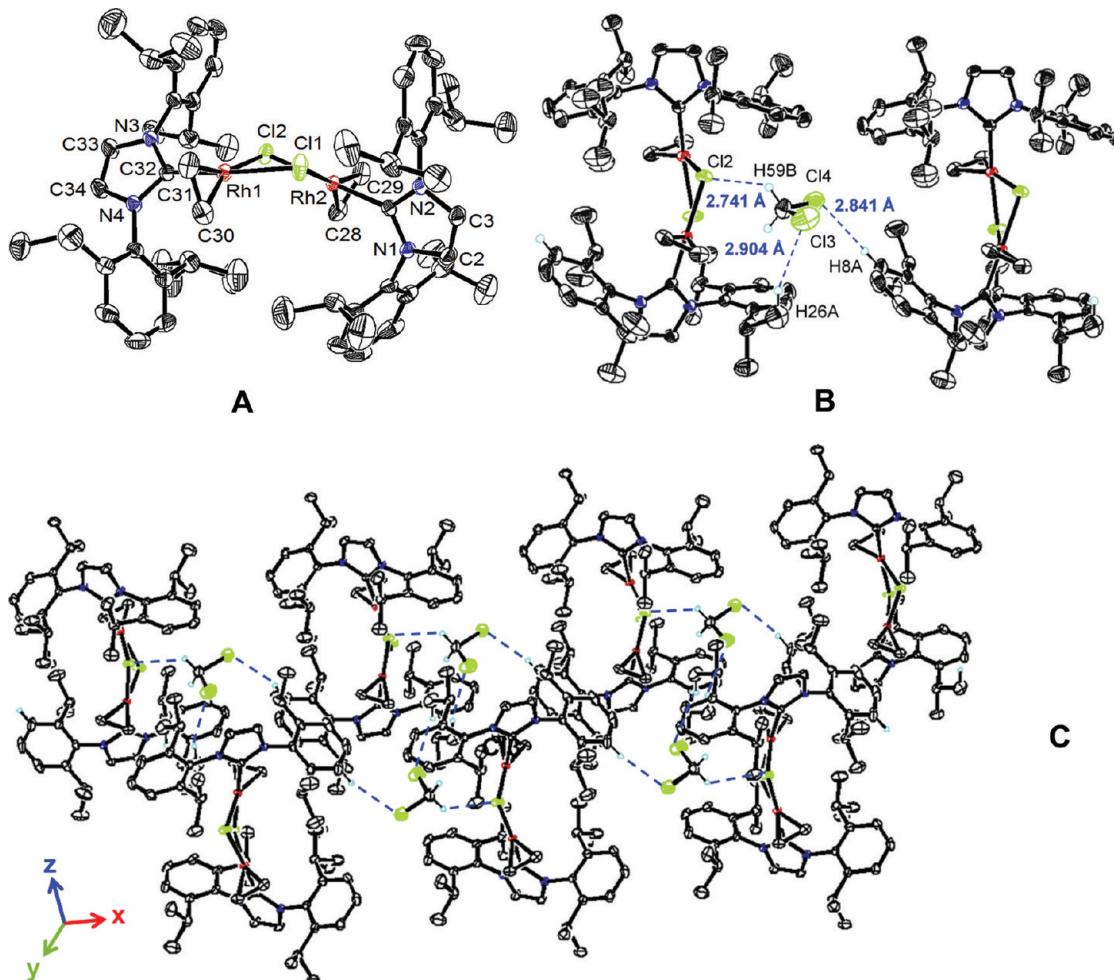


Figure 1. (A) Crystallographically determined structure of $[\text{Rh}(\text{IPr})(\text{C}_2\text{H}_4)\text{Cl}]_2 \cdot \text{CH}_2\text{Cl}_2$ (**2**), displaying thermal ellipsoids drawn at the 50% confidence level. CH_2Cl_2 and hydrogen atoms are omitted for clarity. Selected interatomic distances [\AA] and angles [deg]: $\text{Rh}(2)-\text{Cl}(1)$, 2.3826(5); $\text{Rh}(2)-\text{C}(1)$, 1.9681(17); $\text{Rh}(2)-\text{C}(28)$, 2.0985(19); $\text{Rh}(2)-\text{C}(29)$, 2.0986(19); $\text{C}(28)-\text{C}(29)$, 1.389(3); $\text{Rh}(2)-\text{Cl}(2)$, 2.4259(4); $\text{N}(1)-\text{C}(1)$, 1.372(2); $\text{N}(2)-\text{C}(1)$, 1.378(2); $\text{C}(2)-\text{C}(3)$, 1.337(3); $\text{C}(1)-\text{Rh}(2)-\text{C}(28)$, 98.53(7); $\text{C}(1)-\text{Rh}(2)-\text{C}(29)$, 93.13(8); $\text{C}(1)-\text{Rh}(2)-\text{Cl}(1)$, 93.43(5); $\text{C}(1)-\text{Rh}(2)-\text{Cl}(2)$, 176.15(5); $\text{C}(28)-\text{Rh}(2)-\text{Cl}(1)$, 155.99(6); $\text{C}(29)-\text{Rh}(2)-\text{Cl}(1)$, 160.11(7); $\text{C}(1)-\text{Rh}(2)-\text{Cl}(1)$, 93.43(5); $\text{C}(28)-\text{Rh}(2)-\text{Cl}(2)$, 85.03(6); $\text{C}(29)-\text{Rh}(2)-\text{Cl}(2)$, 90.57(6); $\text{N}(1)-\text{C}(1)-\text{N}(2)$, 102.30(14). (B, C) 2D structure of $[\text{Rh}(\text{IPr})(\text{C}_2\text{H}_4)\text{Cl}]_2 \cdot \text{CH}_2\text{Cl}_2$ showing the hydrogen C-H...Cl bonds. Non-hydrogen-bonding H atoms are omitted for clarity.

different types of C–H...Cl contacts are clearly visible in the crystal structure of **2** (Figure 1B, C). These contacts may reasonably be considered to be nonclassical C–H...Cl hydrogen bonds^{57,58} since they are less than the sum of the van der Waals radii (2.95 Å),⁵⁹ and are charge assisted by the opposite charges of the anion and cation. The strongest interaction exists between the bridging chlorine atom of complex **2** and a hydrogen atom from a CH_2Cl_2 molecule ($\text{H}(59\text{B})-\text{Cl}(2)$ bond length = 2.741 Å). The angles $\text{H}(59\text{B})-\text{Cl}(2)-\text{Rh}(1)$ and $\text{H}(59\text{B})-\text{Cl}(2)-\text{Rh}(2)$ are 90.74 and 91.99 Å, respectively. Since metals can activate bound chlorine atoms, making them quite acidic, M–Cl species are generally much stronger H-bond acceptors than their C–Cl analogues.^{58,60–63} The C–H...Cl motif has been utilized in the literature for the assembly of transition metal-based components in supramolecular structures.^{2,56,62,64–66} The apparent intermolecular hydrogen bonds between a chlorine atom of CH_2Cl_2 and an aromatic CH group from an aromatic wingtip of the NHC are certainly less strong: ($\text{Cl}(4)-\text{H}(8\text{A})$ bond length = 2.841 Å). Furthermore, fairly weak interactions between the chlorine atoms of the CH_2Cl_2 and the aliphatic hydrogens of an isopropyl group of the DiPP

wingtip group were also detectable in complex **2** (($\text{Cl}(3)-\text{H}(26\text{A})$ bond length = 2.904 Å).

Complex **3** was crystallized from a THF–hexanes mixture, and thus no CH_2Cl_2 was observed in the crystal. However, the solid-state structure of complex **3** was also stabilized by weak noncovalent C–H...Cl interactions. In this case, the interactions are between one of the bridging chlorine atoms and one of the backbone hydrogens in the NHC heterocyclic ring (($\text{H}(23\text{A})-\text{Cl}(1)$ bond length = 2.817 Å), Figure 2B).

It should be noted that no such intermolecular noncovalent C–H...Cl interactions, similar to those in complexes **2** and **3**, were found in the crystal structure of complex **1**, which was also crystallized from a THF–hexane mixture.

Stability Studies. Complexes **1–4** exhibit relatively high stability except upon prolonged storage in solution, but the same is not true for the considerably more bulky $\text{I}^{\prime}\text{Bu}$ derivative **5**. The preparation of this compound was achieved by reacting $[\text{Rh}(\text{C}_2\text{H}_4)\text{Cl}]_2$ with 2 equiv of $\text{I}^{\prime}\text{Bu}$ in pentene at room temperature for 2 h. This resulted in the quantitative formation of dimeric complex **5** (Scheme 2).

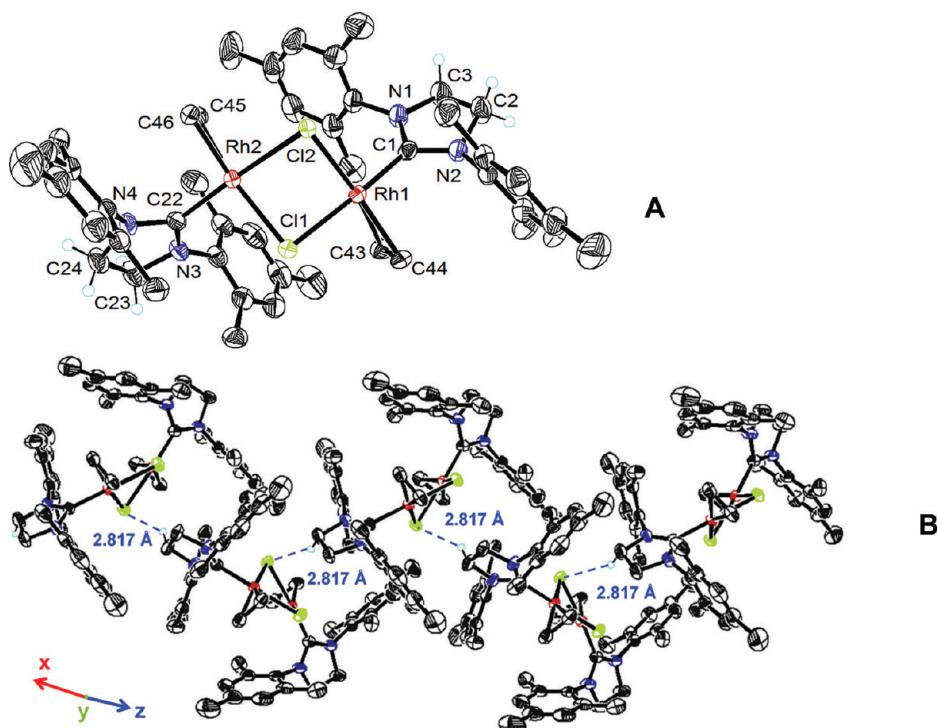


Figure 2. (A) Crystallographically determined structure of $[\text{Rh}(\text{SIMes})(\text{C}_2\text{H}_4)\text{Cl}]_2$ (3), displaying thermal ellipsoids drawn at the 50% confidence level. Hydrogen atoms (except for the SIMes backbone hydrogens) are omitted for clarity. Selected interatomic distances [\AA] and angles [deg]: Rh(1)–C(1), 1.943(3); Rh(1)–Cl(1), 2.4486(8); Rh(1)–C(43), 2.092(3); Rh(1)–C(44), 2.098(3); C(43)–C(44), 1.399(5); Rh(1)–Cl(2), 2.3900(8); N(1)–C(1), 1.352(4); N(2)–C(1), 1.368(4); C(2)–C(3), 1.513(5); C(1)–Rh(1)–C(44), 96.72(14); C(1)–Rh(1)–C(43), 89.74(14); C(1)–Rh(1)–Cl(1), 176.24(10); C(1)–Rh(1)–Cl(2), 95.17(9); C(43)–Rh(1)–Cl(1), 90.91(11); C(44)–Rh(1)–Cl(1), 86.10(10); C(1)–Rh(1)–Cl(1), 176.24(10); C(43)–Rh(1)–Cl(2), 163.05(11); C(44)–Rh(1)–Cl(2), 154.83(11); N(1)–C(1)–N(2), 105.9(3). (B) 2D structure of $[\text{Rh}(\text{SIMes})(\text{C}_2\text{H}_4)\text{Cl}]_2$ showing the hydrogen C–H...Cl bonds. Non-hydrogen bonding H atoms are omitted for clarity.

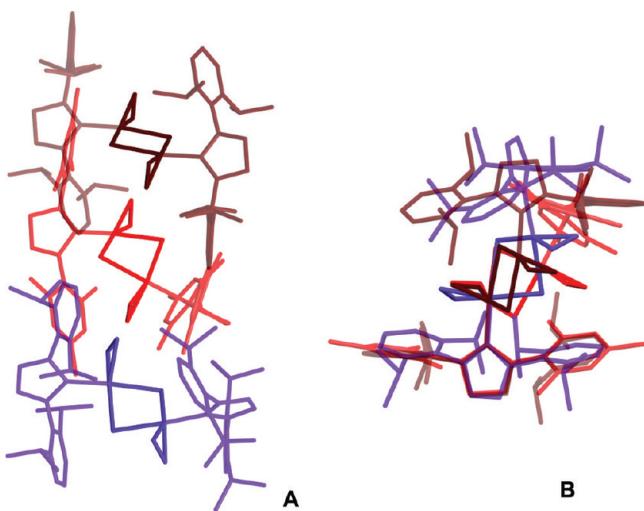


Figure 3. Stacked overlay (A) and superposition (B) of crystal structures of complexes 1–3. (Colors: complex 1(SIPr), brown; complex 2(IPr), blue; complex 3(SIMes), red.) Weak noncovalent C–H...Cl interactions cause significant distortion of the Rh–Cl–Rh–Cl square in complexes 2 and 3, compared to complex 1.

η^2 -Coordination of ethylene to each metal center is evident from the ^1H NMR spectra, which exhibit a characteristic broad resonance at 2.89 ppm typical of such interactions. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, the characteristic ethylene peak appears as a doublet due to ^{103}Rh – ^{13}C coupling at 40.57 ppm with $J = 18.1$ Hz. However, complex 5 is highly unstable and appears to

undergo C–H activation of one of the ^3Bu wingtip groups (one per rhodium center) followed by insertion of the resulting Rh–H into the ethylene moiety of complex 5, resulting in the formation of complex 6. During the measurement of ^{13}C NMR spectra (12 h), compound 5 decomposed such that no clean $^{13}\text{C}\{^1\text{H}\}$ NMR spectra could be obtained. Crystals of complex 6 were grown from a C_6D_6 solution after 2 days. Complex 6 was isolated in a very small quantity, as single crystals suitable for X-ray crystallographic analysis.

The molecular structure of complex 6 in the solid state is depicted in Figure 4. The X-ray structure revealed two rhodium centers interconnected by two μ -chlorine bridges. Each Rh is coordinated to one NHC ligand and one ethyl group. Each NHC has undergone cyclometalation via intramolecular C–H activation of the ^3Bu wingtip group. In complex 6, the two rhodium centers and two chlorine atoms define a plane. The dihedral angle between this plane and the heterocyclic ring of the corresponding carbene ligand (N1C1N2) is 77.54° . Two isomers of 6 cocrystallize together: 6a and 6b in a 23:77 ratio. In 6a, the two cyclometalated wingtip groups of the NHC are arranged *syn* to each other, while in 6b, they are *anti*. The NCN bond angle is 105.42° . The distance between the two Rh centers is 3.705 Å.

In complex 6, noncovalent intermolecular C–H...Cl interactions between one of the bridged chlorine atoms and a backbone hydrogen atom from a heterocyclic ring of a second molecule of complex 6 are clearly detectable but very weak ($\text{H}(16\text{A})$ – $\text{Cl}(1)$ bond length = 2.873 Å) (Figure 4C).

Scheme 2. Formation of Dimeric Rhodium NHC Ethylene Complex **5** Followed by C–H Activation and Addition of the Resulting Rhodium Hydride across an η^2 -Bound Ethylene To Afford Complex **6**, Which Disproportionates with the Formation of Bis-carbene Complex **7**^{45,46}

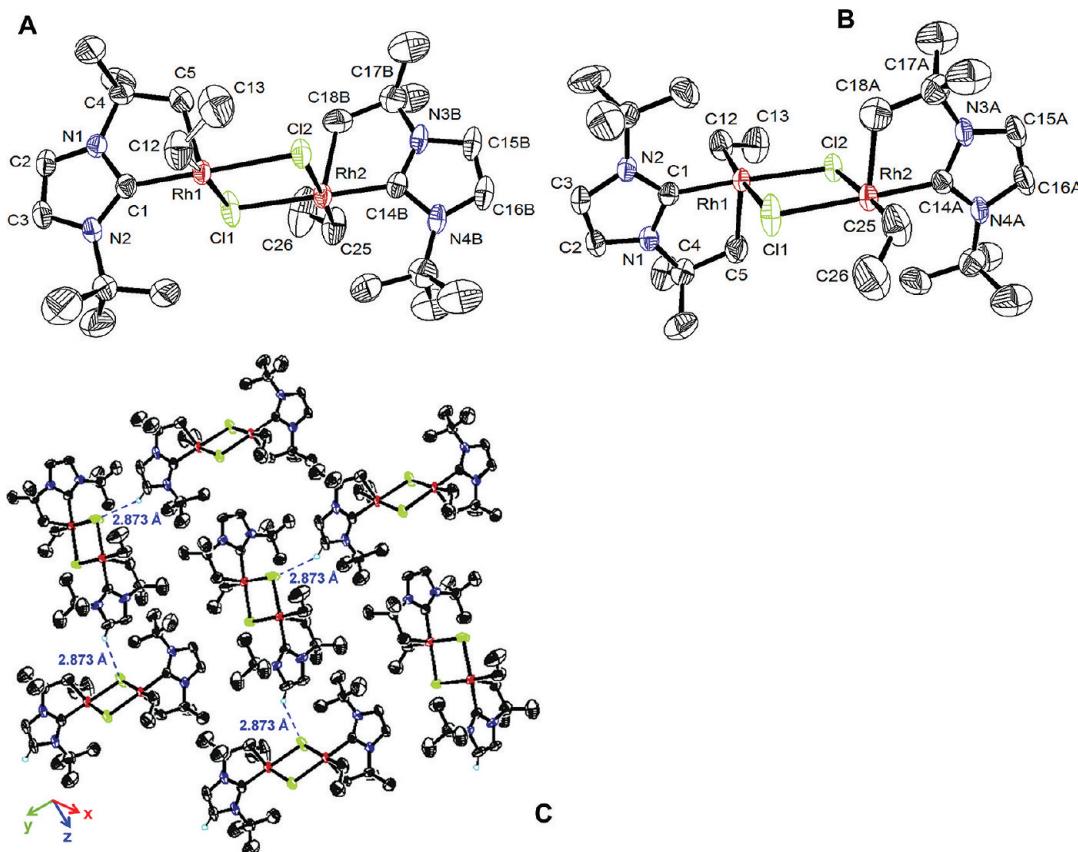
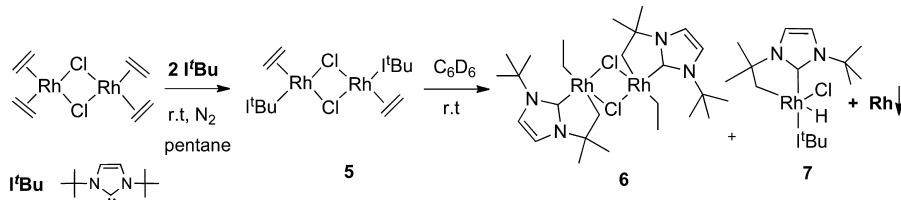


Figure 4. (A, B) Crystallographically determined structure of **6a** (A) *syn* (77%) and **6b** (B) *anti* (23%) $[Rh(I'Bu)'(CH_2CH_3)Cl]_2$ (**6a** and **6b**), displaying thermal ellipsoids drawn at the 50% confidence level. Hydrogen atoms are omitted for clarity. Selected interatomic distances [\AA] and angles [deg]: Rh(1)–C(1), 1.928(2); Rh(1)–Cl(1), 2.5446(7); Rh(1)–Cl(2), 2.4585(6); Rh(1)–C(12), 2.051(3); Rh(1)–C(5), 2.013(3); C(4)–C(5), 1.551(4); Rh(1)–Cl(2), 2.4585(6); N(1)–C(1), 1.357(3); N(2)–C(1), 1.377(3); C(2)–C(3), 1.336(4); C(12)–C(13), 1.469(5); C(25)–C(26), 1.408(5); Rh(2)–Cl(2), 2.5447(7); Rh(2)–Cl(1), 2.4483(7); Rh(2)–C(14A), 1.935(1); Rh(2)–C(14B), 1.977(3); Rh(2)–C(18A), 2.102(5); Rh(2)–C(18B), 2.180(12); Rh(2)–C(25), 2.045(3); C(1)–Rh(1)–C(12), 88.94(11); C(1)–Rh(1)–C(5), 80.90(11); C(5)–Rh(1)–C(12), 93.57(16); C(1)–Rh(1)–Cl(1), 92.33(7); C(1)–Rh(1)–Cl(2), 176.01(7); C(5)–Rh(1)–Cl(2), 97.49(9); C(12)–Rh(1)–Cl(1), 171.42(11); C(12)–Rh(1)–Cl(2), 94.81(9); N(1)–C(1)–N(2), 105.4(2). (C) 2D structure of $[Rh(I'Bu)'(CH_2CH_3)Cl]_2$ showing the hydrogen C–H...Cl bonds. Non-hydrogen bonding H atoms are omitted for clarity.

After several days in solution at room temperature, further decomposition of complex **6** was observed, giving a mixture of this species, Rh black, and complex **7**, whose NMR data matched those of the same species described previously in the literature.^{45,46} Complex **6** rapidly disproportionates to form the previously reported bis-carbene complex **7** $[RhClH(I'Bu)'(I'Bu)]$.⁴⁵

Returning to complexes **1–4**, as previously noted, these are stable in the solid state under an N_2 atmosphere for weeks; however in solution it appears that complexes **1–4** slowly decompose to form paramagnetic Rh(II) complexes $[Rh(NHC)(Cl)_2]_2$ **8–11** and $[Rh(NHC)_2(Cl)_2]$ **12–15**. Paramagnetic complex **8** was crystallized from a THF solution of

ethylene dimer **1** that was left at room temperature for 10 days. Visible decomposition and precipitation of Rh black occurs as well during the crystallization. This decomposition route appears to be general, as single crystals of complex **11** suitable for X-ray crystallographic analysis were obtained from a slow diffusion of hexanes into a concentrated THF solution of complex **4** after a period of 14 days. These decomposition products appear in addition to monomeric paramagnetic complexes **12–15**, which are common decomposition products observed in a variety of Rh-NHC complex preparations.^{17,18,48} This may not be the only existing decomposition pathway, as the yield of formation

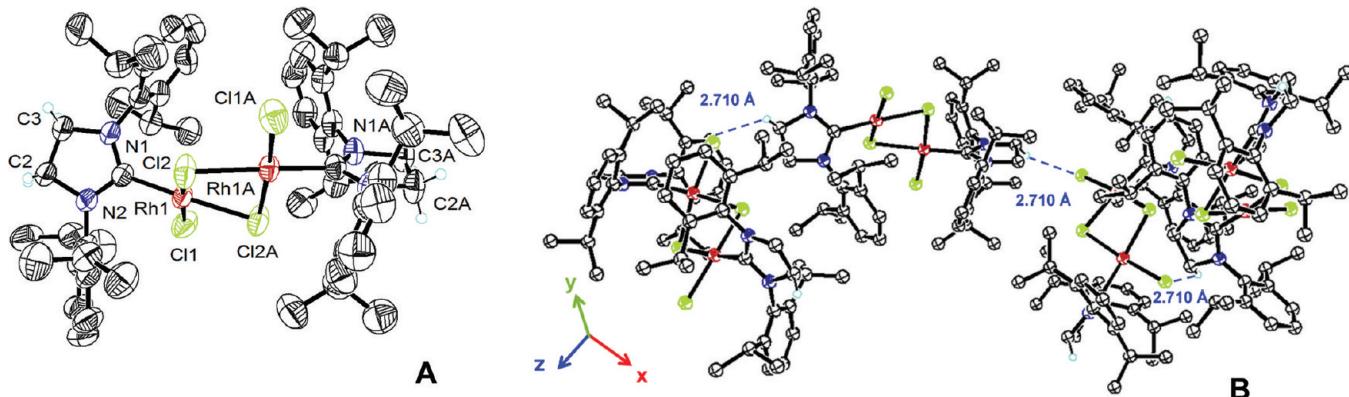
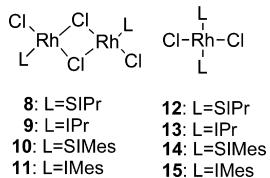


Figure 5. (A) Crystallographically determined structure of $\text{Rh}_2(\text{SIPr})_2(\text{Cl})_2(\mu\text{-Cl})_2$ (**8**), displaying thermal ellipsoids drawn at the 50% confidence level. There is half a molecule of complex **8** per asymmetric unit. Hydrogen atoms (except for the SIMes backbone hydrogens) are omitted for clarity. Selected interatomic distances [\AA] and angles [deg]: $\text{Rh}(1)-\text{C}(1)$, 1.959(3); $\text{Rh}(1)-\text{Cl}(1)$, 2.2919(11); $\text{Rh}(1)-\text{Cl}(2)$, 2.3416(10); $\text{Rh}(1)-\text{Cl}(2\text{A})$, 2.4363(10); $\text{N}(1)-\text{C}(1)$, 1.343(5); $\text{N}(2)-\text{C}(1)$, 1.343(4); $\text{C}(2)-\text{C}(3)$, 1.505(5); $\text{C}(1)-\text{Rh}(1)-\text{Cl}(1)$, 93.25(11); $\text{C}(1)-\text{Rh}(1)-\text{Cl}(2)$, 92.07(10); $\text{C}(1)-\text{Rh}(1)-\text{Cl}(2\text{A})$, 176.14(10); $\text{Cl}(1)-\text{Rh}(1)-\text{Cl}(2)$, 173.73(4); $\text{N}(1)-\text{C}(1)-\text{N}(2)$, 108.5(3). (B) 2D structure of $\text{Rh}_2(\text{SIPr})_2(\text{Cl})_2(\mu\text{-Cl})_2$ showing the hydrogen $\text{C}-\text{H}\cdots\text{Cl}$ bonds. Non-hydrogen-bonding H atoms are omitted for clarity.

Table 2. Characteristic NMR Features of Complexes 16–19

compound	^1H		$^{31}\text{P}\{^1\text{H}\}$			$^{13}\text{C}\{^1\text{H}\}$			
	Rh ($\eta^2\text{-CH}_2=\text{CH}_2$)	δ , ppm	δ , ppm	J_{RhP} , Hz	Rh ($\eta^2\text{-CH}_2=\text{CH}_2$)	δ , ppm	J_{RhC} , Hz	NCN–Rh	
[$\text{Rh}(\text{PPh}_3)(\text{SIPr})(\text{C}_2\text{H}_4)\text{Cl}$] (16)	1.68	37.75	111.6		41.38	15.4	215.71	44.6	132.9
[$\text{Rh}(\text{PPh}_3)(\text{IPr})(\text{C}_2\text{H}_4)\text{Cl}$] (17)	1.67	40.12	116.9		41.45	15.3	188.89	47.5	141.4
[$\text{Rh}(\text{PPh}_3)(\text{SIMes})(\text{C}_2\text{H}_4)\text{Cl}$] (18)	1.82	39.11	111.5		41.46	15.3	214.91	45.2	133.9
[$\text{Rh}(\text{PPh}_3)(\text{IMes})(\text{C}_2\text{H}_4)\text{Cl}$] (19)	1.50	40.48	116.3		41.37	15.3	187.57	47.5	141.8

of complexes **8–11** was far too low for isolation and intractable mixtures always resulted.

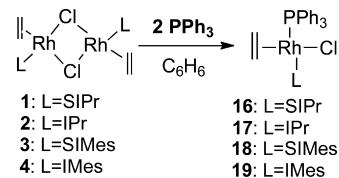


The molecular structure of complex **8** in the solid state is shown in Figure 5. In complex **8**, the planes containing each rhodium center and the two central chlorine atoms have a dihedral angle of 31.24° . The heterocyclic rings of the NHCs are not planar, as the C3 and C2 atoms are distorted out of the plane containing the N1C1N2 atoms. Deviation from planarity is represented by the torsion angle (N1C2C3N2) of 13.05° . The NCN angle is 108.87° , which is larger than in the ethylene dimer **1** (105.61°). The distance between the two Rh centers is 3.401 Å. The solid-state structure of complex **8** is clearly stabilized by weak noncovalent interactions between both terminal chlorine atoms and one of the adjacent backbone hydrogens in the SIPr ligand. These interactions are stronger than in complexes **2** and **3**, since the terminal M–Cl is a stronger hydrogen bond acceptor.⁶⁰ (($\text{H}_2\text{B}-\text{Cl}(1)$ bond length = 2.710 Å), Figure 5B).

Preparation of Tetra-heteroleptic Complexes. The reactivity of complexes **1–4** toward phosphines was investigated in order to determine if these complexes could be utilized as precursors for the formation of monomeric tetra-heteroleptic complexes with the formula $[\text{ClRh}(\text{CH}_2=\text{CH}_2)(\text{NHC})(\text{PPh}_3)]$. Indeed, treatment of complexes **1–4** with 2

equiv of PPh_3 in C_6H_6 for 2 h under anaerobic conditions resulted in the formation of complexes **16–19**. Complexes **16–19** were isolated in 89–92% yield and were fully characterized by ^1H , $^{31}\text{P}\{^1\text{H}\}$, and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy and elemental analysis (C, H, N). Complexes **16**, **17**, and **19** were also characterized by high-resolution mass spectrometry.

Scheme 3. Formation of Heteroleptic Monomeric Rhodium NHC Ethylene Phosphine Complexes **16–19**



Due to the significant steric bulk of the NHC ligand, it is expected that the most stable conformation would have the phosphine *trans* to this ligand. This effect has been previously observed by our group in the case of $[\text{Rh}(\text{IMes})(\text{PR}_3)_2\text{Cl}]$ -type complexes, where the two phosphines prefer to be *cis* to one another to minimize interactions with the bulky NHC ligand.¹³ The exceptionally large $^2J_{\text{PC}}$ coupling constants observed in compounds **16–19** ($^2J_{\text{PC}} = 133–142$ Hz, Table 2) are consistent with the formulation of these compounds as *trans* isomers,^{40,13} which typically have $^2J_{\text{PC}}$ values of ca. 120 Hz. By comparison, the $^2J_{\text{PC}}$ of *cis* NHC phosphine complexes are an order of magnitude lower ($^2J_{\text{PC}} = 10–20$ Hz).^{13,41} Complex **18** was crystallized at room temperature from a mixture of THF and hexanes, and the X-ray crystallographic analysis confirmed

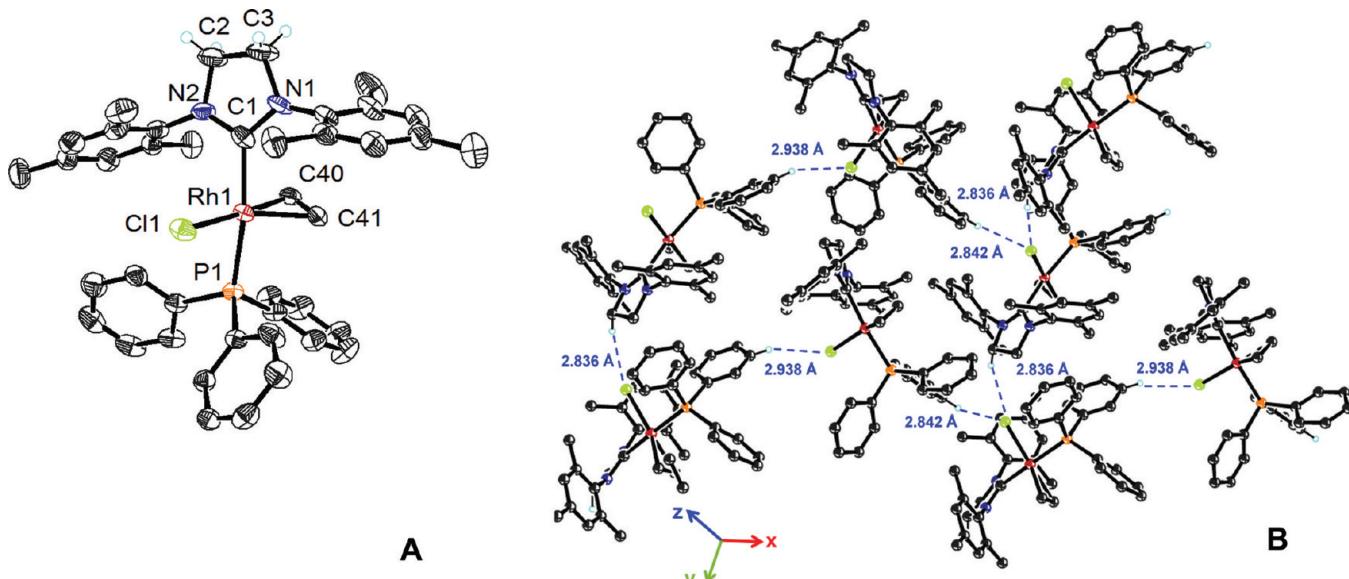


Figure 6. (A) Crystallographically determined structure of $[\text{Rh}(\text{SIMes})(\text{CH}_2=\text{CH}_2)(\text{PPh}_3)\text{Cl}]$ (**18**), displaying thermal ellipsoids drawn at the 50% confidence level. Hydrogen atoms (except for the SIMes backbone hydrogens) are omitted for clarity. There are two independent molecules of **18** per asymmetric unit. Selected interatomic distances [\AA] and angles [deg]: For **18**: Rh(1)–C(40), 2.128(6); Rh(1)–C(41), 2.099(5); Rh(1)–C(1), 2.071(6); Rh(1)–Cl(1), 2.3918(14); C(40)–C(41), 1.408(9); N(1)–C(1), 1.352(2); N(2)–C(1), 1.342(7); C(2)–C(3), 1.523(9); C(40)–Rh(1)–C(1), 85.5(2); C(41)–Rh(1)–C(1), 95.4(2); C(1)–Rh(1)–P(1), 169.62(16); C(1)–Rh(1)–Cl(1), 93.06(15); P(1)–Rh(1)–Cl(1), 93.06(15); N(1)–C(1)–N(2), 108.0(5). (B) 2D structure of $[\text{Rh}(\text{SIMes})(\text{CH}_2=\text{CH}_2)(\text{PPh}_3)\text{Cl}]$ showing the hydrogen C–H···Cl bonds. Non-hydrogen-bonding H atoms are omitted for clarity.

the *trans* relationship between the carbene and phosphine ligands (Figure 6).

The X-ray structure of complex **18** is pseudo-square-planar with slight distortions arising from a subtle tilting of the rhodium–carbene and rhodium–phosphine bonds toward the chloride ligand. The heterocyclic rings of the carbene ligand are nearly planar, with deviations from planarity represented by the torsion angles (N1C2C3N2) of 16.68° or 19.05° . The heterocyclic ring of the carbene ligand is almost perpendicular to the mesityl wingtip groups with a dihedral angle of 80.15° . The coordination of ethylene to the rhodium center induces significant lengthening of the C=C bond, $1.408(9)$ \AA , in comparison with that of uncomplexed ethylene, $1.3391(13)$ \AA .^{51,53} Complex **18** is a distorted-square-planar species with an angle between the carbene atom, rhodium, and phosphine of 169.62° (C1–Rh1–P1).

The solid-state structure of complex **18** was stabilized by two types of weak noncovalent C–H···Cl interactions (Figure 6B). In this case, the interactions are between the chlorine atoms and one of the backbone hydrogens in the NHC heterocyclic ring (H(43B)–Cl(1) bond length = 2.836 \AA) and interactions between chlorine atoms and hydrogens of the phenyl group of PPh_3 (H(26B)–Cl(1) bond length = 2.842 \AA ; H(67A)–Cl(1) bond length = 2.936 \AA).

With a straightforward and high-yielding route to complexes **16–19** in hand, we then studied the stability of these species. Previously we showed that $[\text{Rh}(\text{IMes})(\text{PR}_3)_2\text{Cl}]$ -type complexes are stable indefinitely in the solid state under an atmosphere of argon or nitrogen, but when exposed to higher temperatures in solutions of chlorinated solvents with even relatively small excesses of phosphine ligand, Wilkinson's catalyst is readily formed.¹³ Since this report, there have been several examples demonstrating even more facile cleavage of metal–NHC bonds. For example, $[(\text{IPr})\text{Pd}(\eta^3\text{-allyl})\text{Cl}]$ was reported to react with 4 equiv of PPh_3 in the presence of ${}^i\text{PrOH}$, generating $\text{Pd}(\text{PPh}_3)_4$

in quantitative yield at room temperature, obviously by Pd–NHC bond cleavage.⁶⁷ In addition, Cavell and Nechaev reported that $[(\text{NHC})\text{Pd}(\text{allyl})\text{PR}_3]^+$ complexes (NHC = tmiy-tetramethylimidazolin-2-ylidene) undergo autocatalytic NHC/X ligand exchanges, in which multiple Pd–NHC bonds are cleaved.⁶⁸

Relative to the previously mentioned bis(triarylphosphine) complexes $[\text{Rh}(\text{IMes})(\text{PAR}_3)_2\text{Cl}]$,⁴³ complexes **16–19** appear to be significantly more stable. Solutions of complexes **16–19** stored in THF under a nitrogen atmosphere underwent only trace amounts (<2%) of decomposition after three weeks at 30°C . This increase in stability may be due to the presence of the π -back-bonding ethylene ligands which may help to stabilize the relatively electron rich Rh(I) center, combined with the significant reduction of steric strain in comparison to the bis(phosphine) analogues.

However, the addition of 2 equiv of PPh_3 to the reaction mixture increased the amount of decomposition products up to 10%. The major decomposition product appears to be Wilkinson's catalyst, whose formation can easily be monitored by ^{31}P NMR (Figure S2). Prolonged reaction time (21 days) results in a very minor increase of the amount of Wilkinson's catalyst in the solution (<2% increase up to 12%), as judged by $^{31}\text{P}\{^1\text{H}\}$ NMR. This also illustrates the stability of complexes **16–19**.

This relative stability can be overcome upon treatment with a large excess of phosphine, resulting in decomposition to Wilkinson's catalyst. For example, a solution of complex **17** in C_6D_6 treated with 10 equiv of PPh_3 in a nitrogen atmosphere was fully converted to Wilkinson's catalyst in only 3 days. The nature of the decomposition described herein indicates a surprising lability of the NHCs from the rhodium centers in the presence of other ligands. This is in stark contrast to the well-held view that NHCs generally form such strong bonds to metals that they do not dissociate easily.¹⁹ Although it is not clear if similar behavior would be observed with the less stable

free NHCs such as IMe or C4-bound abnormal carbenes, clearly the lability of the metal–NHC bond needs to be considered in complexes prepared from NHCs such as those examined herein. These results, in addition to others in the literature,^{20,67,68} indicate that a revision of the generally held views on the stability of metal NHC complexes is likely in order. Most importantly, as illustrated herein, it is clear that the stability of these complexes can be controlled and predicted.

SUMMARY

Five dinuclear rhodium NHC complexes of the type $[\text{Rh}(\text{NHC})(\text{C}_2\text{H}_4)\text{Cl}]_2$ have been synthesized and fully characterized. Analysis of the packing of these dimeric complexes reveals the importance of noncovalent CH–Cl interactions on the stabilization of the crystal lattice. These dimeric ethylene complexes were found to be intermediates for the formation of monomeric heteroleptic rhodium NHC, ethylene, and phosphine complexes. The ready formation of these derivatives proves the generality of this method for the synthesis of such compounds. In addition, a dimeric complex has been observed with the formula $\text{Rh}_2(\text{L})_2(\text{Cl})_2(\mu\text{-Cl})_2$, which may be an intermediate en route to the formation of a common paramagnetic impurity with the formula $[\text{Rh}(\text{NHC})_2(\text{Cl})_2]$. Interestingly, when the very sterically bulky I^tBu ligand was used, X-ray structural analysis indicated that rapid C–H activation of the wingtip group followed by insertion of the newly formed metal hydride into the ethylene occurs without breakage of the dimeric nature of the complex. Further, we demonstrated the utility of these dimeric complexes in the formation of the new tetra-heteroleptic, mixed-ligand metal complexes, which were not synthetically accessible before. Stability studies of these compounds illustrate that they are more stable than the corresponding mixed phosphine/carbene complexes, although decomposition with loss of the NHC is still observed upon treatment with an excess of phosphine. The use of these complexes as catalysts in organic transformations is currently under investigation in our laboratories.

EXPERIMENTAL DETAILS

General Considerations. All manipulations were carried out in a nitrogen atmosphere in a glovebox (M. Braun) with oxygen and water levels of ≤ 2 ppm. Solvents were purified on a PureSolv solvent purification system, distilled, degassed, and stored over 4 Å molecular sieves prior to use. $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$,⁶⁹ SIPr,⁷⁰ IPr,⁷¹ SIMes,^{29,70} IMes,³¹ and I^tBu⁹ were prepared according to previously reported literature procedures. ¹H NMR spectra were recorded on a 400 or 500 MHz spectrometer. Chemical shifts are expressed in parts per million (ppm) downfield from tetramethylsilane using residual protonated solvent as an internal standard (C_6D_6 , 7.15 ppm; CDCl_3 , 7.24 ppm; CD_2Cl_2 , 5.32 ppm). ¹³C NMR spectra were recorded at 100 or 125 MHz. Chemical shifts are reported as above using the solvent as an internal standard (C_6D_6 , 128.0 ppm; CDCl_3 , 77.23 ppm; CD_2Cl_2 , 53.8 ppm). Elemental analyses were performed by Canadian Microanalytical Systems Ltd. X-ray data collection was performed on a Bruker SMART APEX II X-ray diffractometer.

[Rh(IPr)(C₂H₄)Cl]₂ (2). Free IPr carbene (100 mg, 0.257 mmol) was dissolved in 20 mL of benzene and added dropwise to a stirred solution of $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$ (50.0 mg, 0.129 mmol) in 15 mL of benzene at room temperature, and the solution was stirred for 12 h. Afterward, all volatiles were removed under vacuum, affording complex 2 as a dark yellow powder with 92% overall yield (131 mg). Complex 2 is stable as a powder at -20°C under nitrogen for 2–4 weeks, as judged by ¹H NMR spectroscopy. X-ray quality dark orange crystals were obtained after 4 days by slow diffusion of hexane into a concentrated solution of the product in a mixture of THF– CH_2Cl_2 (10:1) at room temperature.

¹H NMR (CD_2Cl_2 , 400 MHz, 293 K): δ 7.49 (t, 4H, ArH, ³J_{HH} = 7.6 Hz), 7.33 (br, 8H, ArH), 6.8 (s, 4H, $\text{CH}=\text{CH}$), 2.92 (septet, ³J_{HH} = 7.6 Hz, 8H, CH), 2.23 (br, 4H, $\eta^2\text{-CH}_2=\text{CH}_2$), 1.96 (br, 4H, $\eta^2\text{-CH}_2=\text{CH}_2$), 1.38 (d, 24H, ³J_{HH} = 6.6 Hz CH₃), 1.02 (d, 24H, ³J_{HH} = 5.9 Hz CH₃). ¹H NMR (CD_2Cl_2 , 600 MHz, 273 K): δ 7.46 (t, 4H, ArH, ³J_{HH} = 7.6 Hz), 7.29 (br, 8H, ArH), 6.75 (s, 4H, $\text{CH}=\text{CH}$), 2.92 (br, ³J_{HH} = 7.6 Hz, 8H, CH), 2.23 (d, 4H, $\eta^2\text{-CH}_2=\text{CH}_2$, ³J_{HH} = 11.3 Hz), 1.89 (d, 4H, $\eta^2\text{-CH}_2=\text{CH}_2$, ³J_{HH} = 11.42 Hz), 1.33 (d, 24H, ³J_{HH} = 6.7 Hz CH₃), 0.98 (d, 24H, CH₃). ¹³C{¹H} NMR (CD_2Cl_2 , 125.6 MHz): δ 179.05 (d, ¹J_{RhC} = 62.52 Hz, C_q, C-carbene), 146.99 (C_q, C-N), 137.56 (C_q, C-CH-(CH₃)₃), 129.75 (C-Ar), 124.88 (C-Ar), 124.19 (CH=CH), 43.7 (d, $\eta^2\text{-CH}_2=\text{CH}_2$, ¹J_{RhC} = 16.55 Hz), 29.15 (s, CH₃), 26.41 (s, CH₃), 23.38 (s, CH₃). MS *m/e*: calcd for $\text{C}_{58}\text{H}_{80}\text{N}_4\text{Rh}_2\text{Cl}_2$ 1108.3870, found 1108.3822. Anal. Calcd for $\text{C}_{58}\text{H}_{80}\text{N}_4\text{Rh}_2\text{Cl}_2 \cdot 1.85 \text{ H}_2\text{O}$: C 60.93, H 7.38, N 4.90. Found: C 61.14, H 7.17, N 4.68.

[Rh(SIMes)(C₂H₄)Cl]₂ (3). Free SIMes carbene (63.0 mg, 0.206 mmol) was dissolved in 15 mL of benzene and added dropwise to a stirred solution of $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$ (40.0 mg, 0.103 mmol) in 8 mL of benzene and 8 mL of THF at room temperature, and the solution was stirred for 16 h. Then the reaction mixture was filtered through a plug of Celite, and all volatiles were removed under vacuum, affording spectroscopically pure complex 3 as a yellow powder with 78% overall yield (76 mg). Complex 3 is stable as a powder at -20°C under nitrogen. However, in THF or DCM solution after 6–12 h some decomposition and precipitation of some Rh black occur. X-ray quality crystals were obtained after 12 days by slow diffusion of hexane into a concentrated THF solution of the product at -20°C .

For complex 3 two isomers were observed in solution:

3a: ¹H NMR (CD_2Cl_2 , 600 MHz, 273K): δ 7.07 (s, 4H, ³J_{HH} = 7.5 Hz, ArH), 6.92 (br, 4H, ArH), 3.75 (d, 4H, NCH₂), 3.68 (d, 4H, NCH₂), 2.56 (br, 4H, $\eta^2\text{-CH}_2=\text{CH}_2$), 2.43 (br, 4H, $\eta^2\text{-CH}_2=\text{CH}_2$), 2.43 (12H, CH₃), 2.38 (12H, CH₃), 2.20 (12H, CH₃). ¹³C{¹H} NMR (CD_2Cl_2 , 150.9 MHz): δ 207.02 (d, ¹J_{RhC} = 58.5 Hz, C-carbene), 137.84, 137.55, 137.96, 129.64, 129.40, 129.13, 51.62 (N-CH₂), 45.93 (d, $\eta^2\text{-CH}_2=\text{CH}_2$, ¹J_{RhC} = 16.1 Hz), 20.94 (s, CH₃), 19.63 (s, CH₃), 18.64 (s, CH₃).

3b: ¹H NMR (CD_2Cl_2 , 600 MHz, 273K): δ 6.95 (s, 4H, ArH), 6.77 (br, 4H, ArH), 3.59 (d, 4H, NCH₂), 3.51 (d, 4H, NCH₂), 2.34 (12H, CH₃), 2.32 (12H, CH₃), 2.22 (br, 4H, $\eta^2\text{-CH}_2=\text{CH}_2$), 2.07 (br, 4H, $\eta^2\text{-CH}_2=\text{CH}_2$), 2.17 (12H, CH₃). ¹³C{¹H} NMR (CD_2Cl_2 , 150.9 MHz): δ 204.02 (d, ¹J_{RhC} = 55.9 Hz, C-carbene), 137.63, 137.97, 135.88, 129.55, 129.33, 128.76, 51.52 (N-CH₂), 45.14 (d, $\eta^2\text{-CH}_2=\text{CH}_2$, ¹J_{RhC} = 16.8 Hz), 20.91(s, CH₃), 19.45(s, CH₃), 18.46 (s, CH₃). Anal. Calcd for $\text{C}_{46}\text{H}_{60}\text{N}_4\text{Cl}_2\text{Rh}_2$: C 58.42, H 6.39, N 5.92. Found: C 58.41, H 6.24, N 6.14.

[Rh(IMes)(C₂H₄)Cl]₂ (4). Free IMes carbene (100.8 mg, 0.207 mmol) was dissolved in 10 mL of benzene and added dropwise to a stirred solution of $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$ (40.0 mg, 0.103 mmol) in 10 mL of benzene at room temperature, and the solution was stirred for 4 h. The solution was filtered twice through a plug of Celite. Afterward, all volatiles were removed under vacuum, affording complex 4 as a light yellow powder with 89% overall yield (85 mg). Complex 4 is unstable in solution at room temperature and decomposes slowly, as judged by ¹H NMR spectroscopy. Crystals of 4 were subjected to an X-ray analysis, and although the data set was poor since crystals were highly disordered, the connectivity of 4 could be established and confirmed the dimeric nature of complex 4 with a η^2 -bonding motif for the ethylene ligand. Crystals of 4 were obtained after 7–12 days by slow diffusion of hexane into a concentrated THF solution of the product at -20°C .

¹H NMR (CD_2Cl_2 , 600 MHz, 273 K): δ 7.00 (br, 8H, ArH), 6.69 (br, 2H, br, 4H, $\text{CH}=\text{CH}$), 2.40 (m, 24H, CH₃), 2.25 (d, 4H, $\eta^2\text{-CH}_2=\text{CH}_2$), 2.14 (d, 4H, $\eta^2\text{-CH}_2=\text{CH}_2$), 2.20 (m, 12H, CH₃). ¹³C{¹H} NMR (CD_2Cl_2 , 150.9 MHz): δ 176.03 (d, ¹J_{RhC} = 61.8 Hz, C-carbene), 137.96 (s, C_q, C-N), 136.90 (s, C_q, C-CH-(CH₃)₃), 128.50 (C-Ar), 123.32 (CH=CH), 43.3 (d, $\eta^2\text{-CH}_2=\text{CH}_2$, ¹J_{RhC} = 16.5 Hz), 20.97 (s, CH₃), 19.46 (s, CH₃), 18.59 (s, CH₃). Anal. Calcd for $\text{C}_{46}\text{H}_{56}\text{N}_4\text{Rh}_2\text{Cl}_2 \cdot 0.9 \text{ H}_2\text{O}$: C 57.68, H 6.08, N 5.85. Found: C 58.06, H 6.39, N 5.46.

[Rh(I^tBu) η^2 (C₂H₄)Cl]₂ (5). To a yellow pentane slurry (2 mL) of [Rh(C₂H₄)Cl]₂ (15.0 mg, 0.0386 mmol) was added dropwise a pentane solution (5 mL) of I^tBu-free carbene (13.8 mg, 0.0765 mmol). Continued aggressive stirring led to the precipitation of a pale yellow solid after 30 min. After stirring for another 2 h, the suspension was decanted and dried *in vacuo*. The sample was quickly dissolved in C₆D₆ and loaded into an NMR tube. ¹H NMR demonstrates the quantitative formation of complex 5. However, compound 5 is unstable, and it decomposes rapidly with formation of complex 7.

¹H NMR (C₆D₆, 400 MHz): δ 7.27 (s, 2H, CH-imidazole), 6.62 (s, 2H, CH-imidazole), 2.89 (br, 8H, η^2 -CH₂=CH₂), 2.19 (s, 36H, C(CH₃)₃).

[Rh(I^tBu)'(I^tBu)((C₂H₅)Cl)]₂ (6). A 0.0386 M solution of complex 7 in benzene was left for 2 days at room temperature and resulted in the formation of a mixture of complexes 6 and 7,^{45,46} as judged by X-ray spectroscopy and ¹H and ¹³C{¹H} NMR. In addition, significant amounts of rhodium black precipitated from the solution. Crystals of complex 6 were grown from C₆D₆ solution after 2 days. We were able to isolate 6 in small quantities as single crystals suitable for X-ray analysis to confirm the structure, but our attempts to obtain solely complex 6 were hampered due to the unstable nature of the complex. It is likely that complex 6 is a reactive intermediate for the formation of 7 and decomposes at room temperature after 2–4 days with formation of complex 7.^{45,46}

[Rh(PPh₃)(SiPr)(C₂H₄)Cl] (16). A 20 mL vial was charged with complex 1 (44.0 mg, 0.039 mmol). Then, a solution of PPh₃ (21 mg, 0.080 mmol) in 10 mL of C₆H₆ was added dropwise. The resulting orange solution was stirred for 1 day, and then the volatiles were removed *in vacuo*. The yellow residue was then triturated with cold hexane and collected by filtration. Yield: 62 mg (81%).

¹H NMR (CD₂Cl₂, 600 MHz): δ 7.47 (t, 2H, ArH, ${}^3J_{HH}$ = 7.7 Hz), 7.36 (br, 4H, ArH), 7.28 (br, 9H, ArH), 7.25 (t, 6H, ${}^3J_{HH}$ = 6.8 Hz ArH), 3.96 (br, 2H, NCH₂), 3.89 (br, 2H, NCH₂), 3.82 (septet, ${}^3J_{HH}$ = 6.6 Hz, 2H, CH), 3.48 (septet, ${}^3J_{HH}$ = 6.7 Hz, 2H, CH), 1.68 (br, 4H, η^2 -CH₂=CH₂), 1.52 (d, 6H, CH₃, ${}^3J_{HH}$ = 6.08 Hz), 1.38 (d, 6H, CH₃, ${}^3J_{HH}$ = 6.6 Hz), 1.28 (d, 6H, CH₃, ${}^3J_{HH}$ = 6.5 Hz), 1.22 (d, 6H, CH₃, ${}^3J_{HH}$ = 6.80 Hz). ¹³C{¹H} NMR (100.6 MHz, C₆D₆): δ 215.71 (d, ${}^1J_{RHC}$ = 44.6 Hz, ${}^2J_{PC}$ = 132.91 Hz, C-carbene), 149.44, 147.02, 135.68 (d, ${}^1J_{PC}$ = 10.71), 134.06, 133.70, 129.06, 127.60 (d, ${}^1J_{PC}$ = 8.83), 125.26, 123.92, 54.38 (s, N-CH₂), 54.33 (s, N-CH₂), 41.38 (d, η^2 -CH₂=CH₂, ${}^1J_{RHC}$ = 15.4 Hz), 30.57 (s, CH), 29.44 (s, CH), 27.11 (s, CH₃), 26.88 (s, CH₃), 24.90 (s, CH₃), 23.95 (s, CH₃). ³¹P{¹H} NMR (C₆D₆, 161.95 MHz, 293 K): δ 37.75 (d, ${}^1J_{RHP}$ = 111.6 Hz). MS *m/e* for C₄₇H₅₅N₂PRhCl: calcd 818.3003, found 818.2978. Anal. Calcd for C₄₇H₅₅N₂RhCl·1.1H₂O: C 67.27, H 7.11, N 3.34. Found: C 67.04, H 7.03, N 3.64.

[Rh(PPh₃)(IPr)(C₂H₄)Cl] (17). During the review process of the manuscript, an alternate procedure for the preparation of complex 17 was reported.⁷² A 20 mL vial was charged with complex 2 (44.0 mg, 0.040 mmol). A solution of PPh₃ (21 mg, 0.080 mmol) in 10 mL of C₆H₆ was then added dropwise. The resulting orange solution was stirred for 1 day, and then the volatiles were removed *in vacuo*. The yellow residue was then triturated with cold hexane and collected by filtration. Yield: 57 mg (87%).

¹H NMR (600 MHz, CH₂Cl₂): δ 7.57 (t, 2H, ArH, ${}^3J_{HH}$ = 7.7 Hz), 7.42 (br, 4H), 7.35 (br d, 6H), 7.29 (d, 3H, ArH, ${}^3J_{HH}$ = 7.0 Hz), 7.18 (d, 6H, ArH, ${}^3J_{HH}$ = 3.4 Hz), 7.06 (br, 4H, CH=CH), 3.54 (septet, ${}^3J_{HH}$ = 5.7 Hz, 4H, CH), 3.10 (septet, ${}^3J_{HH}$ = 5.6 Hz, 4H, CH), 1.67 (br, 8H, η^2 -CH₂=CH₂), 1.47 (d, 6H, CH₃, ${}^3J_{HH}$ = 5.2 Hz), 1.33 (d, 6H, CH₃, ${}^3J_{HH}$ = 5.3 Hz), 1.17 (d, 6H, CH₃, ${}^3J_{HH}$ = 5.5 Hz), 1.07 (d, 6H, CH₃, ${}^3J_{HH}$ = 5.6 Hz). ³¹P{¹H} NMR (C₆D₆, 161.95 MHz, 293 K): δ 40.12 (d, ${}^1J_{RHP}$ = 116.9 Hz). ¹³C{¹H} NMR (100.6 MHz, C₆D₆): δ 188.89 (d, ${}^1J_{RHC}$ = 47.5 Hz, ${}^2J_{PC}$ = 141.4 Hz, C-carbene), 148.57, 146.13, 137.48, 135.92 (d, ${}^1J_{PC}$ = 10.8 Hz), 134.34, 133.89, 129.95, 129.23, 127.71 (d, ${}^1J_{PC}$ = 9.0 Hz), 124.85, 124.33 (CH=CH), 123.52, 41.35 (d, η^2 -CH₂=CH₂, ${}^1J_{RHC}$ = 15.3 Hz), 29.31 (s, CH), 29.04 (s, CH), 26.52 (s, CH₃), 26.43 (s, CH₃), 23.69 (s, CH₃), 23.06 (s, CH₃). MS *m/e* for C₄₇H₅₅N₂PRhCl: calcd 816.2847, found 816.3390. Anal. Calcd for C₄₇H₅₅N₂PRhCl: C 69.07, H 6.78, N 3.43. Found: C 69.18, H 7.01, N 3.13.

[Rh(PPh₃)(SIMes)(C₂H₄)Cl] (18). A 20 mL vial was charged with complex 3 (38.0 mg, 0.040) and dissolved in C₆H₆ (5 mL). Then a solution of PPh₃ (21 mg, 0.080 mmol) in 10 mL of C₆H₆ was added dropwise. The resulting yellow-orange solution was stirred for 1 day, and then the volatiles were removed *in vacuo*. The yellow residue was then triturated with cold hexane and collected by filtration. Yield: 48 mg (82%).

¹H NMR (400 MHz, C₆D₆): δ 7.72 (t, SH, ArH, ${}^3J_{HH}$ = 8.0 Hz), 7.25 (br, 2H, ArH), 7.09 (d, br, 6H, ArH, ${}^3J_{HH}$ = 2.1 Hz), 7.07 (d, 6H, ArH, ${}^3J_{HH}$ = 6.1 Hz), 6.96 (br, 2H, ArH), 3.75 (m, 4H, NCH₂), 2.96 (d, 3H, CH₃), 2.55 (d, 3H, CH₃), 2.44 (s, 3H, CH₃), 2.30 (s, 3H, CH₃), 2.17 (s, 3H, CH₃), 2.04 (s, 3H, CH₃), 1.82 (4H, η^2 -CH₂=CH₂). ¹³C{¹H} NMR (125.6 MHz, C₆D₆): δ 214.91 (d, ${}^1J_{RHC}$ = 45.2 Hz, ${}^2J_{PC}$ = 133.9 Hz, C-carbene), 163.87, 139.25, 137.50, 135.15, 135.90 (d, ${}^1J_{PC}$ = 10.9 Hz), 134.50, 134.22, 130.49, 130.17, 129.06, 129.06 (d, ${}^1J_{PC}$ = 8.9 Hz), 51.73 (s, N-CH₂), 51.40 (s, N-CH₂), 41.46 (d, η^2 -CH₂=CH₂, ${}^1J_{RHC}$ = 15.32 Hz), 21.33 (s, CH₃), 20.80 (s, CH₃), 19.03 (s, CH₃). ³¹P{¹H} NMR (C₆D₆, 161.95 MHz, 293 K): δ 39.11 (d, ${}^1J_{RHP}$ = 111.5 Hz). Anal. Calcd for C₄₁H₄₃N₂PRhCl: C 66.99, H 6.17, N 3.81. Found: C 66.38, H 6.29, N 3.94.

[Rh(PPh₃)(IMes)(C₂H₄)Cl] (19). A 20 mL vial was charged with complex 4 (37.7 mg, 0.040 mmol) and dissolved in C₆H₆ (5 mL). Then a solution of PPh₃ (21 mg, 0.080 mmol) in 10 mL of C₆H₆ was added dropwise. The resulting orange solution was stirred for 1 day, and then the volatiles were removed *in vacuo*. The yellow residue was then triturated with cold hexane and collected by filtration. Yield: 50 mg (85%).

¹H NMR (400 MHz, C₆D₆): δ 7.78 (t, 3H, ArH, ${}^3J_{HH}$ = 8.0 Hz), 7.27 (br, 6H, ArH), 7.10 (d, 6H, ArH, ${}^3J_{HH}$ = 7.5 Hz), 7.03 (d, 2H, ArH), 6.96 (br, 2H, ArH), 6.30 (s, 2H, CH=CH), 2.81 (d, 6H, CH₃), 1.50 (br, 4H, CH₂=CH₂), 2.24 (br, 6H, CH₃), 2.46 (d, 6H, CH₃). ¹³C{¹H} NMR (100.6 MHz, C₆D₆): δ 187.57 (d, ${}^1J_{RHC}$ = 47.5 Hz, ${}^2J_{PC}$ = 141.9 Hz, C-carbene), 138.64, 138.35, 135.95 (d, ${}^1J_{PC}$ = 11.0 Hz), 135.21, 134.58, 134.29, 130.16, 129.31, 128.68, 127.65 (d, ${}^1J_{PC}$ = 9.0 Hz), 41.37 (d, η^2 -CH₂=CH₂, ${}^1J_{RHC}$ = 15.3 Hz), 21.34 (s, CH₃), 20.60 (s, CH₃), 18.87 (s, CH₃). ³¹P{¹H} NMR (C₆D₆, 161.95 MHz, 293 K): δ 40.48 (d, ${}^1J_{RHP}$ = 116.3 Hz). MS *m/e* for C₄₁H₄₃N₂PRhCl: calcd 732.1907, found 732.2189. Anal. Calcd for C₄₁H₄₃N₂PRhCl: C 67.17, H 5.91, N 3.82. Found: C 67.34, H 6.01, N 3.67.

ASSOCIATED CONTENT

Supporting Information

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