

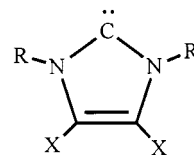
# Intramolecular C–H Activation Involving a Rhodium–Imidazol-2-ylidene Complex and Its Reaction with H<sub>2</sub> and CO

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**Summary:** An orthometalated rhodium–carbene complex  $\text{Rh}(\text{IMes})(\text{H})(\text{IMes}')\text{Cl}$  (**2**) was obtained in high yield by reacting 2 equiv of a nucleophilic carbene, 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) with  $[\text{Rh}(\text{COE})_2\text{Cl}]_2$  (**1**). The X-ray structure of **2** shows an intramolecular C–H activation of one aryl ortho methyl group. Complex **2** reacts rapidly with H<sub>2</sub> and CO at room temperature, leading to the formation of  $\text{Rh}(\text{IMes})_2(\text{H})_2\text{Cl}$  (**3**) and  $\text{Rh}(\text{IMes})_2(\text{CO})\text{Cl}$  (**4**), respectively.



R = alkyl, aryl, amine, ether... X = alkyl, H, halide

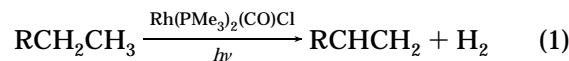
## Introduction

The use of tertiary phosphines as ligands is ubiquitous in organometallic chemistry and homogeneous catalysis.<sup>1</sup> Recent developments in the area of nucleophilic carbenes have indicated that these compounds could act as supporting ligation-mimicking tertiary phosphines. Herrmann<sup>2</sup> and more recently Cavell<sup>3</sup> have utilized members of this ligand family to assist in palladium-mediated Heck coupling. Based on the stereoelectronic properties of these nucleophilic carbenes, we have developed a methodology for C–C<sup>4</sup> and C–N<sup>5</sup> bond formation mediated by palladium. Furthermore, we have also recently reported on the synthesis and use of thermally tolerant ruthenium olefin metathesis-active complexes modified with these nucleophilic carbene ligands.<sup>6</sup>

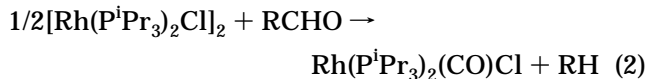
Solution calorimetric and structural studies on complexes bearing this ligand family help explain the improved catalytic behavior encountered in the palladium and ruthenium systems.<sup>7</sup> In a recent contribution, we have shown that the carbene ligand 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) pos-

sesses similar electron-donating and significantly more demanding steric properties than the bulky tertiary phosphine ligands PCy<sub>3</sub> and P<sup>i</sup>Pr<sub>3</sub>.<sup>6a,7</sup>

Rhodium phosphine complexes such as Wilkinson's Catalyst have played a major role in the development of homogeneous catalysis and continue to be a very active area of investigation. The "RhL<sub>2</sub>Cl" fragment, where L is a tertiary phosphine, is a key intermediate in olefin hydrogenation and in alkane dehydrogenation catalyzed by  $\text{Rh}(\text{PMe}_3)_2(\text{CO})\text{Cl}$ .<sup>8</sup>



Goldman and co-workers have recently investigated alkane dehydrogenation and aldehyde decarbonylation mediated by  $\text{Rh}(\text{P}^i\text{Pr}_3)_2\text{Cl}$ .<sup>8</sup>



In the  $\text{Rh}(\text{P}^i\text{Pr}_3)_2\text{Cl}$  complex, the bulky tertiary phosphine ligands are used to assist in stabilizing the coordinatively unsaturated Rh(I) species. It is also of note that tertiary alkyl phosphines are used in these complexes which render the metal center highly electron rich. Having recently examined the enhanced activity in systems where the nucleophilic carbenes can replace bulky tertiary phosphines and in view of the important catalytic behavior of RhL<sub>2</sub>Cl species, we became interested in examining rhodium complexes of this type bearing nucleophilic carbenes. We now report our initial synthetic and reactivity studies in this area.

## Results and Discussion

When 4 equiv of IMes are reacted with 1 equiv of  $[\text{Rh}(\text{COE})_2\text{Cl}]_2$  (**1**) in THF at room temperature, an orange

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(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Parshall, G. W.; Ittel, S. *Homogeneous Catalysis*; J. Wiley and Sons: New York, 1992. (c) Pignolet, L. H., Ed. *Homogeneous Catalysis with Metal Phosphine Complexes*; Plenum: New York, 1983.

(2) (a) Herrmann, W. A.; Goosen, L. J.; Spiegler, M. *J. Organomet. Chem.* **1997**, *547*, 357–366. (b) For a comprehensive review see: Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2163–2187.

(3) McGuinness, D. S.; Green, M. J.; Cavell, K. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1998**, *565*, 165–178.

(4) (a) For Suzuki coupling see: Zhang, C.; Huang, J.; Trudell, M. L.; Nolan, S. P. *J. Org. Chem.* **1999**, *64*, 3804–3805. (b) For Kumada coupling see: Huang, J.; Nolan, S. P. *J. Am. Chem. Soc.* **1999**, *121*, 9889–9890.

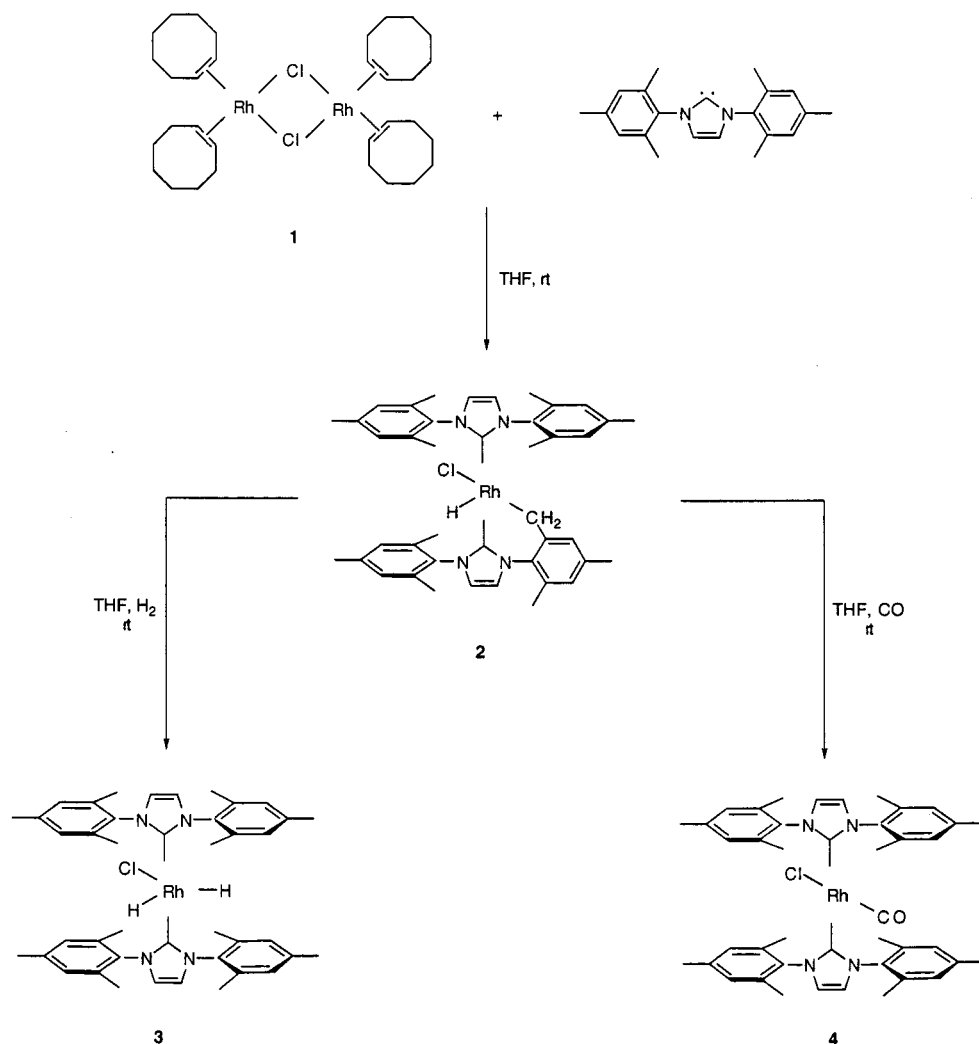
(5) Huang, J.; Grasa, G.; Nolan, S. P. *Org. Lett.* **1999**, *1*, 1307–1309.

(6) (a) Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674–2678. (b) Scholl, M.; Trnka, T. M.; Morgan, J. T.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247–2250.

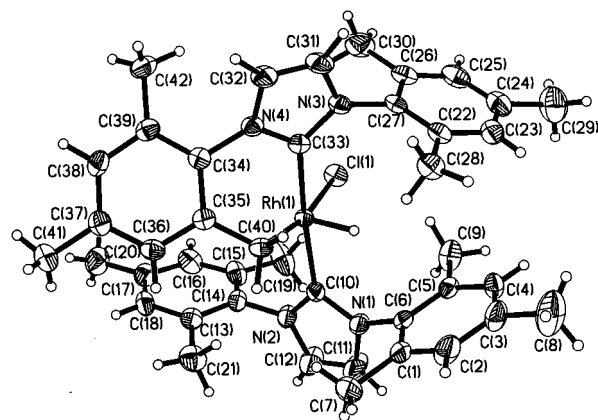
(7) Huang, J.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 2370–2375.

(8) (a) Hun, K.; Rosini, G. P.; Goldman, A. S.; Nolan, S. P. *J. Am. Chem. Soc.* **1995**, *117*, 5082–5088, and references cited. (b) Hun, K.; Goldman, A. S.; Li, C.; Nolan, S. P. *Organometallics* **1995**, *14*, 4010–4013. (c) Hun, K.; Emge, T. J.; Goldman, A. S.; Li, C.; Nolan, S. P. *Organometallics* **1995**, *14*, 4929–4936. (d) Liu, F.; Pak, E. B.; Singh, B.; Jensen, C. M.; Goldman, A. S. *J. Am. Chem. Soc.* **1999**, *121*, 4086–4087, and references therein.

Scheme 1



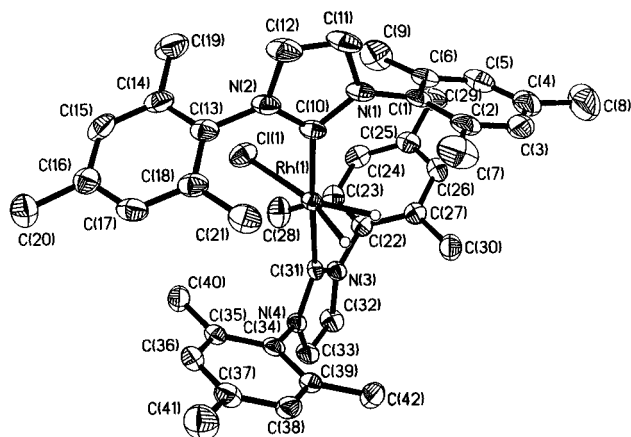
solution rapidly develops. The microcrystalline product is isolated in high yield after a simple workup. The <sup>1</sup>H NMR spectrum of the complex was surprisingly complex and showed no coordinated COE moiety present. A <sup>1</sup>H signal at -27 ppm indicated the presence of a Rh-H moiety in the new complex. The spectroscopy also indicated nonequivalent IMes ligands bound to the rhodium center. To unequivocally establish the structure of the complex, a single-crystal diffraction was performed on a crystal grown by slow diffusion of hexane over a saturated THF solution of **2**. The X-ray structure shows that **2** is actually an orthometalated complex resulting from C-H bond activation of an internal aryl methyl C-H bond of one of the IMes ligands, producing a five-coordinate Rh(III) alkyl hydride complex. (Scheme 1 and Figure 1). This was somewhat unexpected since Herrmann and co-workers<sup>9</sup> had recently reported on a related ligand substitution occurring from the [Rh(COD)Cl]<sub>2</sub> complex [COD = cyclooctadiene] resulting in [CODRhCl] products [L = nucleophilic carbene]. The COE ligand is a more weakly coordinating ligand than COD, and the relative ease of COE dissociation may prove the key in accessing RhL<sub>2</sub>Cl complexes. The



**Figure 1.** ORTEP of Rh(IMes)(H)(IMes)Cl (**2**) with ellipsoids drawn at 50% probability. Selected bond distances and angles: Rh(1)-C(33), 2.0242(17); Rh(1)-C(10), 2.0480(17); Rh(1)-C(40), 2.0793(18); Rh(1)-Cl(1), 2.4363(5); Rh(1)-H(1), 1.455(17); C(33)-Rh(1)-C(10), 172.33(7); C(33)-Rh(1)-C(40), 81.21(7); C(10)-Rh(1)-C(40), 95.66(7); C(33)-Rh(1)-Cl(1), 93.05(5); C(10)-Rh(1)-Cl(1), 91.13(5); C(40)-Rh(1)-Cl(1), 169.07(5); C(33)-Rh(1)-H(1), 87.4(7); C(10)-Rh(1)-H(1), 85.3(7); C(40)-Rh(1)-H(1), 83.5(7); Cl(1)-Rh(1)-H(1), 105.6(7).

structure of **2** shows the complex to be a slightly distorted trigonal bipyramid with IMes moieties trans to one another (172.33(7)°). One of the IMes aryl methyl

(9) (a) Herrmann, W. A.; Goosen, L. J.; Spiegler, M. *Organometallics* **1998**, *17*, 2162-2168. (b) Herrmann, W. A.; Elison, M.; Fischer, J.; Kocher, C.; Ofele, K., US Patent 5,728,839, Mar 17, 1998.



**Figure 2.** ORTEP of  $\text{Rh}(\text{IMes})_2(\text{H})_2\text{Cl}$  (**3**) with ellipsoids drawn at 50% probability. Selected bond distances and angles:  $\text{Rh}(1)-\text{C}(10)$ , 2.0183(18);  $\text{Rh}(1)-\text{C}(31)$ , 2.0216(18);  $\text{Rh}(1)-\text{Cl}(1)$ , 2.4185(6);  $\text{Rh}(1)-\text{H}(1)$ , 1.44(2);  $\text{Rh}(1)-\text{H}(2)$ , 1.647(17);  $\text{C}(10)-\text{Rh}(1)-\text{C}(31)$ , 177.24(8);  $\text{C}(10)-\text{Rh}(1)-\text{Cl}(1)$ , 89.93(5);  $\text{C}(31)-\text{Rh}(1)-\text{Cl}(1)$ , 92.68(5);  $\text{C}(10)-\text{Rh}(1)-\text{H}(1)$ , 90.7(8);  $\text{C}(31)-\text{Rh}(1)-\text{H}(1)$ , 86.7(8);  $\text{Cl}(1)-\text{Rh}(1)-\text{H}(1)$ , 143.5(8);  $\text{C}(10)-\text{Rh}(1)-\text{H}(2)$ , 90.8(5);  $\text{C}(31)-\text{Rh}(1)-\text{H}(2)$ , 86.8(5);  $\text{Cl}(1)-\text{Rh}(1)-\text{H}(2)$ , 169.4(6);  $\text{H}(1)-\text{Rh}(1)-\text{H}(2)$ , 47.1(8).

C–H bonds has been activated with a Rh–C bond length of 2.0793(18) Å and a Rh–H bond distance<sup>10</sup> of 1.455(17) Å. To minimize the steric congestion about the metal center, the IMes ligands are staggered with the imidazole rings displaying a dihedral angle of 49.19(7)°.

Reacting a THF solution of **2** with 1 atm of  $\text{H}_2$  at room temperature leads to the rapid formation of the dihydride complex **3**. The complex was successfully crystallized from THF/hexane, and an ORTEP of **3** is presented in Figure 2.

The  $\text{Rh}(\text{IMes})_2(\text{H})_2\text{Cl}$  (**3**) complex also adopts a trigonal bipyramidal structure where the two IMes ligands are now 177.24(8)° apart. A more nearly trans arrangement of the IMes ligands results from the formal release of the ortho position by Rh in **2**. A dihedral angle between the two imidazole rings of 47.43(6)° is found in **3**. Two Rh–H bonds are present in the structure:  $\text{Rh}(1)-\text{H}(1)$ , 1.44(2) Å, and  $\text{Rh}(1)-\text{H}(2)$ , 1.647(17) Å.<sup>11</sup>

Reaction involving **2** and CO affords  $\text{Rh}(\text{IMes})_2(\text{CO})\text{Cl}$ . The carbonyl stretching frequency of **2** ( $\nu_{\text{CO}} = 1935 \text{ cm}^{-1}$ ) clearly indicates the increased electron density provided by IMes compared to the  $\text{P}^i\text{Pr}_3$  ( $\nu_{\text{CO}} = 1943.2 \text{ cm}^{-1}$ ).<sup>8a</sup> This trend is similar to the one observed in our initial thermochemical studies on  $\text{Cp}^*\text{Ru}(\text{L})\text{Cl}$  complexes where the IMes ligand displays enthalpies of reaction on the order of 6 kcal/mol more exothermic than  $\text{P}^i\text{Pr}_3$ .<sup>6a</sup>

## Summary

We have shown that the reaction of the IMes nucleophilic carbene with  $[\text{Rh}(\text{COE})_2\text{Cl}]_2$  forms an orthometalated complex **2**. This complex is very reactive and in the presence of  $\text{H}_2$  rapidly forms the five-coordinate

trigonal bipyramidal dihydride  $\text{Rh}(\text{IMes})_2(\text{H})_2\text{Cl}$  (**3**). The orthometalated complex also reacts rapidly with CO to effectively reverse the orthometalation and produce a four-coordinate, square planar  $\text{Rh}(\text{IMes})_2(\text{CO})\text{Cl}$  (**4**). The carbonyl stretching frequency of **4** shows the IMes ligand to be more electron donating than the phosphine in  $\text{Rh}(\text{P}^i\text{Pr}_3)_2(\text{CO})\text{Cl}$ . The mechanism by which the orthometalation is reversed as well as the catalytic activity of these complexes is presently being investigated in our laboratories.

## Experimental Section

**General Considerations.** All manipulations involving organorhodium complexes were performed under inert atmospheres of argon or nitrogen using standard high-vacuum or Schlenk tube techniques or in an argon-filled MBraun glovebox containing less than 1 ppm oxygen and water. Solvents including deuterated solvents for NMR analysis were dried and distilled under nitrogen before use employing standard drying agents.<sup>12</sup> For example, tetrahydrofuran was stored over sodium wire, distilled from sodium benzophenone ketyl, stored over Na/K alloy, and vacuum transferred into flame-dried glassware prior to use. 1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes)<sup>13</sup> and  $[\text{Rh}(\text{COE})_2\text{Cl}]_2$ <sup>14</sup> were synthesized according to literature procedures.  $\text{H}_2$  and CO were purchased from Matheson and purified prior to use (passed through columns of molecular sieves/manganese oxide). NMR spectra were recorded using a Oxford-400 MHz spectrometer. Infrared spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer. Elemental analyses were performed by Desert Analysis, Tucson, AZ.

**Synthesis.** Experimental procedures, leading to isolation of previously unreported complexes, are described below.

**$\text{Rh}(\text{IMes})(\text{H})(\text{IMes}')\text{Cl}$  (**2**).** A 100 mL flask was charged with 0.995 g (1.387 mmol) of  $[\text{Rh}(\text{COE})_2\text{Cl}]_2$ , 1.700 g (5.547 mmol) of IMes, and 50 mL of dry THF in the glovebox. The flask was taken out of the box and connected to a Schlenk line. The clear orange solution was stirred at room temperature for 60 min, after which the solvent was removed under vacuum. The residue was washed with pentane ( $2 \times 10 \text{ mL}$ ), filtered, and dried under vacuum, which afforded the yellow powder. Yield: 1.702 g, 82%.  $^1\text{H}$  NMR (400 MHz,  $\text{THF}-d_6$ )  $\delta$ : –27.30 (br, Rh–H), 2.10 (s, 18 H, Mes-2, 6- $\text{CH}_3$ ), 2.20 (s, 3 H, Mes-2,6- $\text{CH}_3$ ), 2.24 (s, 3 H, Mes-4- $\text{CH}_3$ ), 2.36 (s, 9 H, Mes-4- $\text{CH}_3$ ), 2.41 (s, 2 H, Rh– $\text{CH}_2$ ), 6.42 (s, 1 H, NCHCHN of IMes'), 6.66 (s, 1 H, NCHCHN of IMes'), 6.76 (s, 2 H, NCHCHN of IMes'), 6.84 (s, 4 H, Mes-3, 5-H), 6.95 (s, 2 H, Mes-3, 5-H), 6.87 (d, 1 H,  $J = 2 \text{ Hz}$ , Mes'-3(5)-H), 7.42 (d,  $J = 2 \text{ Hz}$ , Mes'-3(5)-H) ppm. Anal. Calcd for  $\text{C}_{42}\text{H}_{48}\text{ClN}_4\text{Rh}$ : C, 67.51; H, 6.47; N, 7.50. Found: C, 67.69; H, 6.34; N, 7.14.

**$\text{Rh}(\text{IMes})_2(\text{H})_2\text{Cl}$  (**3**).** A 50 mL flask was charged with 0.202 g (0.270 mmol) of  $\text{Rh}(\text{IMes})(\text{H})(\text{IMes}')\text{Cl}$  and 20 mL of dry THF in the glovebox. The flask was taken out of the box and connected to a Schlenk line. The clear yellow solution was purged with  $\text{H}_2$  at room temperature for 60 min, after which the solvent was removed under vacuum. The residue was washed with pentane ( $2 \times 10 \text{ mL}$ ), filtered, and dried under vacuum, which afforded the light yellow powder. Yield: 0.188

(12) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, 1988.

(13) (a) Arduengo, A. J., III; Harlow, R. L.; Kline, M. J. *J. Am. Chem. Soc.* **1991**, *113*, 361–363. (b) Arduengo, A. J., III; Gamper, S. F.; Calabrese, J. C.; Davidson, F. J. *J. Am. Chem. Soc.* **1994**, *116*, 4391–4393. (c) Adducts of a related carbene ligand with group II and XII metallocenes have been reported: Arduengo, A. J., III; Davidson, F.; Kraftczyk, R.; Marshall, W. J.; Tamm, M. *Organometallics* **1998**, *17*, 3375–3382. (d) Arduengo, A. J., III. *Acc. Chem. Res.* **1999**, *32*, 913–921.

(14) Werner, H.; Wolf, J.; Hohn, A. *J. Organomet. Chem.* **1985**, *287*, 395–407.

(10) All hydrogens contained in complex **2** were located on a difference Fourier map and refined in full-matrix least-square refinements.

(11) All hydrogens contained in complex **3** were located on a difference Fourier map and refined in full-matrix least-square refinements.

Table 1. Crystal Data and Structure Refinement for **2** and **3**

	<b>2</b>	<b>3</b>
empirical formula	C <sub>42</sub> H <sub>48</sub> ClN <sub>4</sub> Rh	C <sub>42</sub> H <sub>50</sub> ClN <sub>4</sub> Rh
fw	747.23	749.22
wavelength (Å)	0.71073	0.71073
cryst syst	monoclinic	Orthorhombic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>Pbca</i>
unit cell dimens	<i>a</i> = 16.1160(6) Å <i>b</i> = 12.2405(5) Å <i>c</i> = 20.8719(8) Å $\alpha = 90^\circ$ , $\beta = 103.1^\circ$ , $\gamma = 90^\circ$	<i>a</i> = 16.935(2) Å <i>b</i> = 19.226(3) Å <i>c</i> = 23.173(3) Å $\alpha = 90^\circ$ , $\beta = 90^\circ$ , $\gamma = 90^\circ$
volume (Å <sup>3</sup> )	4010.4(3)	7545.1(18)
<i>Z</i>	4	8
density (g/cm <sup>3</sup> )	1.302	1.319
abs coeff	0.528 mm <sup>-1</sup>	0.558 mm <sup>-1</sup>
<i>F</i> (000)	1644	3136
crysta size (mm <sup>3</sup> )	0.10 × 0.20 × 0.30	0.15 × 0.45 × 0.50
$\theta$ range for data collection	1.81–30.00°	2.12–27.50°
index ranges	–22 ≤ <i>h</i> ≤ 22, –17 ≤ <i>k</i> ≤ 17, –29 ≤ <i>l</i> ≤ 29	–22 ≤ <i>h</i> ≤ 17, –24 ≤ <i>k</i> ≤ 24, –29 ≤ <i>l</i> ≤ 30
no. of reflns collected	66 596	59 394
no. of ind reflns	11 697 [ <i>R</i> (int) = 0.0665]	8661 [ <i>R</i> (int) = 0.0542]
no. of data/restraints/params	11697/36/674	8661/434/633
goodness-of-fit on <i>F</i> <sup>2</sup>	0.829	0.690
final <i>R</i> indices	<i>R</i> 1 = 0.0291, <i>wR</i> 2 = 0.0544	<i>R</i> 1 = 0.0239, <i>wR</i> 2 = 0.0364
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0647, <i>wR</i> 2 = 0.0585	<i>R</i> 1 = 0.0640, <i>wR</i> 2 = 0.0378

g, 93%. <sup>1</sup>H NMR (400 MHz, THF-*d*<sub>8</sub>)  $\delta$ : –23.04 (d, *J* = 34.8 Hz, 2 H, Rh-*H*), 1.86 (s, 24 H, Mes-2,6-CH<sub>3</sub>), 2.42 (s, 12 H, Mes-4-CH<sub>3</sub>), 6.765 (d, 8 H, Mes-3, 5-*H*), 6.86 (s, 4 H, NCHCHN) ppm. Anal. Calcd for C<sub>42</sub>H<sub>50</sub>ClN<sub>4</sub>Rh: C, 67.33; H, 6.73; N, 7.48. Found: C, 67.05; H, 6.57; N, 7.10.

**Rh(IMes)<sub>2</sub>(CO)Cl (4).** A 50 mL flask was charged with 0.1935 g (0.259 mmol) of Rh(IMes)(H)(IMes')Cl and 10 mL of dry THF in the glovebox. The flask was taken out of the box and connected to a Schlenk line. The clear yellow solution was purged with CO at room temperature for 60 min, after which the solvent was removed under vacuum. The residue was washed with pentane (2 × 10 mL), filtered, and dried under vacuum, which afforded the off-white powder. Yield: 0.173 g, 86%. <sup>1</sup>H NMR (400 MHz, THF-*d*<sub>8</sub>)  $\delta$ : 1.81, 1.93 (both br, 24 H, Mes-2,6-CH<sub>3</sub>), 2.43 (s, 12 H, Mes-4-CH<sub>3</sub>), 6.84 (d, 8 H, Mes-3, 5-*H*), 7.00 (s, 4 H, NCHCHN) ppm. IR (CH<sub>2</sub>Cl<sub>2</sub>,  $\nu$ ): 1935 cm<sup>-1</sup>. Anal. Calcd for C<sub>43</sub>H<sub>48</sub>ClN<sub>4</sub>ORh: C, 66.62; H, 6.24; N, 7.23. Found: C, 66.45; H, 6.22; N, 7.48.

**X-ray Diffraction Measurements.** A single crystal of **2** or **3** [grown by slow diffusion of hexane through a saturated THF solution of **2** or by cooling a saturated THF/hexane solution of **3**] was coated with paratone oil and then sealed in a glass capillary tube. The X-ray data were collected at low

temperature using graphite-monochromated Mo K $\alpha$  radiation on a Bruker diffractometer fitted with a CCD detector. The structure was solved using direct methods (SHELXS-86) and refined by full-matrix least-squares techniques. Initial fractional coordinates for the Rh atom were determined by heavy-atom methods, and the remaining non-hydrogen atoms were located by successive difference Fourier calculations, which were performed with algorithms provided by SHELXTL IRIS operating on a Silicon Graphics IRIS Indigo workstation. Crystallographic data can be found in Table 1.

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**Supporting Information Available:** Details of crystal structure determinations for **2** and **3** (PDF) are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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