2616 *Organometallics* **2010,** *29,* 2616–2630
DOI: 10.1021/om1003607

ORGANOMETALLICS
Article

Facile Derivatization of a "Chemo-active" NHC Incorporating an Enolate Backbone and Relevant Tuning of Its Electronic Properties

Laure Benhamou, Nadia Vujkovic, Vincent César,* Heinz Gornitzka, Noël Lugan, and Guy Lavigne*

LCC (Laboratoire de Chimie de Coordination), CNRS, 205 Route de Narbonne, F-31077 Toulouse, France, and Université de Toulouse, UPS, INPT, 31077 Toulouse, France

Received April 28, 2010

The present report discloses a modular synthetic route to a new type of anionic N-heterocyclic carbene ligand incorporating an enolate group as a reactive backbone component of its heterocyclic framework. The presence of such a reactive unit facilitates further tailoring of the ligand, even after its complexation to transition metals, with concomitant tuning of the electronic donor properties of the carbene center. Simple acylation of the formamidine Ar-NH-CH=NAr (**1a**,**b**) (**a**: Ar = mesityl (Mes); **b**: Ar = 2,6-diisopropylphenyl (DIPP)) by chloroacetyl chloride gives an acylated formamidine (**2a**,**b**), which undergoes a thermally induced cyclization to afford the 4-hydroxyimidazolium salt **3a**,**b**. Single deprotonation by NEt_3 gives the zwitterionic imidazolium-4-olate **4**, whereas double deprotonation by 2 equiv of LiHMDS gives the imidazolin-2-ylidene-4-olate ligand $\mathbf{5}^-$, which reacts with 0.5 equiv of $[RhCl(1,5\text{-}COD)]_2$ to give, after acidification with HCl, the complex $[(\mathbf{5_H})RhCl(COD)]$ (**7**), in which the "acidified" carbene ligand noted "$\mathbf{5_H}$" adopts the keto form. By contrast, treatment of **4** with electrophilic reagents **E**-X ($\mathbf{E_1}$ = *t*BuCO; $\mathbf{E_2}$ = Me; $\mathbf{E_3}$ = Tf) results in the O-functionalized imidazolium derivatives $[\mathbf{4}^{\mathbf{E1-3}}]^+X^-$, which can be subsequently complexed under the form of the carbene $\mathbf{5}^{\mathbf{E1-3}}$ to give $[(\mathbf{5}^{\mathbf{E1-3}})RhCl(COD)]$ ($\mathbf{7}^{\mathbf{E1-3}}$). Alternatively, the carbene ligand **5** can be post-functionalized from its complex $[(\mathbf{5_H})RhCl(COD)]$ (**7**) by a simple sequence involving (i) base-induced deprotonation and (ii) addition of **E**-X, exemplified by the generation of $[(\mathbf{5}^{\mathbf{E4-5}})RhCl(COD)]$ ($\mathbf{7}^{\mathbf{E4-5}}$) (with $\mathbf{E_4}$ = Ph_2PO; $\mathbf{E_5}$ = *t*BuSiMe$_2$ (TBDMS)). In parallel, C-functionalization of the metal-bound ligand can be achieved from **7** by deprotonation with LiHMDS, leading to $[(\mathbf{5}^-)RhCl(COD)]Li(thf)_n^+$ followed by a classical aldolization/elimination sequence leading to $[(\mathbf{5_{CH2}})RhCl(COD)]$ (**8**), in which the C5 carbon of the NHC bears a methylene group. Parallel direct transformations can be achieved after ligand complexation to copper, as exemplified by the generation of $[(\mathbf{5_H})CuCl]$ (**9**) or $[(\mathbf{5}^{\mathbf{E5}})CuCl]$ ($\mathbf{9}^{\mathbf{E5}}$) ($\mathbf{E_5}$ = TBDMS). The donor properties of all the above NHC ligands were evaluated from the standard complexes $(NHC)RhCl(CO)_2$ against the classical IR ν(CO) scale. The resulting order of nucleophilicities for the modulated carbenes is $\mathbf{5_{CH2}} < \mathbf{5_H} \ll \mathbf{5}^{\mathbf{E4}} < \mathbf{5}^{\mathbf{E1}} < \mathbf{5}^{\mathbf{E2}} < \mathbf{5}^{\mathbf{E5}} \ll \mathbf{5}^-$. The X-ray structures analyses of $\mathbf{7}^{\mathbf{E2}}$ and $\mathbf{7}^{\mathbf{E4}}$ are reported.

Introduction

Synthetic versatility and structural modularity are desirable criteria in the selection of ancillary ligands for transition metal complex catalyzed reactions. Indeed, a ligand whose functional "modules" can be easily interchanged will be ideally suited for a rapid precatalyst screening, ultimately allowing a fast optimization of the catalyst's performance. In the specific case of N-heterocyclic carbenes,[1,2] there is a growing diversity in the synthetic approaches that have been recently devised for such compounds,[3] offering attractive possibilities to modify distinctly their *steric* and *electronic* properties.

Whereas the steric properties, quantifiable in terms of "percentage of buried volume",[4] are generally adjusted by

*Corresponding authors. E-mail: vincent.cesar@lcc-toulouse.fr; guy.lavigne@lcc-toulouse.fr.

(1) For monographs, see: (a) *N-Heterocyclic Carbenes in Transition Metal Catalysis* (*Topics in Organometallic Chemistry* 2007; Vol. *21*); Glorius, F., Ed.; Springer: Berlin, 2007; (b) *N-Heterocyclic Carbenes in Synthesis*; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, 2006.

(2) For general reviews on NHCs, see: (a) Schuster, O.; Yang, L.; Raubenheimer, H. G.; Albrecht, M. *Chem. Rev.* **2009**, *109*, 3445. (b) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122. (c) Bourissou, D.; Guerret, O.; Gabbaï, F.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.

(3) For synthetic methods of NHCs, see: (a) Arduengo, A. J., III. U.S. Patent 5 077 414, 1992. (b) Glorius, F.; Altenhoff, G.; Goddard, R.; Lehmann, C. W. *Chem. Commun.* **2002**, 2704. (c) Arduengo, A. J., III; Krafczyk, R.; Schmultzer, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523. (d) Nolan, S. P. U.S. Patent 7 109 348, 2006. (e) Jafarpour, L.; Stevens, E. D.; Nolan, S. P. *J. Organomet. Chem.* **2006**, *606*, 49. (f) Bertogg, A.; Camponovo, F.; Togni, A. *Eur. J. Inorg. Chem.* **2005**, 347. (g) Hirano, K.; Urban, S.; Wang, C.; Glorius, F. *Org. Lett.* **2009**, *11*, 1019. (h) Fürstner, A.; Alcarazo, M.; César, V.; Lehmann, C. W. *Chem. Commun.* **2006**, 2176.

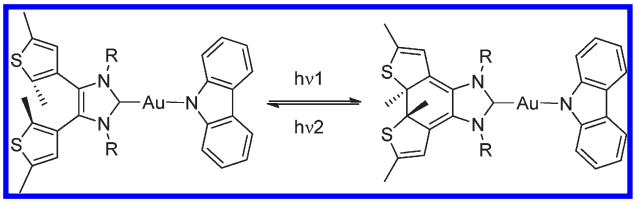
(4) (a) For a general review, see: Diez-Gonzalez, S.; Nolan, S. P. *Coord. Chem. Rev.* **2007**, *251*, 874. (b) For a leading reference on the calculation of the buried volume of monodentate NHCs, see: Poater, A.; Cosenza, B.; Correa, A.; Giudice, S.; Ragone, F.; Scarano, V.; Cavallo, L. *Eur. J. Inorg. Chem.* **2009**, 1759.

 Published on Web 05/19/2010

playing with the ring size or the nature of the nitrogen substituents,[5] the electronic properties may be varied by diverse means including (i) the grafting of various electron-withdrawing or electron-releasing elements, either on the nitrogen substituents[6] or, even more efficiently, on the backbone atoms of the heterocycle (in some cases fused with nitrogen substituents),[7] (ii) the introduction of heteroelements within the backbone,[8] or (iii) the direct replacement of a nitrogen atom of the diaminocarbene unit by a quaternary or ylidic carbon.[9]

In practice, however, the structural modularity of these systems is not always readily exploitable for a precatalyst screening, since most ligand modifications have to be planned in advance and introduced in the early stages of the synthesis, even often requiring a total reconstruction of the heterocyclic framework. So, there is still a need for the development of N-heterocyclic carbenes incorporating a functional backbone susceptible to allowing further chemical modifications allowing a real-time tuning of the electronic properties.

Chart 1. Literature Example of Post-functionalization of a Coordinated Carbene Induced by Reversible UV−Visible Excitation[13]



In this context, the recent transposition of the concept of "redox-active" ligands[10] to the case of N-heterocyclic carbenes, by Bielawski[11] and Siemelink,[12] has proven to be particularly useful, with the spectacular example of a metallacyclic N-heterocyclic carbene possessing an electro-active 1,1′-ferrocenediyl backbone. Indeed, the electronic properties of the latter could be remotely switched by oxidation or reduction of the iron center, albeit offering the possibility to obtain only two stable states.

In the same vein, a remarkable example of ligand post-functionalization can be found in the recent report, by Yam and co-workers, of a *photoswitchable* NHC incorporating a di(thiophenyl)ethene backbone, which was seen to undergo a reversible skeletal reorganization via a C−C bond activation triggered by UV−visible irradiation at specific wavelengths (Chart 1).[13]

With these results in mind, we became interested in the search for simple routes to *chemo-active* NHC ligands. Our first investigation in this area led to the disclosure of a series of anionic six-membered N-heterocyclic carbenes incorporating a malonate backbone (Chart 2).[14] Later on, we demonstrated that they are effectively *chemo-active*, in the sense that they are sensitive to an external chemical modification applicable even after their coordination to a transition metal.[15] It was found that their electronic properties can be smoothly modified by addition of a variety of electrophilic reagents interacting directly with the oxygen of the backbone malonate unit in the outer coordination sphere of the complex, and a logical correlation could be established between the ligand's donor properties and the catalytic performances of its complexes. In parallel, it was also noted that formal addition of the electrophile to the central carbon of the malonate group also results in an important decrease of the ligand's donicity.[16,17]

Beyond this, we were also interested in a transposition of this concept to the case of five-membered heterocycles. While thinking of a representative chemically reactive function

(5) For a comparison of the catalytic performances of a series of electronically identical NHCs exhibiting different steric constraints, see: (a) Würtz, S.; Glorius, F. *Acc. Chem. Res.* **2008**, *41*, 1523. (b) Altenhoff, G.; Goddard, R.; Lehmann, C. W.; Glorius, F. *J. Am. Chem. Soc.* **2004**, *126*, 15195. (c) Altenhoff, G.; Goddard, R.; Lehmann, C. W.; Glorius, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 3690.

(6) (a) Sashuk, V.; Peeck, L. H.; Plenio, H. *Chem.—Eur. J.* **2010**, *16*, 3983. (b) Ogle, J. W.; Miller, S. A. *Chem. Commun.* **2009**, 5728. (c) Leuthäusser, S.; Schmidts, V.; Thiele, C. M.; Plenio, H. *Chem.—Eur. J.* **2008**, *14*, 5465. (d) Leuthäusser, S.; Schwarz, D.; Plenio, H. *Chem.—Eur. J.* **2007**, *13*, 7195.

(7) (a) Hahn, F. E.; Wittenbecher, L.; Boese, R.; Bläser, D. *Chem.—Eur. J.* **1999**, *5*, 1931. (b) Khramov, D. M.; Rosen, E. L.; Er, J. A. V.; Vu, P. D.; Lynch, V. M.; Bielawski, C. W. *Tetrahedron* **2008**, *64*, 6853. (c) Fürstner, A.; Alcarazo, M.; Krause, H.; Lehmann, C. W. *J. Am. Chem. Soc.* **2007**, *129*, 12676. (d) Gomez-Bujedo, S.; Alcarazo, M.; Pichon, C.; Alvarez, E.; Fernandez, R.; Lassaletta, J. M. *Chem. Commun.* **2007**, 1180. (e) Hadei, N.; Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Org. Lett.* **2005**, *7*, 1991. (f) Saravanakumar, S.; Oprea, A. I.; Kindermann, M. K.; Jones, P. G.; Heinicke, J. *Chem.—Eur. J.* **2006**, *12*, 3143. (g) Saravanakumar, S.; Kindermann, M. K.; Heinicke, J.; Köckerling, M. *Chem. Commun.* **2006**, 640. (h) Kascatan-Nebioglu, A.; Panzner, M. J.; Garrison, J. C.; Tessier, C. A.; Youngs, W. J. *Organometallics* **2004**, *23*, 1928. (i) Schütz, J.; Herrmann, W. A. *J. Organomet. Chem.* **2004**, *689*, 2995. (j) Herrmann, W. A.; Schütz, J.; Frey, G. D.; Herdtweck, E. *Organometallics* **2006**, *25*, 2437. (k) Tapu, D.; Owens, C.; VanDerveer, D.; Gwaltney, K. *Organometallics* **2009**, *28*, 270. (l) Ullah, F.; Kindermann, M. K.; Jones, P. G.; Heinicke, J. *Organometallics* **2009**, *28*, 2441. (m) Nonnenmacher, M.; Kunz, D.; Rominger, F.; Oeser, T. *Chem. Commun.* **2006**, 1378. (n) Nonnenmacher, M.; Kunz, D.; Rominger, F.; Oeser, T. *J. Organomet. Chem.* **2005**, *690*, 5647. (o) Alcarazo, M.; Roseblade, S. J.; Cowley, A. R.; Fernandez, R.; Brown, J. M.; Lassaletta, J. M. *J. Am. Chem. Soc.* **2005**, *127*, 3290. (p) Würtz, S.; Glorius, F. *Acc. Chem. Res.* **2008**, *41*, 1523. (q) While the present work was reviewed, a new, nice method to functionalize the backbone atoms of an unsaturated five-membered-ring NHC has appeared; see: Mendosa-Espinosa, D.; Donnadieu, B.; Bertrand, G. *J. Am. Chem. Soc.* **2010**, asap, 10.1021/ja102639a.

(8) (a) Präsang, C.; Donnadieu, B.; Bertrand, G. *J. Am. Chem. Soc.* **2005**, *127*, 10182. (b) Krahulic, K. E.; Enright, G. D.; Parvez, M.; Roesler, R. *J. Am. Chem. Soc.* **2005**, *127*, 4142. (c) Despagnet-Ayoub, E.; Grubbs, R. H. *J. Am. Chem. Soc.* **2004**, *126*, 10198.

(9) (a) Fürstner, A.; Alcarazo, M.; Radkowski, K.; Lehmann, C. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 8302. (b) Nakafuji, S.; Kobayashi, J.; Kawashima, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 1141. (c) Frey, G. D.; Lavallo, V.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *Science* **2007**, *316*, 439. (d) Lavallo, V.; Canac, Y.; DeHope, A.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 7236. (e) Lavallo, V.; Canac, Y.; Präsang, C.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 5705.

(10) For leading references on redox-active ligands and catalysts, see: (a) Allgeier, A. M.; Mirkin, C. A. *Angew. Chem.. Int. Ed.* **1998**, *37*, 894. (b) Ringenberg, M. R.; Kokatam, S. L.; Heiden, Z. M.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2008**, *130*, 788. (c) Gregson, C. K. A.; Gibson, V. C.; Long, N. L.; Marshall, E. L.; Oxford, P. J.; White, A. J. P. *J. Am. Chem. Soc.* **2006**, *128*, 7410. (d) Siemeling, U.; Schrock, R. R.; Stammler, A.; Stammler, H.-G.; Kuhnert, O. *Z. Anorg. Allg. Chem.* **2001**, *627*, 925. (e) Lorkovic, I. M.; Duff, R. R., Jr.; Wrighton, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 3617.

(11) (a) Tennyson, A. G.; Ono, R. J.; Hudnall, T. W.; Khramov, D. M.; Er, J. A. V.; Kamplain, J. W.; Lynch, V. M.; Sessler, J. L.; Bielawski, C. W. *Chem.—Eur. J.* **2010**, *16*, 304. (b) Rosen, E. L.; Varnado, C. D., Jr.; Tennyson, A. G.; Khramov, D. M.; Kamplain, J. W.; Sung, D. H.; Cresswell, P. T.; Lynch, V. M.; Bielawski, C. W. *Organometallics* **2009**, *28*, 6695. (c) Varnado, C. D., Jr.; Lynch, V. M.; Bielawski, C. W. *Dalton Trans.* **2009**, 7253. (d) Khramov, D. M.; Rosen, E. L.; Lynch, V. M.; Bielawski, C. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 2267. (e) Sanderson, M.; Kamplain, J. W.; Bielawski, C. W. *J. Am. Chem. Soc.* **2006**, *128*, 16514.

(12) (a) Siemeling, U.; Färber, C.; Leibold, M.; Bruhn, C.; Mücke, P.; Winter, R. F.; Sarkar, B.; von Hopffgarten, M.; Frenking, G. *Eur. J. Inorg. Chem.* **2009**, 4607. (b) Siemeling, U.; Färber, C.; Bruhn, C. *Chem. Commun.* **2009**, 98.

(13) Yam, V. W.-W.; Lee, J. K.-W.; Ko, C.-C.; Zhu, N. *J. Am. Chem. Soc.* **2009**, *131*, 912.

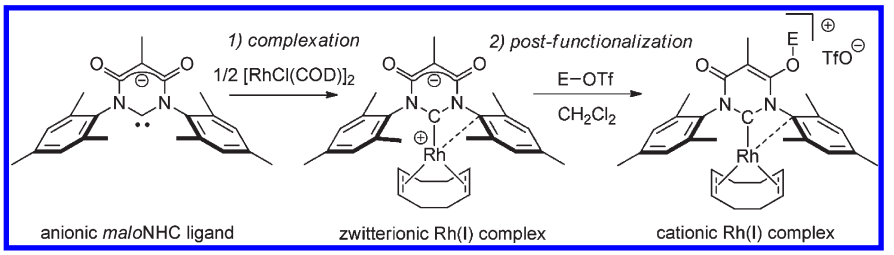
(14) César, V.; Lugan, N.; Lavigne, G. *J. Am. Chem. Soc.* **2008**, *130*, 11286.

(15) César, V.; Lugan, N.; Lavigne, G. Submitted for publication.

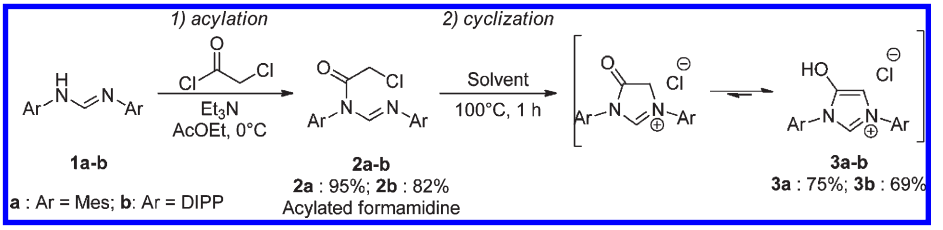
(16) Hudnall, T. W.; Bielawski, C. W. *J. Am. Chem. Soc.* **2009**, *131*, 16039.

(17) César, V.; Lugan, N.; Lavigne, G. *Eur. J. Inorg. Chem.* **2010**, 361.

Chart 2. Post-functionalization of an Anionic N-Heterocyclic Carbene after Its Coordination to Rhodium[15]



Scheme 1. Synthesis of the 4-Hydroxyimidazolium Ligand



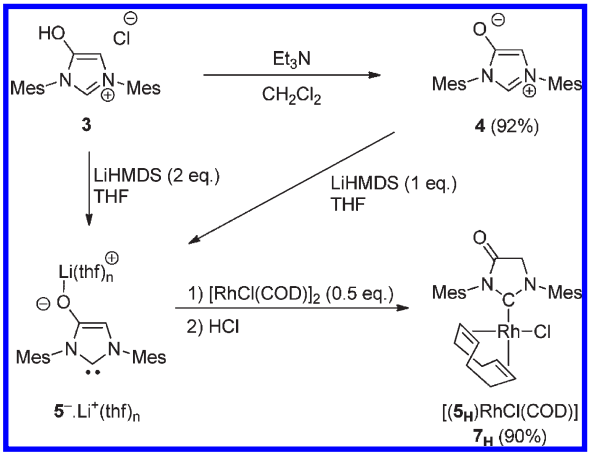
susceptible to serve as a backbone for the targeted heterocycle, we came to the idea that an enolate group, possessing a readily exploitable intrinsic chemical reactivity, could be an attractive candidate, provided one could find a simple synthetic strategy to incorporate it.

Results and Discussion

As previously disclosed in a preliminary communication of the present work,[18,19] the target 4-hydroxyimidazolium cation **3** (Scheme 1) was easily prepared on a gram scale by an original modular synthetic route involving a simple acylation of the formamidine **1** by chloroacetyl chloride in air, giving an acylformamidine (**2**), which, upon heating, was subsequently cyclized via an intramolecular nucleophilic substitution leading to the precipitation of the salt **3**. The elusive intermediate 4-oxo-1,3-diarylimidazolinium salt was not detected, due to the existence of a tautomeric keto/enol equilibrium being strongly favorable to the formation of the 4-hydroxyimidazolium cation, representing the preferred enol form.

The method effectively proved to work with a good efficiency. The cationic precursor **3**, possessing two acidic functions differentiable by their pK_a values, namely, a phenol-type OH group (pK_a ~9−10) and an acidic imidazolium proton on the C2 center (pK_a ~22−24),[20] could be engaged in single or double deprotonation depending on the pK_a of the added base. Typically, deprotonation of the OH group was made to occur by reaction with a weak base such as triethylamine (pK_a = 10.75), generating the zwitterionic imidazolium-4-olate **4** (Scheme 2). Besides, a double deprotonation was observed in the presence of a stronger base such as LiHMDS, giving directly the anionic imidazol-2-yliden-4-olate $\mathbf{5}^{-}\cdot Li^{+}$, which was identified as a carbene through its reaction with sulfur to give the thiourea-type ligand **6** (not represented here).[18] It could be trapped with half an

Scheme 2. *In Situ* Generation of the Imidazol-2-ylidene-4-olate and Subsequent Trapping with a Transition Metal Complex



equivalent of the classical rhodium dimer $[RhCl(COD)]_2$ to give, after acidification by HCl, the new complex $[(\mathbf{5_H})RhCl(COD)]$ (**7**), representing the principal starting compound of the present investigation. The analogous NHC species incorporating DIPP as nitrogen substituent is also accessible, but we will deliberately restrict our comments here to the case of the mesityl derivative.

Whereas our preliminary communication[18] focused mainly on the synthetic procedure and showed that the ligand can be post-functionalized either at the oxygen or at the carbon of the enolate group, the present report gives a more detailed analysis of such modifications and examines their respective consequences in terms of electronic modulation of the carbene center.

Two main strategies are available for functionalizing the reactive enolate backbone of the imidazol-2-yliden-4-olate ligand disclosed in this work. We first briefly describe the classical one, consisting in modifications introduced directly onto the preligand, and then focus more deeply on those implemented after the coordination of the NHC to transition metal complexes, exemplified below by Rh and Cu species.

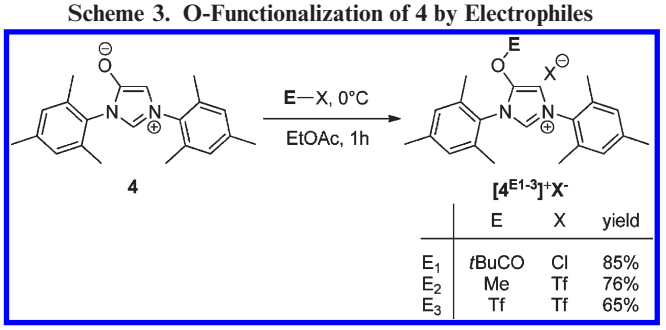
A. Functionalization of the Imidazolium-4-olate by Reaction with Electrophiles and Subsequent Complexation with Rhodium. Our first experiments (Scheme 3) indicated that the

(18) Benhamou, L.; César, V.; Gornitzka, H.; Lugan, N.; Lavigne, G. *Chem. Commun.* **2009**, 4720.

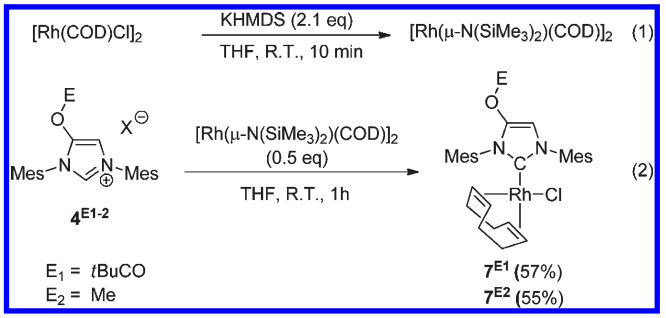
(19) See also the following related work developed by the Glorius' group: Biju, A. T.; Hirano, K.; Fröhlich, R.; Glorius, F. *Chem. Asian J.* **2009**, *4*, 1786.

(20) (a) Kim, Y.-J.; Streitwieser, A. *J. Am. Chem. Soc.* **2002**, *124*, 5757. (b) Alder, R. W.; Allen, P. R.; Williams, S. J. *J. Chem. Soc., Chem. Commun.* **1995**, 1267.

Scheme 3. O-Functionalization of 4 by Electrophiles



Scheme 4. Synthesis of the Rhodium(I) Complexes $7a^{E1-2}$ from the Salts $4a^{E1-2}$



zwitterionic preligand **4** readily reacts with electrophiles ($\mathbf{E_{1-3}}$-X: $\mathbf{E_1}$-X = pivaloyl chloride; $\mathbf{E_2}$-X = methyl triflate; $\mathbf{E_3}$-X = triflic anhydride) at 0 °C in ethyl acetate to give precipitation of the corresponding O-functionalized imidazolium salts $[\mathbf{4^E}]^+X^-$, recovered in good yields as white powders, which were fully characterized both spectroscopically and analytically.

Rhodium complexes incorporating an NHC derived from the above precursors were then prepared by the method originally proposed by Hermann,[21] which is generally used in the case of unstable carbenes.[22] It consists in the generation of a rhodium precursor incorporating a basic ligand susceptible to deprotonating the imidazolium salt, in such a way that the carbene, generated *in situ* in the vicinity of the metal center, can be more efficiently trapped. Although the published procedure generally uses potassium *tert*-butoxide, such a base was not found suitable in the present case since it might undergo nucleophilic attack at the previously introduced functional group. So, we opted for a less nucleophilic base such as potassium bis(trimethylsilyl)amide (KHMDS). In a typical procedure, the amido Rh(I) complex [Rh(μ-N(SiMe$_3$)$_2$)(COD)]$_2$ was generated *in situ* by treatment of [RhCl(COD)]$_2$ with KHMDS (0.5 M solution in toluene) in THF at room temperature (Scheme 4, eq 1).[23] The desired imidazolium salt $[\mathbf{4^E}]^+\mathbf{X}^-$ was then added as a solid at room temperature, and the solution was stirred for 1 h (Scheme 4, eq 2). The resulting Rh(I) complexes $\mathbf{7^{E1-2}}$ were purified by chromatography on neutral alumina in dichloromethane and isolated in satisfactory yields ($\mathbf{7^{E1}}$: 57%; $\mathbf{7^{E2}}$: 55%) as yellow, air-stable solids.

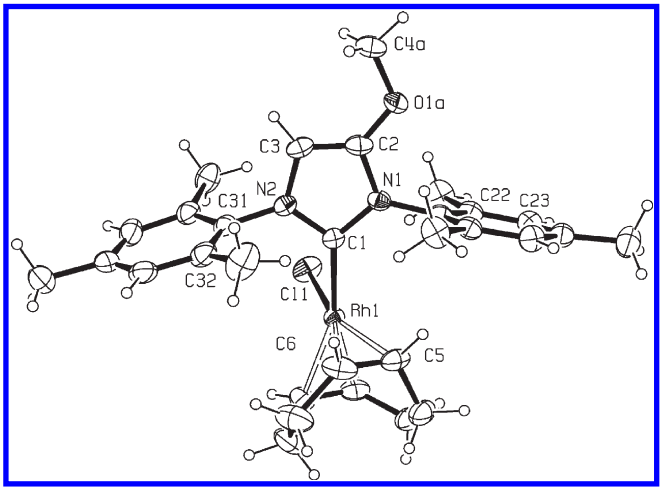


Figure 1. Perspective view of complex $\mathbf{7^{E2}}$. Selected interatomic distances [Å] and bond angles [deg]: Rh−C(1) 2.044(4), Rh−Cl-(1) 2.3653(15), Rh−C(5) 2.097(5), Rh−C(6) 2.101(5), Rh−C(9) 2.186(4), Rh−C(10) 2.195(5), C(2)−C(3) 1.328(6), C(1)−Rh−Cl(1) 88.03(10), C(1)−Rh−C(6) 94.03(15), C(1)−Rh−C(9) 92.44(15), N(1)−C(1)−N(2) 102.8(3).

Both complexes were isolated in analytically pure form and were fully characterized by ^{1}H and ^{13}C NMR. The characteristic signals of the carbenic carbon are observed at $\delta(N_2C)_{piv}$ = 179.6 ppm (d, J_{RhC} = 53.1 Hz) ppm for $\mathbf{7^{E1}}$ and at $\delta(N_2C)_{Me}$ = 178.9 ppm (d, J_{RhC} = 53.1 Hz) for $\mathbf{7^{E2}}$, consistent with literature data for imidazol-2-ylidene complexes of Rh(I).[24]

Yellow single crystals of $\mathbf{7^{E2}}$ were obtained by slow evaporation of a dichloromethane/pentane (1/10) mixture and were subjected to an X-ray structure analysis. The molecular structure is depicted in Figure 1, also giving a selection of interatomic distances (Å) and bond angles (deg). The complex is tetracoordinated and adopts a classical square-planar geometry. The Rh−C1 bond length, 2.044(4) Å, lies within the normal range of those observed for comparable NHC complexes of Rh(I).[25] The mesityl cycles are roughly orthogonal to the plane of the heterocycle (dihedral angles C1−N1−C21−C22 = 89.4(5)° and C1−N2−C31−C32 = 82.5(5)°). It is noteworthy that the interatomic Rh−C_{COD} bond distances corresponding to the olefinic carbon atoms *trans* to the carbene center are slightly longer than those *trans* to the chloride, which indicates that the *trans* influence of the NHC is higher than that of the chloride, in agreement with relevant data on related complexes.

B. Alternate Route to Rh Complexes from the Anionic Imidazol-2-yliden-4-olate. The 4-hydroxyimidazolium cation **3** was deprotonated by two equivalents of LiHMDS, and the incipient carbene $\mathbf{5}^-$ thus generated *in situ* was treated with half an equivalent of [RhCl(COD)]$_2$ in THF at 0 °C to produce, after neutralization, the Rh(I) complex [($\mathbf{5_H}$)RhCl-(COD)] ($\mathbf{7_H}$), isolated in 90% yield after purification through an alumina column using dichloromethane as eluent (Scheme 5). Very characteristically, whereas the imidazolium precursor **3** exists exclusively in the enol form, the complexed carbene in

(21) Köcher, C.; Herrmann, W. A. *J. Organomet. Chem.* **1997**, *532*, 261.

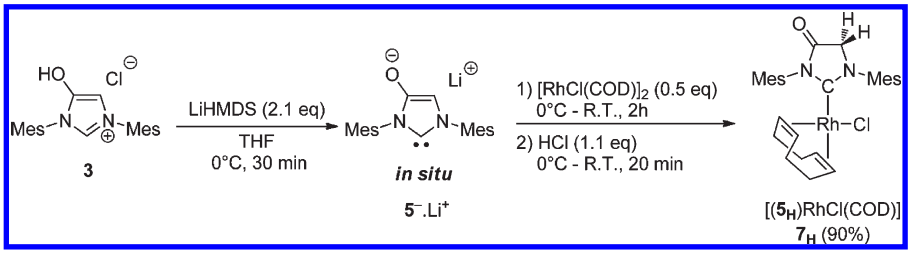
(22) Peris, E. In *N-Heterocyclic Carbenes in Transition Metal Catalysis* (*Topics in Organometallic Chemistry*, 2007; Vol. *21*); Glorius, F., Ed.; Springer: Berlin, 2007; p 83.

(23) Alcarazo, M.; Roseblade, S. J.; Alonso, E.; Fernandez, R.; Alvarez, E.; Lahoz, F. J.; Lassaletta, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 13242.

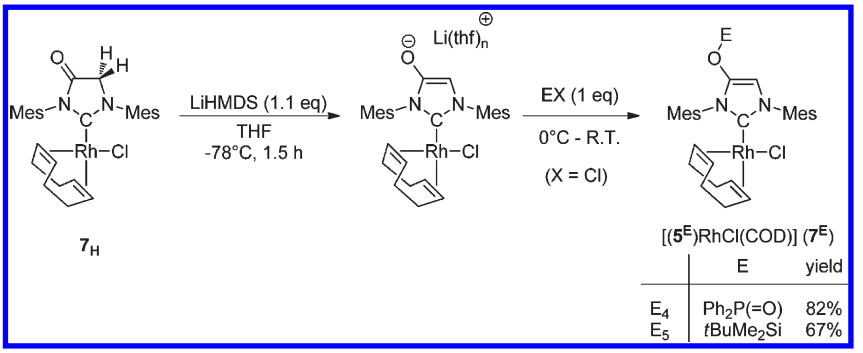
(24) See for instance: (a) Tapu, D.; Dixon, A.; Roe, C. *Chem. Rev.* **2009**, *109*, 3385, and references therein. (b) Wolf, S.; Plenio, H. *J. Organomet. Chem.* **2009**, *694*, 1487. (c) Xiao-Yan, Y.; Brian, O. P.; Brian, R. J. *Organometallics* **2006**, *25*, 2359.

(25) Evans, P. A.; Baum, E. W.; Fazal, A. N.; Pink, M. *Chem. Commun.* **2005**, 63.

Scheme 5. Synthesis of Complex 7_H



Scheme 6. Direct O-Functionalization of the Carbene from 7_H



7_H adopts the keto form. This is consistent with theoretical studies indicating that the aromatic character of imidazol-2-ylidenes is less pronounced than that of their imidazolium precursors.[26]

The formulation of 7_H was established by classical spectroscopic NMR analyses and analytical data. The peak at 531.2 au (100%) appearing in the electrospray mass spectrum corresponds to the cationic fragment $[M - Cl]^+$. In the ^{13}C NMR spectrum, the ketonic carbon resonates at $\delta(CO)$ = 171.2 ppm. Besides, the characteristic signal of the carbene arises as a doublet $\delta(N_2C)$ = 229.7 ppm due to its coupling with the metal (J_{RhC} = 51.5 Hz). Such a value is significantly higher than that observed in the reference complex [(SIMes)-RhCl(COD)], in which $\delta(N_2C)$ = 212.0 ppm, and J_{RhC} = 48.1 Hz.[24a] Such a deshielding of the carbenic carbon signal in 7_H reflects the fact that the ketonic group exerts a withdrawing effect on the electronic density of the heterocycle. It is noteworthy that all spectroscopic analyses are consistent with the keto form. Very characteristically, the rotation around the Rh−NHC bond appears to be hindered by the steric crowding of mesityl groups. So, the molecule adopts C_1 symmetry, and the two signals of the methylene group at position 5 of the heterocycle are becoming diastereotopic and are strongly coupled ($^2J_{HH}$ = 20.7 Hz). Single crystals of the complex were obtained by slow diffusion of pentane into a solution of 7_H in CH_2Cl_2. The complex exists under the form of a racemate, with the two enantiomers coexisting in the centrosymmetric unit cell. Since the molecular structure was already presented in our preliminary communication,[18] it will not be discussed here.

C. Post-functionalization of the Carbene Starting from Its Rh Complex 7_H. In subsequent work, we were able to demonstrate that complex 7_H can be used as a starting material for further modifications of the NHC, first by O-functionalization and, second, by C-functionalization.

1. O-Functionalization. In a series of typical experiments, complex 7_H was readily deprotonated upon reaction with lithium bis(trimethylsilyl)amide (LiHMDS) in THF at −78 °C for 1.5 h, giving the anionic intermediate species $[(5^-)RhCl(COD)]Li(thf)_n^+$ (Scheme 6), which was subsequently treated with electrophilic reagents **E**-X to give the O-functionalized species $[(5^E)RhCl(COD)]$ (7^E). Such a reaction was tested with two new electrophiles, diphenylphosphinic chloride ($Ph_2P(=O)Cl$) and chloro-*tert*-butyldimethylsilane (TBDMSCl), leading to the complexes 7^{E4} and 7^{E5}, respectively.

The success of the reaction was confirmed by ^1H NMR data revealing the disappearance of the AB type signal of the methylene group on the C5 carbon and the concomitant appearance of a singlet at $\delta CH_{Im\text{-}5}$ = 6.22 ppm for 7^{E4} and at $\delta CH_{Im\text{-}5}$ = 6.18 ppm for 7^{E5}, corresponding to the aromatic proton at the C5 position. The presence of the carbene was confirmed by ^{13}C NMR, showing the carbene signals arising respectively at δN_2C = 179.4 ppm (d, J_{RhC} = 52.7 Hz) for 7^{E4} and δN_2C = 176.9 ppm (d, J_{RhC} = 52.7 Hz) for 7^{E5}. These values are indeed consistent with those reported in the literature for Rh(I)-imidazol-2-ylidene complexes.[25]

Single crystals of 7^{E4} were obtained by slow diffusion of pentane in a concentrated solution of the complex in dichloromethane and were subjected to an X-ray structure analysis. The molecular structure of 7^{E4} is depicted in Figure 2 along with a selection of interatomic distances (Å) and bond angles (deg).

Compex 7^{E4} exhibits a slightly distorded square-planar geometry. The interatomic distances Rh−C1 (2.042(3) Å) and Rh−Cl1 (2.3611(9) Å) are similar to those found for the methylated derivative 7^{E2} described above. The C2−C3 distance 1.343(5) Å corresponds to a double-bond length. The mesityl cycles are roughly orthogonal to the plane of the heterocycle (C1−N1−C4−C9 = 101.5° and C1−N2−C4−C9 = −73.9°). As previously noted for related complexes, we still observe the characteristic *trans* influence of the carbene, with $Rh-C_{COD}$ bonds *trans* to the carbene (2.214(2) and 2.174(2) Å) being significantly longer than those *trans* to the chloride (2.096(4) and 2.114(4) Å). Such a phenomenon,

(26) (a) Boehme, C.; Frenking, G. *J. Am. Chem. Soc.* **1996**, *118*, 2039. (b) Tafipolsky, M.; Scherer, W.; Öfele, K.; Artus, G.; Pedersen, B.; Herrmann, W. A.; McGrady, G. S. *J. Am. Chem. Soc.* **2002**, *124*, 5865.

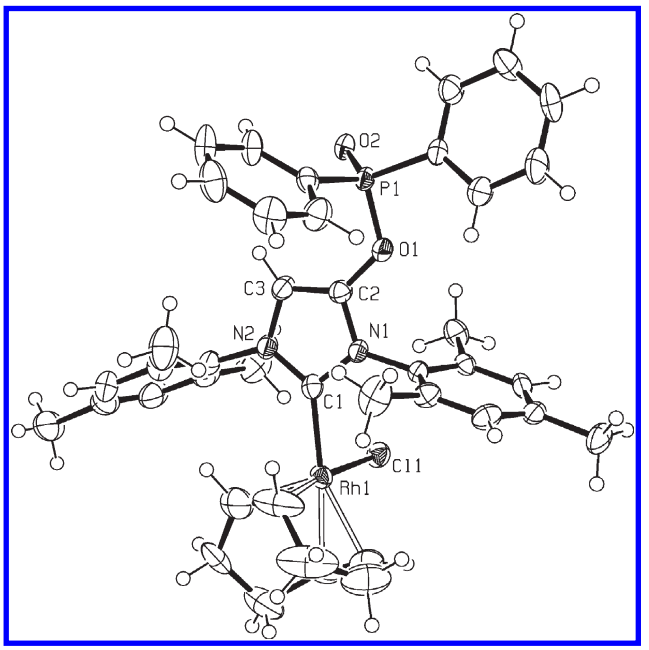


Figure 2. Perspective view of complex $\mathbf{7}^{E4}$. Selected interatomic distances [Å] and bond angles [deg]: Rh−C(1) 2.042(3), Rh−Cl(1) 2.3611(9), Rh−C(35) 2.114(4), Rh−C(36) 2.096(4), Rh−C(39) 2.214(4), Rh−C(40) 2.174(4), C(2)−C(3) 1.343(5), C(2)−O(1) 1.364(4), O(1)−P(1) 1.613(2), P(1)−O(2) 1.470(2), C(35)−C(36) 1.401(8), C(39)−C(40) 1.344(6) C(1)−Rh−Cl(1) 89.50(9), Cl(1)−Rh−C(39) 172.78(17), Cl(1)−Rh−C(35) 171.5(2), C(1)−Rh−C(35) 96.97(16), C(1)−Rh−C(39) 172.78(15), O(1)−C(2)−C(3) 134.2(3), N(1)−C(1)−N(2) 103.1(3).

even more pronounced in the present case, is also correlated with differences in the double-bond lengths within the COD ligand. Typically, the length of the double bond that is *trans* to the carbene, 1.344(6) Å, is significantly shorter than the length (1.401(8) Å) of the double bond *trans* to the halogen.

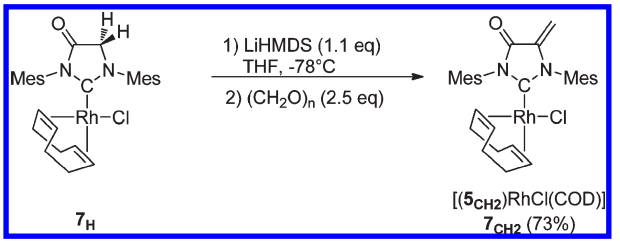
2. C-Functionalization. In parallel to the above experiments, we also performed the C-functionalization of the complex by a classical aldolization/crotonization sequence. As shown in Scheme 7, the anionic complex $[(\mathbf{5}^-)\text{RhCl(COD)}]^-\text{Li(thf)}_n^+$ was generated *in situ* by deprotonation of $\mathbf{7_H}$ and reacted with paraformaldehyde in THF at 0 °C for 1.5 h, producing the new complex $[(\mathbf{5_{CH2}})\text{RhCl(COD)}]$ ($\mathbf{7_{CH2}}$), in which the carbon C5 is now functionalized by a methylene group.

The complex was purified by flash chromatography on neutral alumina (type III), using dichloromethane as eluent. The product, which was obtained as a red-orange solid isolated in good yield (73%), was fully characterized by spectroscopic and analytical methods.

Examination of the ^{1}H NMR spectrum of $\mathbf{7_{CH2}}$ revealed that the olefinic protons arise as two doublets at $\delta(CH_2)$ = 5.68 ppm and $\delta(CH_2)$ = 4.87 ppm coupled with a J_{HH} = 1.8 Hz characteristic of the two geminated protons of an olefin. The proton spectrum also shows that rotation around the Rh−C bond is hindered on the NMR time scale. Indeed, the signals corresponding to the methyl groups of the mesityl substituents appear as six singlets, each integrating for three protons. Similarly, the $=CH_{COD}$ signals, affected by the same phenomenon, arise as four multiplets.

In the ^{13}C NMR, the carbene arises as a doublet, $\delta(N_2C)$ = 227.0 ppm (d, J_{CRh} = 52.6 Hz). The ketonic carbon arises at $\delta(CO)$ = 161.0 ppm (d, J_{CRh} = 1.6 Hz), whereas, in the IR spectrum, the stretching ν(C=O) vibration appears at 1752 cm^{-1}.

Scheme 7. C-Functionalization of the Carbene from Complex $\mathbf{7_H}$



Given that both O- and C-functionalized complexes described above are synthesized from the preformed complex $\mathbf{7_H}$, we also tested the possibility of carrying out a direct one-pot reaction starting from the 4-hydroxyimidazolium **3**, without attempting to isolate the intermediates, but such a simplified synthetic protocol did not give satisfactory product yields. By contrast, however, we found that the one-pot synthetic strategy applies perfectly well to the case of copper, as illustrated below.

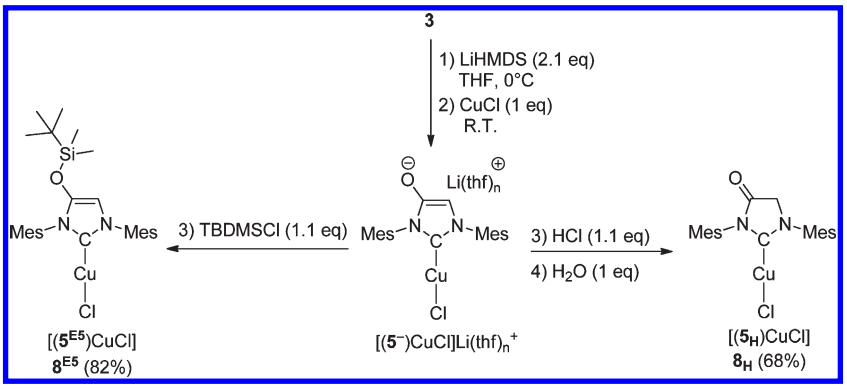
D. Digression into the Case of Copper Complexes. One-Pot Synthesis of Copper(I) Complexes. In a typical experiment, the 4-hydroxyimidazolium cation **3** was doubly deprotonated by reaction with LiHMDS in THF at 0 °C. The incipient anionic carbene thus generated was then reacted *in situ* with 1 equiv of CuCl at ambient temperature to give the intermediate anionic complex $[(\mathbf{5}^-)\text{CuCl}]\text{Li(thf)}_n^+$ (Scheme 8), which was simply neutralized with HCl at 0 °C to give, after addition of degassed water, the complex $\mathbf{8_H}$ in satisfactory yield (68%). Such a complex is air sensitive and should be kept under inert atmosphere.

In practice, the addition of distilled water after the acidification step (Scheme 8, right equation) is necessary to obtain the final product in a clean form. Indeed, in the absence of water, the product $\mathbf{8_H}$ appears to be contaminated by an additional silylated derivative $\mathbf{8}^{SiMe3}$ resulting from the competing reaction of the intermediate enolate copper complex $[(\mathbf{5}^-)\text{CuCl}]\text{Li(thf)}_n^+$ with the silylated base HMDS generated through the deprotonation of the carbene by KHMDS (Scheme 9). The existence of a mixture of both $\mathbf{8_H}$ and $\mathbf{8}^{SiMe3}$ in a ratio of 0.6/1 (evaluated by integration of NMR signals) is confirmed by the ^{1}H NMR spectrum exhibiting both the δCH_2 signal at 4.29 ppm, belonging to $\mathbf{8_H}$, and the $\delta CH_{Im\text{-}5}$ signal at 6.31 ppm, corresponding to the silylated derivative $\mathbf{8}^{SiMe3}$.

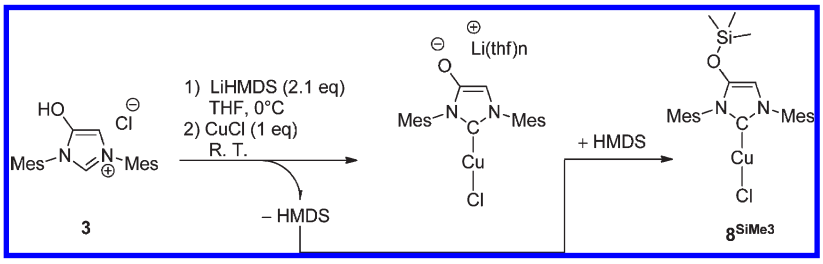
Attempts to prevent this side reaction by using lithium diisopropylamide as a base effectively led to compound $\mathbf{8_H}$, albeit contaminated by impurities, which we were unable to eliminate. So, the treatment with water, as depicted in Scheme 8, remains the best procedure to obtain $\mathbf{8_H}$ in analytically pure form.

Just like in the rhodium complex $\mathbf{7_H}$ described above, the functionalized backbone of the NHC ligand in $\mathbf{8_H}$ (Scheme 8) exhibits the preferred keto form, reflecting a lack of aromaticity of the heterocycle. This can be inferred from the occurrence of the IR ν(CO) band at 1750 cm^{-1} and from the presence of the characteristic ^{13}C NMR signal $\delta(CO)$ = 172.0 ppm. The resonance of the carbene $\delta(N_2C)$ = 213.5 ppm is considerably deshielded as compared with that of the corresponding carbene center in [(SIMes)CuCl], $\delta(N_2C)$ = 202.8 ppm.[24a] Such a difference is ascribed to the fact that the ketonic function releases part of the electron density from the

Scheme 8. Straightforward One-Pot Generation of Copper Complexes 8_H and 8^{E5} from 4-Hydroxyimidazolium Salt 3



Scheme 9. Parasite Side Reaction of the *in Situ* Generated Anionic Intermediate [(5⁻)CuCl] with HMDS



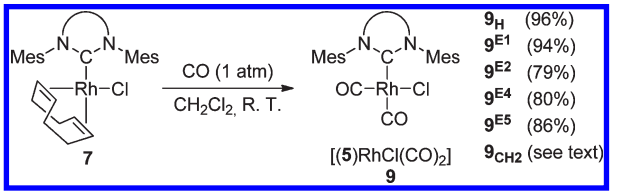
heterocycle, thereby reducing the overall nucleophilicity of the carbene. Such a phenomenon was in fact corroborated by complementary investigations reported below. Further evidence for the existence of the ligand in the keto form here comes from the observation of the CH_2 signal at $\delta(CH_2)$ = 4.29 ppm arising as a singlet, since the complex now exhibits C_s symmetry.

Quite logically, these observations led us to think of another silylated electrophile, *tert*-butyldimethylsilyl chloride (TBDMSCl) (Scheme 8, left equation), the addition of which was found to proceed cleanly at room temperature to give $\mathbf{8^{E5}}$ in high yield (82%). The formation of the latter was inferred from the existence of a ^{13}C NMR signal δN_2C at 173.1 ppm. Let us note that the corresponding chemical shift for the closely related IMes compound [(IMes)CuCl] was detected at $\delta(N_2C)$ = 178.7 ppm ($CDCl_3$).[24a] The observed difference clearly indicates that the presence of the silylated electrophilic group enriches the electron density on the heterocycle, thereby rendering the carbene more nucleophilic. Finally, the existence of a proton signal at $\delta CH_{Im\text{-}5}$ = 6.27 ppm ($CDCl_3$) in the ^1H NMR spectrum corroborates the fact that the heterocycle is unsaturated and O-functionalized.

E. Examination of the Effects of Various Types of Functionalization on the Donor Properties of the Carbene. Simple transition metal carbonyl complexes incorporating an N-heterocyclic carbene, such as Ni(NHC)$(CO)_3$ or Rh(NHC)-$(CO)_2$Cl, are currently used as standard derivatives for evaluating the donicity of a given NHC ligand relative to the IMes ligand, taken as a reference. Indeed, due to the retrodonation of electrons from the metal to the antibonding π^* of the carbon, IR ν(CO) stretching vibrations of carbonyl ligands constitute a very sensitive probe to estimate the ligand donicity.

In the present work, the cyclooctadiene complexes $\mathbf{7_H}$, $\mathbf{7^E}$, and $\mathbf{7_{CH2}}$ were respectively converted into the corresponding carbonyl chloro Rh(I) derivatives [$\mathbf{(5_H)}$RhCl$(CO)_2$] ($\mathbf{9_H}$),

Scheme 10. Generation of Carbonyl Derivatives [(5)RhCl$(CO)_2$]



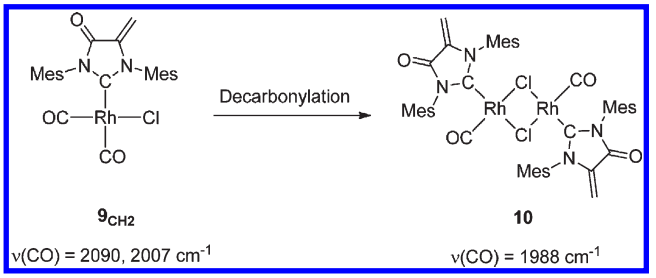
[$\mathbf{(5^E)}$RhCl$(CO)_2$] ($\mathbf{9^E}$), and [$\mathbf{(5_{CH2})}$RhCl$(CO)_2$] ($\mathbf{9_{CH2}}$), upon bubbling CO for a few minutes in dichloromethane solution (Scheme 10). Apart from the complex $\mathbf{9_{CH2}}$, which was found to spontaneously decarbonylate in the absence of CO,[27] all such compounds are stable square-planar dicarbonyl Rh(I) derivatives. The presence of two carbonyl ligands and a carbene is inferred from ^{13}C NMR data showing three doublets coupled with the Rh center, between 170 and 225 ppm (Table 1). Clearly, the chemical shifts of the carbon of carbonyl groups are not influenced by the nature of the carbene. For the unsaturated carbenes $\mathbf{5^E}$, the chemical shifts of the carbenic carbon (171 ppm < $\delta(N_2C)$ < 173 ppm) appear to be insensitive to the nature of the functional group and are within the range of those reported in the literature for comparable imidazol-2-ylidene ligands ($\delta(N_2C)$ = 177.7 ppm in [(IMes)RhCl$(CO)_2$]).[24a] By contrast, the signals of the carbenic carbon center for $\mathbf{9_H}$ (δ = 220.7 ppm) and $\mathbf{9_{CH2}}$ (δ = 218.0 ppm) are significantly higher than that published for the reference compound [(SIMes)RhCl$(CO)_2$], for which $\delta(N_2C)$ = 205.7 ppm.[24a] Such a deshielding can be explained by the fact that the ketone function acts as an electron-withdrawing group relative to the heterocycle. Such an effect was already observed for the cyclooctadiene derivatives $\mathbf{7_H}$ and $\mathbf{7_{CH2}}$.

(27) Related decarbonylation processes have already been observed in Rh(I)-carbonyl complexes incorporating poor electron donors; see: (a) Bittermann, A.; Herdtweck, E.; Härter, P.; Herrmann, W. A. *Organometallics* **2009**, *28*, 6963. (b) See also ref 11e.

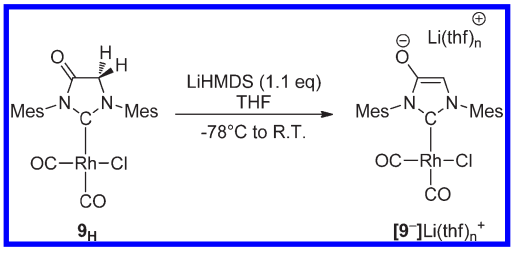
Table 1. ^{13}C NMR Data for the Series of Carbonylated Species 9

compound	δN_2C (ppm)	δCO	δCO
$\mathbf{9^{E1}}$	173.2 (J_{RhC} = 44.3 Hz)	182.7 (J_{RhC} = 74.5 Hz)	184.9 (J_{RhC} = 54.7 Hz)
$\mathbf{9^{E2}}$	172.8 (J_{RhC} = 44.8 Hz)	182.7 (J_{RhC} = 74.2 Hz)	184.9 (J_{RhC} = 54.1 Hz)
$\mathbf{9^{E4}}$	173.4 (J_{RhC} = 45.6 Hz)	182.6 (J_{RhC} = 74.6 Hz)	184.1 (J_{RhC} = 54.0 Hz)
$\mathbf{9^{E5}}$	171.1 (J_{RhC} = 45.1 Hz)	182.9 (J_{RhC} = 74.6 Hz)	185.1 (d, J_{RhC} = 54.1 Hz)
$\mathbf{9_H}$	220.7 (J_{RhC} = 44.2 Hz)	182.3 (J_{RhC} = 73.9 Hz)	184.3 (J_{RhC} = 53.6 Hz)
$\mathbf{9_{CH2}}$	218.0 (J_{RhC} = 45.0 Hz)	183.9 (J_{RhC} = 58.0 Hz)	

Scheme 11. Spontaneous Decarbonylation of 9_{CH2} and Concomitant Condensation into the Dimeric Species 10



Scheme 12. Preparation of the Complex $[(5^-)RhCl(CO)_2][Li(thf)_n]^+$, $[9^-][Li(thf)_n]^+$



The *cis* conformation of the two carbonyls was verified in all cases by IR spectroscopy, systematically giving two intense ν(CO) bands. As noted in Scheme 10, the complex $\mathbf{9_{CH2}}$ could not be isolated in pure form, due to its observed transformation via spontaneous loss of CO, but was investigated in solution by IR and NMR. Its IR spectrum in the ν(CO) shows two bands of equal intensity at 2090 and 2007 cm^{-1}, consistent with the presence of two mutually *cis* carbonyl ligands CO.

In the ^{13}C NMR spectrum of complex $\mathbf{9_{CH2}}$ (Table 1), the signals of the corresponding carbons are fortuitously overlapped, giving a doublet $\delta(CO)$ at 183.9 ppm. The presence of the carbene is corroborated by the occurrence of a characteristic signal $\delta(N_2C)$ at 218.0 ppm arising as a doublet (J_{RhC} = 45.0 Hz). The complex was found to slowly decarbonylate, even at low temperature (Scheme 11).

Although the resulting product was not fully characterized, it could be reasonably formulated as the dimeric species **10**. Indeed, when complex $\mathbf{9_{CH2}}$ was heated at 80 °C under reduced pressure, monitoring by IR spectroscopy indicated the progressive disappearance of the two ν(CO) stretching bands and their replacement by a unique absorption band arising at 1988 cm^{-1}. Such a transformation could also be followed by ^1H NMR spectroscopy. After 24 h, the product **10** was isolated in pure form after purification through a chromatographic column (SiO_2), using dichloromethane as eluent. Its ^{13}C NMR spectrum reveals the occurrence of the carbenic carbon center arising as a doublet $\delta(N_2C)$ at 213.5 ppm (J_{RhC} = 54 Hz). The same spectrum shows a doublet ascribed to the unique CO, arising as a doublet at $\delta(CO)$ = 183.1 ppm (J_{RhC} = 88 Hz), whereas the singlet appearing at δ = 161.4 ppm corresponds to the ketonic carbon center. Complex **10** still exhibits the characteristic signals of the functionalized carbene $\mathbf{5_{CH2}}$. In order to corroborate the formation of the above dimer, we carried out a DOSY NMR experiment aimed at determining the respective hydrodynamic radius of both $\mathbf{9_{CH2}}$ and **10**. The results revealed that the volume occupied by the molecular unit of **10** is 1.4 times larger than that of $\mathbf{9_{CH2}}$, which is roughly consistent with the expected value based on the above formulation.

F. Evaluation of the Donor Properties of the Aforementioned NHCs. In order to evaluate the donor properties of the anionic imidazol-2-yliden-4-olate, we still had to prepare the corresponding chloro-carbonyl Rh(I) derivative, which was simply done by deprotonation of $\mathbf{9_H}$, giving the anion $\mathbf{9^-}$, the IR spectrum of which was recorded in dichloromethane.

Table 2. Recorded IR ν(CO) Stretching Vibrations for the Whole Series of Chloro-Carbonyl NHC Rh(I) Complexes Resulting from the Modulation of the Anionic Imidazol-2-yliden-4-olate

entry	NHC ligand	ν(CO) (cm^{-1})[a]	ν_{av}(CO) (cm^{-1})
1	$\mathbf{5_{CH2}}$ in $\mathbf{9_{CH2}}$	2090, 2007	2048.5
2	$\mathbf{5_H}$ in $\mathbf{9_H}$	2090, 2005	2047.5
3	SIMes[b]	2084, 1997	2040.5
4	$\mathbf{5^{E4}}$ in $\mathbf{9^{E4}}$	2080, 1997	2038.5
5	$\mathbf{5^{E1}}$ in $\mathbf{9^{E1}}$	2080, 1997	2038.5
6	IMes[b]	2081, 1996	2038.5
7	$\mathbf{5^{E2}}$ in $\mathbf{9^{E2}}$	2079, 1995	2037
8	$\mathbf{5^{E5}}$ in $\mathbf{9^{E5}}$	2077, 1994	2035.5
9	$\mathbf{5^-}$ in $\mathbf{9^-}$	2071, 1988	2029.5

[a] IR spectra recorded in CH_2Cl_2. [b] Values obtained from ref 23b.

The IR ν(CO) frequencies of the complexes recorded in this work are reported in Table 2 and in Figure 3, the latter also showing relevant literature data on comparable NHCs, recorded under the same conditions.

The results summarized in Figure 3 deserve the following comments:

(1) Our prototype of anionic carbene, the imidazol-2-ylidene-4-olate $\mathbf{5^-}$, appearing on the extreme right side of the IR ν(CO) scale, is thus the more nucleophilic carbene of the whole series of five-membered-ring NHCs shown here, including those directly comparable independently reported by other authors.[7k,o,22,23b,28]

(2) The donor properties of such a ligand are effectively modulated in a simple way and after its complexation to a transition metal, by post-functionalization of its reactive enolate backbone, either at the oxygen or at the carbon. Such a modulation, quantified against the IR ν(CO) scale based on the standard chloro-carbonyl Rh(I) complex [(NHC)RhCl(CO)$_2$], covers 19 cm^{-1}, one of the largest ones reported so far for modulable carbenes.

(3) Interestingly, Figure 3 reveals a distribution of the modified ligands over three different zones. The middle zone includes the O-functionalized carbenes, namely, those resulting from the selective addition of electrophiles to the oxygen.

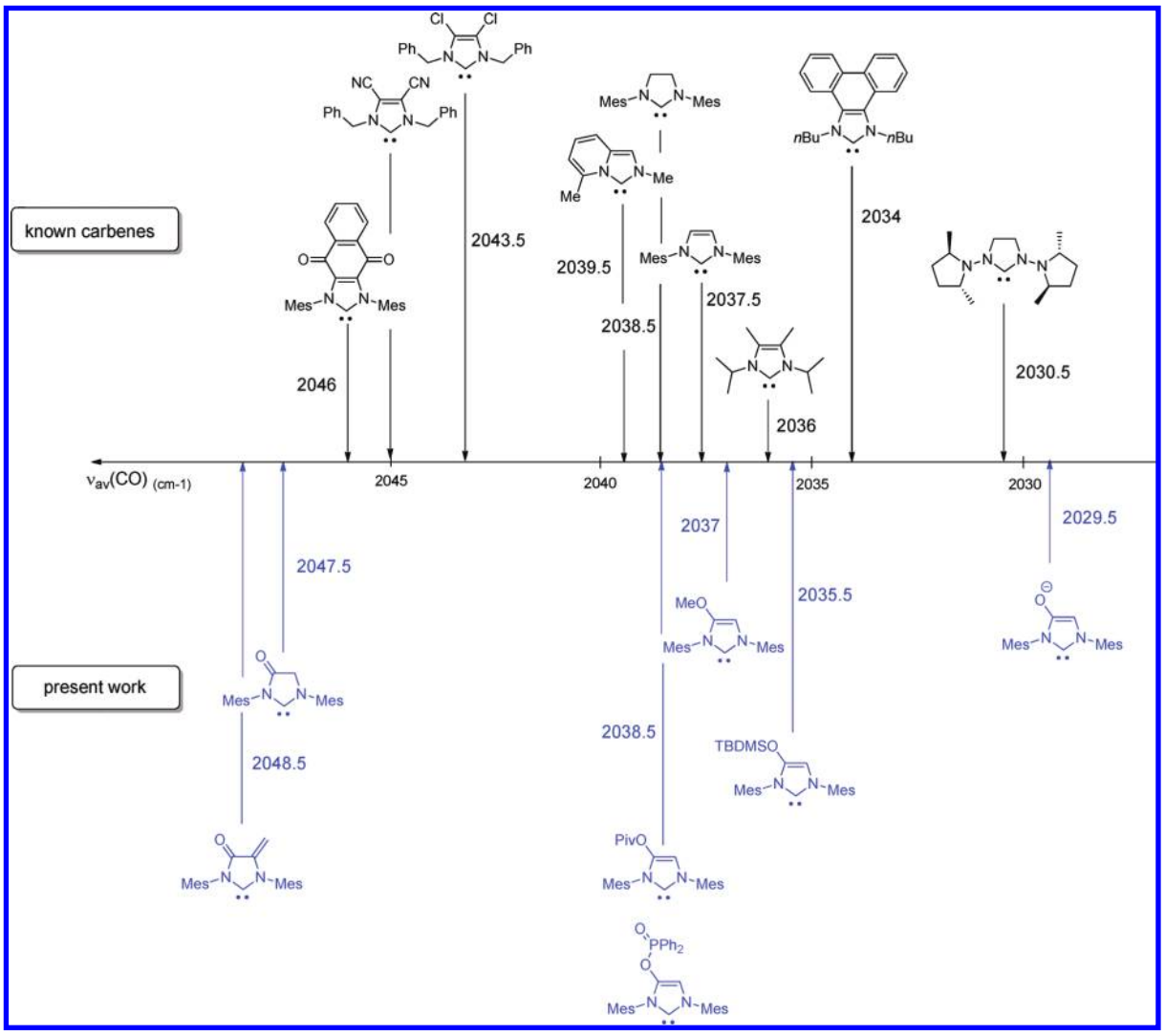
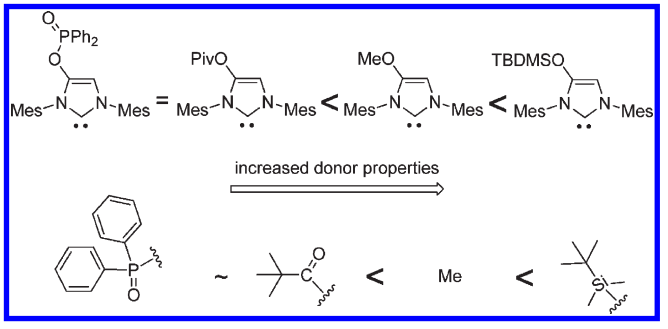


Figure 3. Classification of the carbenes according to their donor properties, determined from the IR ν(CO) frequencies of their respective chloro-carbonyl rhodium complexes of the type [(NHC)RhCl(CO)$_2$].[7k,o,22,23b,28]

Here, the modulation is indeed correlated with the electron-withdrawing properties of the electrophilic group, as represented in the following chart:



However, such a domain is relatively narrow as compared with the one we previously obtained with the six-membered-ring NHCs incorporating a malonate backbone.[15] The extreme left zone corresponds to the less nucleophilic carbenes. One of them results from C-functionalization, whereas the second one represents the case where the addition of H^+ as the incoming electrophile does not give an enol-functionalized-type carbene, but the preferred tautomer, namely, the keto form. It is noteworthy that in the latter cases we no longer have a diaminocarbene, but a mixed amino-amido-carbene, and we now know from earlier studies that diamidocarbenes are among the weakest electron donor carbenes reported so far.[16,17]

Conclusion

As part of a current research program directed to the design of N-heterocyclic carbenes as functional molecules, we have presented here a simple and modulable synthetic strategy for the construction of a new type of NHC incorporating an enolate group in the remote part of its heterocyclic framework. Due to its intrinsic chemical reactivity, such a function confers interesting properties to the N-heterocyclic carbene, which is then prone to be derivatized in a simple way by elementary chemical reactions. Whereas the anionic enolate-based NHC proved to be better electron donor than the closest conventional NHC, IMes, its electronic properties can be modulated in a very simple way and over a relatively broad range, either by simple addition of various electrophiles interacting selectively with the oxygen of the enolate (O-functionalization) or by exploiting the

reactivity of the enolate-type carbon atom (C-functionalization). A beneficial interest of such transformations is that they can be achieved after the ligand's coordination to transition metals, as illustrated here by the cases of rhodium and copper complexes. Since the ligands presented here exhibit the same steric hindrance as IMes, currently used in many catalytic systems, they represent a potentially useful alternative to such a widely used prototype, with the additional advantage of offering readily modulable electronic properties.

Experimental Section

General Considerations. All manipulations were carried out under an inert atmosphere of dry nitrogen by using standard vacuum line and Schlenk tube techniques. Glassware was dried at 120 °C in an oven for at least three hours. THF and diethyl ether were freshly distilled from sodium/benzophenone, and toluene was distilled from molten sodium, prior to use. Pentane, ethyl acetate, and dichloromethane were dried over CaH_2 and subsequently distilled. DMF was dried over CaH_2 and distilled under reduced pressure. NMR spectra were recorded on Bruker ARX250, AV300 AV400, and AV500 spectrometers, in the solvents indicated; chemical shifts (δ) are reported in ppm compared to TMS using the residual peak of deuterated solvent as internal standard; coupling constants (J) are in Hz. Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Microanalyses were performed by the Laboratoire de Chimie de Coordination Microanalytical Service and MS spectra by the mass spectrometry service of Paul Sabatier University. Melting points were obtained with a Stuart Scientific SMP1 melting point apparatus and were not corrected.

Starting Materials and Reagents. *N*,*N*′-Dimesitylformamidine, *N*,*N*′-di(2,6-diisopropylphenyl)formamidine,[29] and [RhCl-(1,5-COD)]$_2$[30] were synthesized according to literature procedures. Lithium bis(trimethylsilyl)amide (LiHMDS) was prepared just before use and was obtained by reacting *n*BuLi (1.6 M in hexane) with an excess of distilled hexamethyldisilazane (1.1 equiv) in pentane and subsequent evaporation of all volatiles *in vacuo*. It was then dissolved in THF to obtain a solution of approximately 1 M.

Synthetic Procedures. 1-(1-Oxo-2-chloroeth-1-yl)-1,3-dimesitylformamidine (2a). This reaction was carried out without any special precaution to exclude air and moisture. Solvent and reagents were used as received. 1,3-Dimesitylformamidine (3.0 g, 10.7 mmol) was suspended in ethyl acetate (75 mL), and the round-bottomed flask was placed in an ice bath. Triethylamine (2.3 mL, 16.1 mmol) was added, and chloroacetyl chloride (1.0 mL, 12.8 mmol) was dropwise added at 0 °C. After reacting 40 min (TLC control), the mixture was filtered through a Büchner funnel to remove triethylammonium chloride. The solvent was evaporated and the sticky residue was purified by flash chromatography (SiO_2, hexane/EtOAc, 2/1) to afford a white solid (3.6 g, 95%): mp 123−124 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.03 (s, 6H, C$H_{3\ ortho}$), 2.22 (s, 3H, C$H_{3\ para}$), 2.27 (s, 6H, C$H_{3\ ortho}$), 2.33 (s, 3H, C$H_{3\ para}$), 3.82 (br s, 2H, CH_2), 6.79 (s, 2H, CH_{Mes}), 7.04 (s, 2H, CH_{Mes}), 8.77 (br s, 1H, N_2CH); ^{13}C{^{1}H} NMR (62.9 MHz, $CDCl_3$) δ 17.9 (*C*H$_{3\ ortho}$), 18.6 (*C*H$_{3\ ortho}$), 20.7 (*C*H$_{3\ para}$), 21.2 (*C*H$_{3\ para}$), 42.5 (*C*H$_2$), 127.6 (C_{Mes}), 128.7 (*C*H$_{Mes}$), 130.1 (*C*H$_{Mes}$), 131.3 (C_{Mes}), 132.9 (C_{Mes}), 135.7 (C_{Mes}), 139.8 (C_{Mes}), 145.3 (C_{Mes}), 147.9 (N_2CH); IR (ATR) $\tilde{\nu}$ 2942, 2914, 2854, 1706 (m, ν_{CO} conformer 1), 1697 (m, ν_{CO} conformer 2), 1660 (m, $\nu_{C=N}$ conformer 1), 1647 (m, $\nu_{C=N}$ conformer 2), 1608, 1482, 1439, 1406, 1360, 1315, 1279, 1235, 1190, 1143, 1088, 1032, 849, 826, 790, 743, 719 cm^{-1}; MS (ESI) *m*/*z* (%): 735.3 (45) [2 M + Na]$^+$, 379.2 (100) [M + Na]$^+$, 357.2 (34) [M + H]$^+$. Anal. Calcd (%) for $C_{21}H_{25}ClN_2O$ (356.89): C 70.67, H 7.06, N 7.85. Found: C 69.48, H 7.05, N 7.57.

1-(1-Oxo-2-chloroeth-1-yl)-1,3-(2,6-diisopropylphenyl)formamidine (2b). This reaction was carried out without any special precaution to exclude air and moisture. Solvent and reagents were used as received. 1,3-(2,6-Diisopropylphenyl)formamidine (1.0 g, 2.76 mmol) was suspended in ethyl acetate (20 mL). Triethylamine (0.58 mL, 4.1 mmol) and chloroacetyl chloride (0.27 mL, 3.3 mmol) were added at 0 °C. After reacting 1 h, the mixture was filtered through a Büchner funnel and the filtrate was evaporated. The sticky residue was purified by flash chromatography (SiO_2, hexane/CH_2Cl_2, 1/2) to afford a white solid (1.0 g, 82%): mp 116 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.15 (d, 12H, J_{HH} = 6.9 Hz, C$H_{3\ iPr}$), 1.26 (d, 6H, J_{HH} = 6.8 Hz, C$H_{3\ iPr}$), 1.29 (d, 6H, J_{HH} = 6.9 Hz, C$H_{3\ iPr}$), 2.95 (m, 4H, CH_{iPr}), 3.97 (br s, 2H, CH_2), 7.09 (m, 3H, CH_{DIPP}), 7.35 (m, 2H, CH_{DIPP}), 7.49 (m, 1H, CH_{DIPP}), 8.80 (br s, 1H, N_2CH); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$) δ 24.0 (*C*H$_{3\ iPr}$), 24.6 (*C*H$_{3\ iPr}$), 27.5 (*C*$_{iPr}$), 28.6 (*C*H$_{iPr}$), 42.6 (*C*H$_2$), 123.0 (*C*H$_{DIPP}$), 124.3 (*C*H$_{DIPP}$), 124.9 (*C*H$_{DIPP}$), 130.5 (*C*H$_{DIPP}$), 130.9 (C_{DIPP}), 138.8 (C_{DIPP}), 145.3 (C_{DIPP}), 146.3 (C_{DIPP}), 148.3 (N_2CH), 168.3 (*C*=O); IR (ATR) $\tilde{\nu}$ 2963, 2929, 2868, 1712 (m, ν_{CO}), 1647 (m, $\nu_{C=N}$), 1590, 1572, 1465, 1456, 1441, 108, 1383, 1361, 1313, 1283, 1221, 1180, 1169, 1124, 1098, 1081, 1058, 1042, 934, 923, 849, 796, 764, 756, 711, 694 cm^{-1}; MS (ESI) *m*/*z* (%) 463.4 (10) [M + Na]$^+$, 441.5 (8) [M]$^+$, 427.5 (26) [M + Na − Cl]$^+$, 405.5 (16) [M − Cl]$^+$, 365.5 (100) [M + H − (CO − CH_2 − Cl)]$^+$. Anal. Calcd (%) for $C_{27}H_{37}ClN_2O$ (441.04): C 73.53, H 8.46, N 6.35. Found: C 73.46, H 8.09, N 6.18.

4-Hydroxy-1,3-dimesitylimidazolium Chloride (3a). 1-(1-Oxo-2-chloroethyl)-1,3-dimesitylformamidine (**2a**) (1.078 g, 3.0 mmol) was solubilized in DMF (7.5 mL, 0.4 mol·L^{-1}), and the mixture was heated at 100 °C for 1 h. During this period, the product started to precipitate. After cooling at room temperature, Et_2O (40 mL) was added and the supernatant solution was evacuated through a filter canula. The white to off-white solid residue was washed with Et_2O (2 × 10 mL) and dried *in vacuo* to yield the imidazolium salt as a white to off-white powder (810 mg, 75%): mp 277 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.13 (s, 12H, C$H_{3\ ortho}$), 2.35 (s, 6H, C$H_{3\ para}$), 7.02 (s, 2H, CH_{Mes}), 7.04 (s, 2H, CH_{Mes}), 7.22 (d, J_{HH} = 2.1 Hz, 1H, C$H_{Im\text{-}5}$), 7.54 (d, 1H, J_{HH} = 2.1 Hz, N_2CH); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$) δ 17.1 (*C*H$_{3\ ortho}$), 17.6 (*C*H$_{3\ ortho}$), 21.1 (*C*H$_{3\ para}$), 21.1 (*C*H$_{3\ para}$), 102.6 (*C*H$_{Im\text{-}5}$), 124.8 (N_2CH), 127.3 (C_{ipso}), 129.7 (*C*H$_{Mes}$), 129.8 (*C*H$_{Mes}$), 131.1 (C_{ipso}), 134.0 (C_{ortho}), 135.0 (C_{ortho}), 141.4 (C_{para}), 148.3 (*C*-OH); IR (ATR) $\tilde{\nu}$ 2970, 2298 (br m, ν_{OH}), 1595 (vs, $\nu_{C=N}$), 1543, 1483, 1463, 1375, 1283, 1244, 1223, 1065, 1039, 861, 832, 776, 726, 683, 673 cm^{-1}; MS (ESI) *m*/*z* (%) 343.2 (93) [M − Cl + Na]$^+$, 321.3 (100) [M − Cl]$^+$. Anal. Calcd (%) for $C_{21}H_{25}ClN_2O$ (356.17): C 70.67, H 7.06, N 7.85. Found: C 70.89, H 7.05, N 7.79.

4-Hydroxy-1,3-(2,6-diisopropylphenyl)imidazolium chloride (3b). 1-(1-Oxo-2-chloroethyl)-1,3-(2,6-diisopropylphenyl)formamidine (**2b**) (294 mg, 0.7 mmol) was solubilized in toluene and heated at 100 °C for 22 h. The product precipitated along the reaction course. After cooling at room temperature, Et_2O (10 mL) was added and the supernatant liquid was evacuated through a canula. The white solid residue was washed with Et_2O (2 × 5 mL) and dried *in vacuo* to yield the imidazolium salt as a white powder (200 mg, 69%): mp 250 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 (d, 6H, J_{HH} = 6.9 Hz, CH_3), 1.18 (d, 6H, J_{HH} = 6.9 Hz, CH_3), 1.32 (d, 6H, J_{HH} = 6.7 Hz, CH_3), 1.32 (d, 6H, J_{HH} = 6.7 Hz, CH_3), 2.59 (m, 4H, CH_{iPr}), 7.32−7.37 (m, 5H, CH_{DIPP} + C$H_{Im\text{-}5}$), 7.53−7.59 (m, 3H, CH_{DIPP} + C$H_{Im\text{-}2}$); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$) δ 23.6 (*C*H$_3$), 23.8 (*C*H$_3$), 24.4 (*C*H$_3$), 25.2 (*C*H$_3$), 28.8 (*C*H$_{iPr}$), 29.2 (*C*H$_{iPr}$), 103.3 (*C*H$_{Im\text{-}5}$), 124.5 (*C*H$_{m\text{-}DIPP}$), 124.6 (*C*H$_{m\text{-}DIPP}$), 125.9 (*C*H$_{Im\text{-}2}$), 130.5 (C_q), 131.9 (C_q), 132.0 (C_q), 145.3 (*C*H$_{p\text{-}DIPP}$), 146.0 (*C*H$_{p\text{-}DIPP}$); IR (ATR) $\tilde{\nu}$ 2962, 2869, 2324

(28) The known NHC ligands in the figure were also taken from: (a) Bittermann, A.; Härter, P.; Herdtweck, E.; Hoffmann, S. D.; Herrmann, W. A. *J. Organomet. Chem.* **2008**, *693*, 2079. (b) Neveling, A.; Julius, G. R.; Cronje, S.; Esterhuisen, C.; Raubenheimer, H. G. *Dalton Trans.* **2005**, 181.

(29) Krahulic, K. E.; Enright, G. D.; Parvez, M.; Roesler, R. *J. Am. Chem. Soc.* **2005**, *127*, 4142.

(30) Giordiano, G.; Crabtree, R. H. *Inorg. Synth.* **1990**, *28*, 88.

(br m, ν_{OH}), 1620 (s, $\nu_{C=N}$), 1589, 1541, 1496, 1461, 1384, 1364, 1331, 1285, 1271, 1258, 1210, 1181, 1106, 1062, 940, 876, 806, 755, 734, 709, 697, 672 cm^{-1}; MS (ESI) *m*/*z* (%) 427.5 (100) $[M - Cl]^+$, 405.5 (79) $[M - Cl + Na]^+$. Anal. Calcd (%) for $C_{27}H_{37}ClN_2O$ (441.04): C 73.53, H 8.46, N 6.35. Found: C 72.73, H 8.30, N 6.28.

1,3-Dimesitylimidazolium-4-olate (4). Triethylamine (185 μL, 1.32 mmol) was added at room temperature to a solution of 4-hydroxy-1,3-dimesitylimidazolium chloride (**3a**) (429 mg, 1.20 mmol) in CH_2Cl_2 (25 mL). After 15 min, volatiles were removed to dryness *in vacuo*. EtOAc was added (30 mL), and the white suspension was filtered through a pad of Celite. EtOAc was then evaporated, and the residue was washed with pentane (2 × 10 mL) to give a pale yellow powder (355 mg, 92%): mp 104 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.21 (s, 6H, C$H_{3\ ortho}$), 2.22 (s, 6H, C$H_{3\ ortho}$), 2.32 (s, 3H, C$H_{3\ para}$), 2.35 (s, 3H, C$H_{3\ para}$), 5.87 (d, 1H, J_{HH} = 2.0 Hz, C$H_{Im\text{-}5}$), 7.00 (br s, 5H, CH_{Mes} + N_2CH); $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$) δ 16.8 (*C*$H_{3\ ortho}$), 17.9 (*C*$H_{3\ ortho}$), 21.1 (*C*$H_{3\ para}$), 95.0 (*C*$H_{Im\text{-}5}$), 118.6 (N_2CH), 129.3 (*C*H_{Mes}), 129.9 (C_{ipso}), 133.1 (C_{ipso}), 134.7 (C_{ortho}), 135.7 (C_{ortho}), 139.3 (C_{para}), 139.9 (C_{para}), 156.2 (*C*-O^-); IR (ATR) $\tilde{\nu}$ 2962, 2919, 2864, 1742, 1726, 1676, 1636, 1609, 1547, 1484, 1439, 1400, 1378, 1253, 1223, 1167, 1140, 1034, 1014, 850, 785, 713 cm^{-1}.

4-(Pivaloyloxy)-1,3-dimesitylimidazolium Chloride (4^{E1}). Triethylamine (30 μL, 0.22 mmol, 1.1 equiv) was added to a suspension of **3a** (70 mg, 0.2 mmol) in CH_2Cl_2 (2 mL). The solution immediately became pale yellow. After 5 min of stirring, volatiles were removed to dryness. The residue was dissolved in EtOAc, filtered through a pad of Celite, and concentrated until the volume was about half of the initial volume. The solution was then cooled in an ice bath, and pivaloyl chloride (27 μL, 0.22 mmol, 1.1 equiv) was slowly added. The mixture was then allowed to warm at room temperature. The product precipitated during the reaction course. After 1 h, volatiles were removed *in vacuo* and the residue was washed with Et_2O (2 × 5 mL) to afford the imidazolium salt as a white powder (75 mg, 87%): mp 245 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (s, 9H, C$H_{3\ tBu}$), 2.22 (s, 6H, C$H_{3\ ortho}$), 2.28 (s, 6H, C$H_{3\ ortho}$), 2.36 (s, 6H, C$H_{3\ para}$), 7.04 (s, 4H, CH_{Mes}), 7.23 (d, 1H, J_{HH} = 1.5 Hz, C$H_{Im\text{-}5}$), 11.73 (d, 1H, J_{HH} = 1.5 Hz, N_2CH); $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$) δ 17.7 (*C*$H_{3\ tBu}$), 21.2 (*C*$H_{3\ para}$), 26.4 (*C*$H_{3\ ortho}$), 110.1 (*C*$H_{Im\text{-}5}$), 129.8 (*C*H_{Mes}), 129.1 (*C*H_{Mes}), 134.2 (C_q) 134.9 (C_q), 137.1 (N_2CH), 141.6 (C_q), *C*=O and C_{tBu} are not observed on this spectrum; IR (ATR) $\tilde{\nu}$ 2976, 2918, 2867, 2754, 1785 (ν_{CO}), 1621, 1610, 1534, 1479, 1460, 1245, 1065, 1023, 855, 771, 670 cm^{-1}; MS (ESI) *m*/*z* (%) 663 (21) [2(M − Cl − *t*BuCO) − 2H + Na]$^+$, 405 (30) $[M - Cl]^+$, 343 (100) [M − Cl − *t*BuCO + Na]$^+$, 321 (48) $[M - Cl - tBuCO]^+$. Anal. Calcd (%) for $C_{26}H_{33}ClN_2O_2$ (441.0): C 70.81, H 7.54, N 6.35. Found: C 69.28, H 7.73, N 6.17.

4-(Methoxy)-1,3-dimesitylimidazolium Trifluoromethanesulfonate (4^{E2}). Triethylamine (23 μL, 0.15 mmol, 1.1 equiv) was added to a suspension of **3a** (50 mg, 0.14 mmol) in CH_2Cl_2 (2 mL). The solution immediately became pale yellow. After 5 min of stirring, volatiles were removed to dryness. The residue was dissolved in EtOAc, filtered through a pad of Celite, and concentrated until the volume was about half of the initial volume. The solution was then cooled in an ice bath, and methyl triflate (18 μL, 0.15 mmol, 1.1 equiv) was slowly added. The mixture was then allowed to warm at room temperature. The product precipitated during the reaction course. After 1 h, volatiles were removed *in vacuo*, and the residue was washed with Et_2O (2 × 5 mL) to afford the imidazolium salt as a white powder (52 mg, 76%): mp 89 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.15 (s, 6H, C$H_{3\ ortho}$), 2.21 (s, 6H, C$H_{3\ ortho}$), 2.38 (s, 3H, C$H_{3\ para}$), 2.39 (s, 3H, C$H_{3\ para}$), 4.10 (s, 3H, O−CH_3), 7.06 (s, 2H, CH_{Mes}), 7.07 (s, 3H, CH_{Mes}, C$H_{Im\text{-}5}$), 8.74 (d, 1H, J_{HH} = 2.1 Hz, N_2CH); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 17.2 (*C*$H_{3\ ortho}$), 17.4 (*C*$H_{3\ ortho}$), 21.1 (*C*$H_{3\ para}$), 21.2 (*C*$H_{3\ para}$), 60.6 (O-*C*H_3), 101.1 (*C*$H_{Im\text{-}5}$), 129.8 (*C*H_{Mes}), 131.7 (N_2CH), 134.1 (C_{ortho}), 134.9 (C_{ortho}), 141.5 (C_{para}), 141.7 (C_{para}), 148.6 (MeO-*C*); IR (ATR) $\tilde{\nu}$ 1625, 1549, 1482, 1445, 1406, 1276, 1256, 1223, 1149, 1031, 990, 853, 752, 727, 667 cm^{-1}; MS (ESI) *m*/*z* (%) 335 (100) $[M]^+$. Anal. Calcd (%) for $C_{23}H_{27}F_3N_2O_4S$ (484.2): C 57.01, H 5.62, N 5.78. Found: C 56.44, H 5.82, N 5.54.

4-(Trifluoromethanesulfonyloxy)-1,3-dimesitylimidazolium Trifluoromethanesulfonate (4^{E3}). Triethylamine (23 μL, 0.15 mmol, 1.1 equiv) was added to a suspension of **3a** (50 mg, 0.14 mmol), in CH_2Cl_2 (2 mL). The solution immediately became pale yellow. After 5 min of stirring, volatiles were removed to dryness. The residue was dissolved in EtOAc, filtered through a pad of Celite, and concentrated until the volume was about half of the initial volume. The solution was then cooled in an ice bath, and triflic anhydride (26 μL, 0.15 mmol, 1.1 equiv) was slowly added. The mixture was then allowed to warm at room temperature. The product precipitated during the reaction course. After 1 h volatiles were removed *in vacuo*, and the residue was washed with Et_2O (2 × 5 mL) to afford the imidazolium salt as a white powder (55 mg, 65%);: mp 77 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.16 (s, 6H, C$H_{3\ ortho}$), 2.19 (s, 6H, C$H_{3\ ortho}$), 2.38 (s, 3H, C$H_{3\ para}$), 2.40 (s, 3H, C$H_{3\ para}$), 7.09 (s, 2H, CH_{Mes}), 7.12 (s, 2H, CH_{Mes}), 7.44 (d, 1H, J_{HH} = 1.2 Hz, C$H_{Im\text{-}5}$), 9.90 (d, 1H, J_{HH} = 1.2 Hz, N_2CH); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 17.2 (*C*$H_{3\ ortho}$), 17.4 (*C*$H_{3\ ortho}$), 21.2 (*C*$H_{3\ para}$), 21.3 (*C*$H_{3\ para}$), 112.6 (*C*$H_{Im\text{-}5}$), 130.2 (*C*H_{Mes}), 130.4 (*C*H_{Mes}), 133.8 (C_q), 134.8 (C_q), 138.3 (N_2CH), 142.4 (C_q), 142.8 (C_q); IR (ATR) $\tilde{\nu}$ 1605, 1541, 1444, 1432, 1294, 1238, 1217, 1155, 1126, 1028, 1006, 845, 811, 735, 724, 707, 665 cm^{-1}; MS (ESI) *m*/*z* (%) 453 (100) $[M - TfO]^+$; 320 (43) $[M - TfO - TfO]^+$. Anal. Calcd (%) for $C_{23}H_{24}F_6N_2O_6S_2$ (602.6): C 45.84, H 4.01, N 4.65. Found: C 45.01, H 3.79, N 4.48.

Chloro(η^4-cycloocta-1,5-diene)(1,3-dimesitylimidazolin-4-on-2-ylidene)rhodium(I) (7_H). A solution of LiHMDS (2.36 mL, 1 M in THF, 2.36 mmol, 2.1 equiv) was added to a solution of **3a** (400 mg, 1.12 mmol) in THF (15 mL) at 0 °C, and the mixture was stirred for 30 min. To this solution was added $[RhCl(1,5\text{-}COD)]_2$ (277 mg, 0.56 mmol, 0.5 equiv), and the resulting orange mixture was stirred 2 h at room temperature before addition of HCl (1.24 mL, 1 M in Et_2O, 1.24 mmol, 1.1 equiv) at 0 °C. The solution was stirred 5 min and then was allowed to warm to room temperature. After 20 min, THF was removed *in vacuo*, the yellow foam obtained was purified by flash chromatography (SiO_2, CH_2Cl_2/MeOH, 98/2) to afford a yellow powder (575 mg, 90%): mp 194 °C (dec); ^{1}H NMR (250 MHz, CD_2Cl_2) δ 1.59−1.88 (m, 8H, C$H_{2\ COD}$), 2.26 (s, 3H, C$H_{3\ Mes}$), 2.27 (s, 3H, C$H_{3\ Mes}$), 2.43 (s, 3H, C$H_{3\ Mes}$), 2.44 (s, 3H, C$H_{3\ Mes}$), 2.47 (s, 3H, C$H_{3\ Mes}$), 2.60 (s, 3H, C$H_{3\ Mes}$), 3.42 (m, 1H, CH_{COD}), 3.58 (m, 1H, CH_{COD}), 4.20 (d, 1H, J_{HH} = 20.7 Hz, CH_2), 4.30 (d, 1H, J_{HH} = 20.7 Hz, CH_2), 4.57 (m, 1H, CH_{COD}), 4.70 (m, 1H, CH_{COD}), 7.08 (br s, 1H, CH_{Mes}), 7.12 (m, 3H, CH_{Mes}); $^{13}C\{^1H\}$ NMR (62.9 MHz, CD_2Cl_2) δ 18.0 (*C*$H_{3\ Mes}$), 18.5 (*C*$H_{3\ Mes}$), 19.5 (*C*$H_{3\ Mes}$), 19.7 (*C*$H_{3\ Mes}$), 20.8 (*C*$H_{3\ Mes}$), 20.9 (*C*$H_{3\ Mes}$), 27.2 (*C*$H_{2\ COD}$), 28.6 (*C*$H_{2\ COD}$), 31.6 (*C*$H_{2\ COD}$), 33.4 (*C*$H_{2\ COD}$), 54.8 (*C*H_2), 67.9 (d, J_{RhC} = 13.9 Hz, *C*H_{COD}), 69.9 (d, J_{RhC} = 14.1 Hz, *C*H_{COD}), 100.6 (d, J_{RhC} = 6.4 Hz, *C*H_{COD}), 101.6 (d, J_{RhC} = 6.6 Hz, *C*H_{COD}), 128.5 (*C*H_{Mes}), 128.8 (*C*H_{Mes}), 129.6 (*C*H_{Mes}), 130.1 (*C*H_{Mes}), 130.9 (C_{Mes}), 131.2 (C_{Mes}), 134.5 (C_{Mes}), 135.1 (C_{Mes}), 135.3 (C_{Mes}), 137.3 (C_{Mes}), 138.3 (C_{Mes}), 139.4 (C_{Mes}), 171.2 (*C*=O), 229.7 (d, J_{RhC} = 51.5 Hz, N_2C); IR (ATR) $\tilde{\nu}$ 2953, 2915, 2868, 2824, 1748, 1737, 1606, 1480, 1456, 1400, 1376, 1359, 1333, 1300, 1271, 1250, 1167, 1147, 1074, 1033, 951, 846, 782, 734, 692 cm^{-1}; MS (ESI) *m*/*z* (%) 572 (16) $[M - Cl + CH_3CN]^+$, 531.2 (100) $[M - Cl]^+$. Anal. Calcd (%) for $C_{29}H_{36}ClN_2ORh$ (566.96): C 61.43, H 6.40, N 4.94. Found: C 61.19, H 6.67, N 4.85.

Chloro(η^4-cycloocta-1,5-diene)(4-pivaloyloxy-1,3-dimesitylimidazol-2-ylidene)rhodium(I) (7^{E1}). A solution of KHMDS (335 μL, 0.5 M in toluene, 0.17 mmol, 2.1 equiv) was added to a solution of $[RhCl(COD)]_2$ (39 mg, 0.08 mmol) in THF (2 mL) at room temperature. The mixture was stirred 15 min and became dark orange. To this solution was added 4-(pivaloyloxy)-1,3-dimesitylimidazolium chloride (4^{E1}) (70 mg, 0.16 mmol), and the resulting orange mixture was stirred 10 h at room temperature. Then THF

was removed *in vacuo*, and the orange residue obtained was purified by flash chromatography (neutral Al_2O_3 type III, CH_2Cl_2) to afford a bright yellow powder (59 mg, 57%): mp 105 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.00 (s, 9H, C$H_{3\ tBu}$), 1.55 (m, 4H, C$H_{2\ COD}$), 1.85 (m, 4H, C$H_{2\ COD}$), 2.11 (s, 3H, C$H_{3\ ortho}$), 2.13 (s, 3H, C$H_{3\ ortho}$), 2.35 (br s, 6H, C$H_{3\ ortho}$), 2.38 (s, 3H, C$H_{3\ para}$), 2.46 (s, 3H, C$H_{3\ para}$), 3.31 (br s, 2H, =CH_{COD}), 4.52 (br s, 2H, =CH_{COD}), 6.89 (s, 1H, C$H_{Im\text{-}5}$), 7.02 (m, 4H, CH_{Mes}); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$) δ 26.5 (*C*$H_{3\ tBu}$), 28.2 (*C*$H_{2\ COD}$), 28.6 (*C*$H_{2\ COD}$), 32.5 (*C*$H_{2\ COD}$), 32.9 (*C*$H_{2\ COD}$), 18.1 (*C*$H_{3\ ortho}$), 18.2 (*C*$H_{3\ ortho}$), 19.6 (*C*$H_{3\ para}$), 19.7 (*C*$H_{3\ para}$), 21.1 (*C*$H_{3\ ortho}$), 21.2 (*C*$H_{3\ ortho}$), 39.0 (*C*$_{tBu}$), 67.6 (d, J_{RhC} = 14.1 Hz, =*C*H$_{COD}$), 96.4 (d, J_{RhC} = 7.9 Hz, =*C*H$_{COD}$), 110.1 (*C*H$_{Im\text{-}5}$), 127.9 (*C*H$_{Mes}$), 128.1 (*C*H$_{Mes}$), 129.6 (*C*H$_{Mes}$), 129.7 (*C*H$_{Mes}$), 131.9 (*C*$_q$), 134.5 (*C*$_q$), 135.2 (*C*$_q$), 136.5 (*C*$_q$), 137.6 (*C*$_q$), 138.4 (*C*$_q$), 138.7 (*C*$_q$), 138.9 (*C*$_q$), 139.0 (*C*$_q$), 173.1 (*C*=O), 179.6 (d, J_{RhC} = 53.1 Hz, N$_2$*C*); IR (ATR) $\tilde{\nu}$ 2915, 2973, 2827, 1774, 1760, 1626, 1609, 1478, 1461, 1381, 1315, 1267, 1098, 1074, 1028, 851, 816, 729 cm^{-1}; MS (EI) *m*/*z* (%) 615 (100) [M − Cl]$^+$, 531 (12) [M − Cl − *t*BuCO]$^+$; HR-MS (ESI) *m*/*z* calcd for $C_{34}H_{44}N_2O_2Rh$ 615.2458, found 615.2460.

Chloro(η^4-cycloocta-1,5-diene)(4-methoxy-1,3-dimesitylimidazol-2-ylidene)rhodium(I) (7^{E2}). A solution of KHMDS (389 μL, 0.5 M in toluene, 0.20 mmol, 2.4 equiv) was added to a solution of $[RhCl(COD)]_2$ (40 mg, 0.08 mmol) in THF (2 mL) at room temperature. The mixture was stirred 15 min and became dark orange. To this solution was added 4-(methoxy)-1,3-dimesitylimidazolium chloride (4^{E2}) (78 mg, 0.16 mmol), and the resulting orange mixture was stirred 1 h at room temperature. Then THF was removed *in vacuo*, and the yellow residue obtained was purified by flash chromatography (neutral Al_2O_3, CH_2Cl_2) to afford a bright yellow powder (51 mg, 55%): mp 229 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55 (m, 4H, C$H_{2\ COD}$), 1.82 (m, 4H, C$H_{2\ COD}$), 2.22 (s, 6H, C$H_{3\ ortho}$), 2.40 (m, 3H, C$H_{3\ ortho}$, 6H, C$H_{3\ para}$) 2.47 (s, 3H, C$H_{3\ ortho}$), 3.31 (m, 2H, =CH_{COD}), 3.75 (s, 3H, O-CH_3), 4.50 (m, 2H, =CH_{COD}), 6.25 (s, 1H, C$H_{Im\text{-}5}$), 7.03 (m, 4H, CH_{Mes}); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$) δ 18.1 (*C*$H_{3\ ortho}$), 18.2 (*C*$H_{3\ ortho}$), 19.8 (s, *C*$H_{3\ ortho}$), 21.2 (*C*$H_{3\ para}$), 21.3 (*C*$H_{3\ para}$), 28.2 (*C*$H_{2\ COD}$), 28.6 (*C*$H_{2\ COD}$), 32.4 (*C*$H_{2\ COD}$), 33.0 (*C*$H_{2\ COD}$), 58.7 (O-*C*H_3), 67.4 (d, J_{RhC} = 14.5 Hz, =*C*H$_{COD}$), 68.0 (d, J_{RhC} = 14.7 Hz, =*C*H$_{COD}$), 95.7 (d, J_{RhC} = 7.5 Hz, =*C*H$_{COD}$), 96.2 (d, J_{RhC} = 7.9 Hz, =*C*H$_{COD}$), 99.4 *C*H$_{Im\text{-}5}$), 127.9 (*C*H$_{Mes}$), 128.0 (*C*H$_{Mes}$), 129.6 (*C*H$_{Mes}$), 129.7 (*C*H$_{Mes}$), 132.3 (*C*$_q$), 134.4 (*C*$_q$), 136.7 (*C*$_q$), 138.5 (*C*$_q$), 138.8 (*C*$_q$), 150.2 (*C*$_q$), 178.9 (d, J_{RhC} = 53.1 Hz, N$_2$*C*); IR (ATR) $\tilde{\nu}$ 2912, 2872, 2826, 1637, 1609, 1481, 1453, 1428, 1389, 1311, 1285, 1216, 1046; 998, 956, 866, 848, 767, 752, 727, 710, 691, 654 cm^{-1}; MS (EI) *m*/*z* (%) 615 (100) [M − Cl]$^+$, 335 (14) [Imidazolium]$^+$. Anal. Calcd (%) for $C_{30}H_{38}ClN_2ORh$ + 0.25CH_2Cl_2: C 60.33, H 6.44, N 4.65. Found: C 60.04, H 6.88, N 4.45.

Chloro(η^4-cycloocta-1,5-diene)(1,3-dimesityl-4-(diphenylphosphinato)imidazol-2-ylidene)rhodium(I) (7^{E4}). A solution of LiHMDS (0.20 mL, 1 M in THF, 0.20 mmol, 1.1 equiv) was added to a solution of $\mathbf{7_H}$ (100 mg, 0.18 mmol) in THF (5 mL) at −78 °C, and the mixture was stirred for 1.5 h. To this solution was added diphenylphosphinic chloride (41 μL, 0.21 mmol). The resulting orange mixture was allowed to warm to room temperature and was stirred for 1.5 h. THF was removed *in vacuo*. The orange foam obtained was dissolved in toluene and filtered through a pad of Celite. After evaporation, the residue was washed with CH_2Cl_2/pentane (1.5 mL/20 mL) and pentane (10 mL) to afford a yellow powder (110 mg, 82%): mp 132 °C (dec); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 1.58 (m, 4H, C$H_{2\ COD}$), 1.88 (m, 4H, C$H_{2\ COD}$), 2.10 (m, 6H, C$H_{3\ Mes}$), 2.22 (br s, 6H, C$H_{3\ Mes}$), 2.40 (s, 3H, C$H_{3\ Mes}$), 2.49 (s, 3H, C$H_{3\ Mes}$), 3.28 (m, 2H, CH_{COD}), 4.45 (m, 2H, CH_{COD}), 6.71 (d, 1H, J_{HP} = 1.0 Hz, C$H_{Im\text{-}5}$), 7.03 (s, 2H, CH_{Mes}), 7.11 (br s, 2H, CH_{Mes}), 7.54−7.56 (m, 10H, CH_{Ph}); ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2) δ 17.9 (*C*H$_{3\ Mes}$), 18.2 (*C*H$_{3\ Mes}$), 19.3 (*C*H$_{3\ Mes}$), 19.7 (*C*H$_{3\ Mes}$), 20.8 (*C*H$_{3\ Mes}$), 20.9 (*C*H$_{3\ Mes}$), 28.2 (*C*H$_{2\ COD}$), 28.3 (*C*H$_{2\ COD}$), 32.4 (*C*H$_{2\ COD}$), 32.6 (*C*H$_{2\ COD}$), 68.4 (d, J_{RhC} = 14.7 Hz, *C*H$_{COD}$), 68.6 (d, J_{RhC} = 13.9 Hz, *C*H$_{COD}$), 95.9 (d, J_{RhC} = 6.7 Hz, *C*H$_{COD}$), 96.0 (d, J_{RhC} = 7.4 Hz, *C*H$_{COD}$), 107.9 (d, J_{CP} = 3.0 Hz, *C*H$_{Im\text{-}5}$), 128.3 (br s, *C*H$_{Mes}$), 128.7 (d, J_{CP} = 13.4 Hz, *C*H$_{Ph}$), 129.2 (*C*H$_{Mes}$), 129.4 (*C*H$_{Mes}$), 131.4 (d, J_{CP} = 10.7 Hz, *C*H$_{Ph}$), 131.7 (d, J_{CP} = 11.2 Hz, *C*H$_{Ph}$), 133.1 (d, J_{CP} = 4.1 Hz, *C*H$_{Ph}$), 133.2 (d, J_{CP} = 3.4 Hz, *C*H$_{Ph}$), 136.5 (*C*$_q$), 138.6 (*C*$_q$), 139.2 (*C*$_q$), 179.4 (d, J_{RhC} = 52.7 Hz, N$_2$*C*); ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2) δ 33.4; IR (ATR) $\tilde{\nu}$ 2917, 2873, 2827, 1631, 1609, 1591, 1482, 1438, 1379, 1311, 1282, 1243, 1205, 1155, 1129, 1111, 1071, 1036, 1018, 997, 973, 853, 873, 851, 749, 731, 693 cm^{-1}; MS (ESI) *m*/*z* (%) 772 (14) [M − Cl + CH_3CN]$^+$, 731 (100) [M − Cl]$^+$, 531 (10) [M − Cl − Ph_2PO + H]$^+$; HR-MS (ESI) *m*/*z* calcd for $C_{41}H_{45}N_2ORh$ 731.2274, found 731.2267.

Chloro(η^4-cycloocta-1,5-diene)(1,3-dimesitylimidazol-4-(dimethyl-*tert*-butylsilyloxy)-2-ylidene)rhodium(I) (7^{E5}). A solution of LiHMDS (0.19 mL, 1 M in THF, 0.2 mmol, 1.1 equiv) was added to a solution of $\mathbf{7_H}$ (100 mg, 0.18 mmol) in THF (5 mL) at −78 °C, and the mixture was stirred for 1.5 h. To this solution was added chlorodimethyl-*tert*-butylsilane (28 mg, 0.19 mmol), and the solution was allowed to warm to room temperature and to stir for 1.5 h. THF was removed *in vacuo*, and the yellow foam obtained was purified by flash chromatography (SiO_2, hexane/EtOAc, 4/1) to afford a yellow powder (68 mg, 67%): mp 94 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.04 (s, 3H, Si-CH_3), 0.09 (s, 3H, Si-CH_3), 0.69 (s, 9H, C$H_{3\ tBu}$), 1.52 (br, 4H, C$H_{2\ COD}$), 1.85 (br, 4H, C$H_{2\ COD}$), 2.07 (s, 3H, C$H_{3\ Mes}$), 2.18 (s, 3H, C$H_{3\ Mes}$), 2.36 (m, 6H, C$H_{3\ Mes}$), 2.41 (m, 6H, C$H_{3\ Mes}$), 3.28 (br, 2H, CH_{COD}), 4.49 (br, 2H, CH_{COD}), 6.18 (s, 1H, C$H_{Im\text{-}5}$), 6.99 (m, 4H, CH_{Mes}); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ −5.7 (Si-*C*H$_3$), 5.9 (Si-*C*H$_3$), 17.2 (*C*$_{tBu}$), 17.7 (*C*H$_{3\ Mes}$), 17.9 (*C*H$_{3\ Mes}$), 19.4 (*C*H$_{3\ Mes}$), 19.7 (*C*H$_{3\ mes}$), 20.8 (*C*H$_{3\ Mes}$), 24.5 (*C*H$_{3\ tBu}$), 27.9 (*C*H$_{2\ COD}$), 28.1 (*C*H$_{2\ COD}$), 32.4 (*C*H$_{2\ COD}$), 67.1 (d, J_{RhC} = 14.5 Hz, *C*H$_{COD}$), 67.6 (d, J_{RhC} = 14.5 Hz, *C*H$_{COD}$), 95.3 (d, J_{RhC} = 7.5 Hz, *C*H$_{COD}$), 102.4 (*C*H$_{Im\text{-}5}$), 127.3 (*C*H$_{Mes}$), 127.7 (*C*H$_{Mes}$), 128.9 (*C*H$_{Mes}$), 129.2 (*C*H$_{Mes}$), 132.2 (*C*$_q$), 134.9 (*C*$_q$), 135.1 (*C*$_q$), 136.4 (*C*$_q$), 137.6 (*C*$_q$), 137.7 (*C*$_q$), 137.9 (*C*$_q$), 138.0 (*C*$_q$), 143.6 (*C*$_q$), 176.9 (d, J_{RhC} = 52.7 Hz, N$_2$*C*); IR (ATR) $\tilde{\nu}$ 2927, 2859, 2827, 1637, 1610, 1472, 1431, 1376, 1304, 1286, 1254, 1210, 1166, 1076, 1034, 993, 972, 953, 939, 878, 844, 785, 750, 733, 714, 695, 663 cm^{-1}; MS (ESI) *m*/*z* (%) 645 (100) [M − Cl]$^+$, 531 (40) [M − Cl − TBDMS + H]$^+$. Anal. Calcd (%) for $C_{35}H_{50}ClN_2ORhSi$: C 61.71, H 7.40, N 4.11. Found: C 61.42, H 7.79, N 3.94.

Chloro(η^4-cycloocta-1,5-diene)(1,3-dimesityl-5-(methylenyl)-imidazolin-4-on-2-ylidene)rhodium(I) (7_{CH2}). A solution of LiHMDS (0.29 mL, 1 M in THF, 0.29 mmol, 1.1 equiv) was added to a solution of $\mathbf{7_H}$ (150 mg, 0.26 mmol) in THF (10 mL) at −78 °C, and the mixture was stirred for 1.5 h. To this solution was added paraformaldehyde (20 mg, 0.66 mmol), and the mixture was allowed to warm to room temperature. The resulting orange mixture was stirred for 1.5 h at room temperature. THF was removed *in vacuo*, and the orange foam obtained was purified by flash chromatography (neutral Al_2O_3 type III, CH_2Cl_2) to afford an orange powder (112 mg, 73%): mp 183 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.58−1.88 (m, 8H, C$H_{2\ COD}$), 2.13 (s, 3H, C$H_{3\ Mes}$), 2.16 (s, 3H, C$H_{3\ Mes}$), 2.38 (s, 3H, C$H_{3\ Mes}$), 2.39 (s, 3H, C$H_{3\ Mes}$), 2.47 (s, 3H, C$H_{3\ Mes}$), 2.49 (s, 3H, C$H_{3\ Mes}$), 3.44 (m, 1H, CH_{COD}), 3.52 (m, 1H, CH_{COD}), 4.74 (m, 1H, CH_{COD}), 4.82 (m, 1H, CH_{COD}), 4.86 (d, 1H, J_{HH} = 1.9 Hz, =CH_2), 5.66 (d, 1H, J_{HH} = 1.9 Hz, =CH_2), 7.04 (s, 2H, CH_{Mes}), 7.08 (s, 1H, CH_{Mes}), 7.11 (s, 1H, CH_{Mes}); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ 17.7 (*C*H$_{3\ Mes}$), 18.3 (*C*H$_{3\ Mes}$), 19.3 (*C*H$_{3\ Mes}$), 19.6 (*C*H$_{3\ Mes}$), 20.7 (*C*H$_{3\ Mes}$), 20.8 (*C*H$_{3\ Mes}$), 27.2 (*C*H$_{2\ COD}$), 28.0 (*C*H$_{2\ COD}$), 31.7 (*C*H$_{2\ COD}$), 32.7 (*C*H$_{2\ COD}$), 68.6 (d, J_{RhC} = 13.9 Hz, *C*H$_{COD}$), 69.4 (d, J_{RhC} = 14.2 Hz, *C*H$_{COD}$), 102.7 (d, J_{RhC} = 6.1 Hz, *C*H$_{COD}$), 103.1 (=*C*H$_2$), 103.3 (d, J_{RhC} = 6.1 Hz, *C*H$_{COD}$), 128.0 (*C*H$_{Mes}$), 128.3 (*C*H$_{Mes}$), 129.7 (*C*H$_{Mes}$), 130.1 (*C*H$_{Mes}$), 130.8 (*C*$_{ipso}$), 131.9 (*C*$_{ipso}$), 134.6 (*C*$_{ortho}$), 134.7 (*C*$_{ortho}$), 135.4 (d, J_{RhC} = 1.0 Hz, =*C*$_{Im\text{-}5}$), 137.9 (*C*$_{ortho}$), 139.0 (*C*$_{para}$), 139.3 (*C*$_{para}$), 161.0 (d, J_{RhC} = 1.6 Hz, *C*=O), 227.0 (d, J_{RhC} = 52.6 Hz, N$_2$*C*); IR (ATR) $\tilde{\nu}$ 2917, 2872, 2826, 1752 (s, ν_{CO}), 1648, 1608, 1478, 1427, 1362, 1306, 1278, 1210, 1188, 1137, 1087, 1031, 991, 959, 902, 840, 793, 762, 745, 694 cm^{-1}; MS (ESI) *m*/*z* (%) 543(100) [M − Cl]$^+$,

584 (30) $[M - Cl + CH_3CN]^+$; HR-MS (ESI) *m/z* calcd for $C_{30}H_{36}N_2ORh$ 543.1883, found 543.1870.

Chloro(1,3-dimesitylimidazolin-4-on-2-ylidene)copper(I) (8_H). A solution of LiHMDS (1.18 mL, 1 M in THF, 1.18 mmol, 2.1 equiv) was added to a solution of **3a** (200 mg, 0.56 mmol) in THF (10 mL) at 0 °C, and the mixture was stirred for 30 min. To this solution was added CuCl (56 mg, 0.56 mmol), and the resulting mixture was stirred 45 min at room temperature before addition of HCl (618 μL, 1 M in Et_2O, 0.62 mmol, 1.1 equiv) at 0 °C. The solution was stirred 20 min and then was allowed to warm to room temperature before volatiles were removed *in vacuo*. Then, the residue was dissolved in toluene, filtered through a pad of Celite, and washed with pentane (2 × 10 mL) to afford a white powder. This residue was dissolved in CH_2Cl_2, distilled water (10 μL, 1 equiv) was added, and the mixture was stirred for 10 min. Then the solution was dried on Na_2SO_4. After filtration through a canula, volatiles were removed *in vacuo*, and the residue was washed with pentane to afford an off-white powder (159 mg, 68%): mp 115 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.18 (s, 6H, CH_3 ortho), 2.31 (s, 6H, CH_3 ortho), 2.35 (s, 6H, CH_3 para), 4.30 (s, 2H, CH_2), 7.04 (s, 4H, CH_{Mes}); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$) δ 17.7 (*C*H$_3$ ortho), 18.3 (*C*H$_3$ ortho), 21.1 (*C*H$_3$ para), 21.2 (*C*H$_3$ para), 52.9 (*C*H$_2$), 129.9 (*C*H$_{Mes}$), 130.2 (*C*H$_{Mes}$), 134.1 (C_q), 1344 (C_{ortho}), 135.0 (C_{ortho}), 140.2 (C_{para}), 140.5 (C_{para}), 172.0 (*C*=O), 213.5 (N_2C); IR (ATR) $\tilde{\nu}$ 2948, 2916, 2859, 1750, 1608, 1547, 1485, 1444, 1404, 1368, 1315, 1299, 1287, 1248, 1202, 1170, 1154, 1034, 970, 957, 936, 920, 851, 778, 735, 720 cm^{-1}; MS (ESI) *m/z* (%) 424 (30) $[M - Cl + CH_3CN]^+$, 321 (100) $[IMes - OH]^+$. Anal. Calcd (%) for $C_{21}H_{24}ClCuN_2O$ (419.43): C 60.14, H 5.77, N 6.68. Found: C 60.96, H 5.91, N 6.56.

Chloro(4-*tert*-butyldimethylsilyloxy-1,3-dimesitylimidazol-2-ylidene)copper(I) (8^{E5}). A solution of LiHMDS (0.63 mL, 1 M in THF, 0.63 mmol, 2.1 equiv) was added to a solution of **3a** (106 mg, 0.26 mmol) in THF (10 mL) at 0 °C, and the mixture was stirred for 25 min. To this solution was added CuCl (29.5 mg, 0.26 mmol), and the resulting mixture was stirred 1 h at room temperature before addition of *tert*-butyldimethylsilyl chloride (53 mg, 0.31 mmol, 1.2 equiv) at this temperature. The solution was stirred 1 h before volatiles were removed *in vacuo*. The product was then dissolved in CH_2Cl_2 and filtered through Celite. Solvents were evaporated, and the residue was washed with pentane (2 × 5 mL) to obtain a white solid (130 mg, 82%): mp 80 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.11 (s, 6H, Si-CH_3), 0.73 (s, 9H, C$H_{3\ tBu}$), 2.11 (s, 6H, CH_3 ortho), 2.14 (s, 6H, CH_3 ortho), 2.32 (s, 3H, CH_3 para), 2.33 (s, 3H, CH_3 para), 6.27 (s, 1H, C$H_{Im\text{-}5}$), 6.95 (s, 2H, CH_{Mes}), 6.97 (s, 2H, CH_{Mes}); ^{13}C{^{1}H} NMR (62.9 MHz, $CDCl_3$) δ −5.4 (Si-*C*H$_3$), 17.6 (*C*H$_3$ ortho), 17.7 (C_{tBu}), 18.0 (*C*H$_3$ ortho), 21.0 (*C*H$_3$ para), 21.1 (*C*H$_3$ para), 24.8 (*C*H$_{3\ tBu}$), 101.2 (*C*H$_{Im\text{-}5}$), 129.2 (*C*H$_{Mes}$), 129.4 (*C*H$_{Mes}$), 131.5 (C_{ipso}), 134.1 (C_{ortho}), 135.1 (C_{ortho}), 135.9 (C_{ipso}), 139.1 (C_{para}), 139.2 (C_{para}), 143.3 (*C*-O), 173.1 (N_2C); IR (ATR) $\tilde{\nu}$ 2952, 2928, 2857, 1767,1623, 1487, 1472, 1440, 1376, 1303, 1251, 1211, 1170, 1157, 1132, 1034, 1011, 954, 938, 920, 876, 847, 788 732, 695, 665 cm^{-1}; MS (ESI) *m/z* (%) 931 (100) $[Cu(\mathbf{5^{E5}})_2]^+$, 817 (6) $[Cu(\mathbf{5^{E5}})(\mathbf{5_H})]^+$, 435 (13) $[\mathbf{4^{E5}}]^+$, 384 (4) $[Cu(\mathbf{5_H}) + H]^+$. Anal. Calcd (%) for $C_{27}H_{38}ClCuN_2OSi + 0.1CH_2Cl_2$: C 60.03, H 7.10, N 5.17. Found: C 59.71, H 7.60, N 5.50.

General Procedure for the Preparation of [(NHC)RhCl(CO)$_2$] (9). CO gas was bubbled into a solution of **7** in CH_2Cl_2 (or CD_2Cl_2 for $\mathbf{7_{CH2}}$) at room temperature for 15 min. Then CH_2Cl_2 was removed *in vacuo*, and the yellow residue was washed with pentane to remove 1,5-cyclooctadiene and dried to give the product.

Chlorodicarbonyl(1,3-dimesitylimidazolin-4-on-2-ylidene)rhodium-(I) (9_H). The general procedure was followed using complex $\mathbf{7_H}$ (50 mg, 0.09 mmol) in CH_2Cl_2 (3 mL). The initial orange solution became pale yellow after 15 min. After washing with pentane (2 × 5 mL), the complex was isolated as a yellow powder (28 mg, 61%): mp 168 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.34 (s, 6H, CH_3 Mes), 2.38 (s, 6H, CH_3 Mes), 2.41 (s, 6H, CH_3 Mes), 4.42 (s, 2H, CH_2), 7.04 (s, 4H, CH_{Mes}); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$) δ 18.5 (*C*H$_3$ Mes), 18.1 (*C*H$_3$ Mes), 18.9 (*C*H$_3$ Mes), 21.2 (*C*H$_3$ Mes), 21.2 (*C*H$_3$ Mes), 54.3 (*C*H$_2$), 129.5 (*C*H$_{Mes}$), 129.6 (C_q), 129.7 (*C*H$_{Mes}$), 134.0 (C_{Mes}), 135.0 (C_{Mes}), 135.9 (C_{Mes}), 140.0 (C_{Mes}), 140.2 (C_{Mes}), 171.0 (d, J_{RhC} = 1.7 Hz, *C*=O), 182.2 (d, J_{RhC} = 73.8 Hz, *C*O), 184.3 (d, J_{RhC} = 54.5 Hz, *C*O), 220.7 (d, J_{RhC} = 43.8 Hz, N_2C); IR (CH_2Cl_2) $\tilde{\nu}$ 2090 (ν_{CO}), 2005 (ν_{CO}), 1769 ($\nu_{C=O}$) cm^{-1}; MS (ESI) *m/z* (%) 492 (100) $[M - CO - Cl + CH_3CN]^+$, 464 (10) $[M - 2CO - Cl + CH_3CN]^+$, 451 (37) $[M - CO - Cl]^+$, 423 (12) $[M - 2CO - Cl]^+$. Anal. Calcd (%) for $C_{23}H_{24}ClN_2O_3Rh + 0.45C_5H_{12}$: C 55.42, H 5.41, N 5.12. Found: C 55.61, H 5.03, N 5.06.

Chlorodicarbonyl(1,3-dimesityl-4-(*tert*-butylcarbonyloxy)imidazol-2-ylidene)rhodium(I) (9^{E1}). The general procedure was followed using complex $\mathbf{7^{E1}}$ (23 mg, 0.04 mmol), CO(g), and CH_2Cl_2 (2 mL). The initial orange solution became pale yellow after 15 min. After washing with pentane (5 mL), the complex was isolated as a yellow powder (20 mg, 94%): mp 184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (s, 9H, C$H_{3\ tBu}$), 2.23 (s, 6H, CH_3 ortho), 2.28 (s, 6H, CH_3 ortho), 2.38 (s, 3H, CH_3 para), 2.39 (s, 3H, CH_3 para), 7.01 (s, 2H, CH_{Mes}), 7.03 (s, 2H, CH_{Mes}), 7.06 (s, 1H, C$H_{Im\text{-}5}$); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ 18.0 (*C*H$_3$ ortho), 21.0 (*C*H$_3$ para), 26.5 (*C*H$_{3\ tBu}$), 39.1 (C_{tBu}), 110.4 (*C*H$_{Im\text{-}5}$), 29.2 (*C*H$_{Mes}$), 129.3 (*C*H$_{Mes}$), 130.8 (C_q), 135.4 (C_{ortho}), 135.5 (C_q), 136.0 (C_{ortho}), 139.4 (C_{para}), 139.6 (C_{para}), 173.2 (d, J_{RhC} = 44.3 Hz, N_2C), 182.7 (d, J_{RhC} = 74.5 Hz, *C*O), 184.85 (d, J_{RhC} = 54.7 Hz, *C*O); IR (CH_2Cl_2) $\tilde{\nu}$ 2080 (ν_{CO}), 1997 (ν_{CO}) cm^{-1}; MS (ESI) *m/z* (%) 621 (100) $[M + Na]^+$, 567 (68) $[M - Cl - CO + MeOH]^+$, 563 (74) $[M - Cl]^+$, 360 (35). Anal. Calcd (%) for $C_{28}H_{32}ClN_2O_4Rh$ (598.9): C 56.15, H 5.39, N 4.68. Found: C 56.70, H 5.54, N 4.40.

Chlorodicarbonyl(1,3-dimesityl-4-(methoxy)imidazol-2-ylidene)-rhodium(I) (9^{E2}). The general procedure was followed using complex $\mathbf{7^{E2}}$ (70 mg, 0.12 mmol) in CH_2Cl_2 (4 mL). The initial orange solution became pale yellow after 15 min. After washing with pentane (2 × 5 mL), the complex was isolated as a yellow powder (50 mg, 79%): mp 180 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 6H, CH_3 ortho), 2.28 (s, 6H, CH_3 ortho), 2.38 (s, 3H, CH_3 para), 2.39 (s, 3H, CH_3 para), 3.83 (s, 3H, O−CH_3), 6.41 (s, 1H, C$H_{Im\text{-}5}$), 7.01 (s, 2H, CH_{Mes}), 7.03 (s, 2H, CH_{Mes}); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ 18.4 (*C*H$_3$ ortho), 18.5 (*C*H$_3$ ortho), 21.2 (*C*H$_3$ para), 21.3 (*C*H$_3$ para), 59.1 (O-*C*H$_3$), 99.6 (*C*H$_{Im\text{-}5}$), 129.2 (*C*H$_{Mes}$), 129.3 (*C*H$_{Mes}$), 131.2 (C_{Mes}), 135.4 (C_{ortho}), 135.8 (C_{Mes}), 136.1 (C_{ortho}), 139.2 (C_{para}), 139.5 (C_{para}), 150.1 (*C*-O), 172.5 (d, J_{RhC} = 45.0 Hz, N_2C), 182.7 (d, J_{RhC} = 74.2 Hz, *C*O), 184.9 (d, J_{RhC} = 54.1 Hz, *C*O); IR (CH_2Cl_2) $\tilde{\nu}$ 2079 (ν_{CO}), 1995 (ν_{CO}) cm^{-1}; MS (ESI) *m/z* (%) 547 (100) $[M - CO - Cl + 2CH_3CN]^+$, 533 (22) $[M - Cl + CH_3CN]^+$, 519 (12) $[M - 2CO - Cl + 2CH_3CN]^+$, 506 (28) $[M - CO - Cl + CH_3CN]^+$. Anal. Calcd (%) for $C_{24}H_{26}ClN_2O_3Rh$ (528.8): C 54.51, H 4.96, N 5.30. Found: C 52.99, H 5.02, N 5.08.

Chlorodicarbonyl(1,3-dimesityl-4-diphenylphosphinatoimidazol-2-ylidene)rhodium(I) (9^{E4}). The general procedure was followed using complex $\mathbf{7^{E4}}$ (40 mg, 0.052 mmol). The initial orange solution became pale yellow after 15 min. After washing with a mixture of CH_2Cl_2/pentane (0.5 mL/10 mL), the complex was isolated as a yellow powder (30 mg, 80%): mp 175 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.10 (s, 6H, CH_3 ortho), 2.12 (s, 6H, CH_3 ortho), 2.36 (s, 3H, CH_3 para), 2.42 (s, 3H, CH_3 para), 6.90 (d, 1H, J_{PH} = 1.2 Hz, C$H_{Im\text{-}5}$), 6.98 (s, 2H, CH_{Mes}), 7.02 (s, 2H, CH_{Mes}), 7.40−7.62 (m, 10H, CH_{Ph}); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$) δ 34.6 (s, *P*(=O)Ph_2); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ 18.2 (*C*H$_3$ ortho), 18.6 (*C*H$_3$ ortho), 21.2 (*C*H$_3$ para), 21.3 (*C*H$_3$ para), 108.0 (d, J_{PC} = 3.1 Hz, *C*H$_{Im\text{-}5}$), 128.8 (d, J_{PC} = 13.8 Hz, *C*H$_{ortho}$), 129.2 (s, *C*H$_{Mes}$), 131.7 (d, J_{PC} = 10.9 Hz, *C*H$_{meta}$), 133.6 (d, J_{PC} = 2.8 Hz, *C*H$_{para}$), 125.2 (C_{ortho}), 136.2 (C_{ortho}), 139.4 (C_{para}), 139.6 (C_{para}), 173.4 (d, J_{RhC} = 45.6 Hz, N_2C), 182.6 (d, J_{RhC} = 74.6 Hz, *C*O), 184.1 (d, J_{RhC} = 54.0 Hz, *C*O); IR (CH_2Cl_2) $\tilde{\nu}$ 2080 (ν_{CO}), 1997 (ν_{CO}) cm^{-1}; MS (ESI) *m/z* (%) 733 (100) $[M - CO - Cl + 2CH_3CN]^+$, 692 (34) $[M - CO - Cl + CH_3CN]^+$, 651 (6) $[M - CO - Cl]^+$, 533 (42) $[M - CO - Cl - P(=O)Ph_2 + 2CH_3CN]^+$, 492 (21) $[M - CO - Cl - P(=O)Ph_2 + CH_3CN]^+$,

Table 3. X-ray Experimental Data for Complexes 7^{E2} and 7^{E4}

	7^{E2}	7^{E4}
formula	$C_{30}H_{38}ClN_2ORh$	$C_{41}H_{45}ClN_2O_2PRh$
molecular weight	580.98	767.12
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a (Å)	13.200(5)	18.6377(5)
b (Å)	11.630(5)	11.2954(4)
c (Å)	18.518(5)	19.2758(6)
α (deg)	90	90
β (deg)	100.288(5)	107.192(2)
γ (deg)	90	90
V (Å^3)	2797.1(18)	3876.6(2)
Z	4	4
cryst dimens (mm)	0.15 × 0.15 × 0.15	0.40 × 0.30 × 0.10
ρ_{calc} (g cm^{-3})	1.380	1.314
$F000$	1208	1592
μ (mm^{-1})	0.731	0.586
temp (K)	180(2)	110(2)
wavelength (Å)	0.71073	0.71073
radiation	Mo Kα	Mo Kα
no. of data measd	78 899	68 541
no. of data with $I > 2\sigma(I)$	4471	6446
no. of variables	361	439
R	0.0385	0.0386
R_w	0.1028	0.0935
goodness-of-fit on F^2	1.21	1.047
largest peak in final difference (e Å^3)	0.87 and −0.53	0.924 and −0.381

321 (38) [ImOH]$^+$. Anal. Calcd (%) for $C_{35}H_{33}ClN_2O_4PRh$ + $0.7CH_2Cl_2$: C 55.37, H 4.48, N 3.62. Found: C 55.36, H 4.78, N 3.72.

Chlorodicarbonyl(1,3-dimesityl-4-*tert*-butyldimethylsilyloxyimidazol-2-ylidene)rhodium(I) (9^{E5}). The general procedure was followed using complex 7^{E5} (40 mg, 0.07 mmol), CO(g), and CH_2Cl_2 (5 mL). After washing with pentane (2 × 5 mL), the complex was isolated as a yellow powder (38 mg, 86%): mp 172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.14 (s, 6H, Si-CH_3), 0.75 (s, 9H, C$H_{3\ tBu}$), 2.24 (s, 6H, C$H_{3\ ortho}$), 2.28 (s, 6H, C$H_{3\ ortho}$), 2.37 (s, 3H, C$H_{3\ para}$), 2.38 (s, 3H, C$H_{3\ para}$), 6.35 (s, 1H, C$H_{Im\text{-}5}$), 6.99 (s, 2H, CH_{Mes}), 7.01 (s, 2H, CH_{Mes}); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ −5.4 (Si-CH_3), 17.6 (C_{tBu}), 18.4 ($CH_{3\ ortho}$), 18.7 ($CH_{3\ ortho}$), 21.1 ($CH_{3\ para}$), 21.2 ($CH_{3\ para}$), 24.8 ($CH_{3\ tBu}$), 102.8 ($CH_{Im\text{-}5}$), 128.9 (CH_{Mes}), 129.2 (CH_{Mes}), 131.5 (C_q), 135.9 (C_{ortho}), 136.0 (C_{ortho}), 139.0 (C_{para}), 139.1 (C_{para}), 144.0 (*C*-O), 171.1 (d, J_{RhC} = 45.1 Hz, N_2C), 182.9 (d, J_{RhC} = 74.6 Hz, *C*O), 185.1 (d, J_{RhC} = 54.1 Hz, *C*O); IR (CH_2Cl_2) $\tilde{\nu}$ 2077 (ν_{CO}), 1994 (ν_{CO}) cm^{-1}; MS (ESI) m/z (%) 621 (100) [M − Cl + MeOH + Na]$^+$, 567 (38) [M − Cl − CO + CH_3CN]$^+$. Anal. Calcd (%) for $C_{29}H_{38}ClN_2O_3RhSi$ (629.1): C 55.37, H 6.09, N 4.45. Found: C 55.28, H 6.49, N 4.22.

Chlorodicarbonyl(1,3-dimesityl-5-(methylenyl)imidazolin-4-on-2-ylidene)rhodium(I) (9_{CH2}). The general procedure was followed using complex 7_{CH2} (23 mg, 0.04 mmol), CO(g), and $CDCl_3$ (2 mL). The initial orange solution became pale yellow after 15 min. The solution was poured into a NMR tube, and NMR analyses were performed: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.31 (s, 12H, C$H_{3\ ortho\text{-}mes}$), 2.39−2.41 (C$H_{3\ para\text{-}mes}$ + C$H_{2\ COD}$), 5.19 (d, 1H, J_{HH} = 2.4 Hz, =CH_2), 5.60 (br s, 4H, =CH_{COD}), 5.03 (d, 1H, J_{HH} = 2.4 Hz, =CH_2), 7.05 (s, 2H, CH_{Mes}); 7.08 (s, 2H, CH_{Mes}); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$) δ 18.4 ($CH_{3\ ortho\text{-}mes}$), 18.7 ($CH_{3\ ortho\text{-}mes}$), 21.2 ($CH_{3\ para\text{-}mes}$), 21.2 ($CH_{3\ para\text{-}mes}$), 28.0 ($CH_{2\ COD}$), 108.8 (=CH_2), 128.6 (=CH_{COD}), 129.6 (CH_{Mes}), 129.8 (CH_{Mes}), 131.2 (C_q), 135.2 (C_q), 135.8 (C_q), 140.0 (C_q), 140.5 (C_q), 162.0 (*C*=O), 183.9 (d, J_{RhC} = 58 Hz, *C*O), 218.0 (d, J_{RhC} = 45 Hz, N_2C); IR (CH_2Cl_2) $\tilde{\nu}$ 2090 (ν_{CO}), 2007 (ν_{CO}) cm^{-1}; MS (FAB, MNBA matrix) m/z (%) 527 (29) [M]$^+$, 498 (100) [M − CO]$^+$, 471 (42) [M − 2CO]$^+$, 440 (43).

Generation of the Dimeric Species 10. Compound 9_{CH2} was heated *in vacuo* at 80 °C for 8 h. The red residue was washed with pentane (2.5 mL) and dried *in vacuo* to afford an orange solid (quantitative yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.19 (s, 6H, C$H_{3\ ortho\text{-}mes}$), 2.20 (s, 6H, C$H_{3\ ortho\text{-}mes}$), 2.36 (s, 3H, C$H_{3\ para\text{-}mes}$), 2.37 (s, 3H, C$H_{3\ para\text{-}mes}$), 4.87 (d, J_{HH} = 1.2 Hz, 1H, =CH_2) 5.74 (d, J_{HH} = 1.2 Hz, 1H, =CH_2), 6.97 (s, 2H, CH_{Mes}), 6.99 (s, 2H, CH_{Mes}); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$) δ 18.7 ($CH_{3\ ortho\text{-}mes}$), 19.0 ($CH_{3\ ortho\text{-}mes}$), 21.2 ($CH_{3\ para\text{-}mes}$), 103.7 (=CH_2), 129.4 (CH_{Mes}), 129.8 (CH_{Mes}), 130.8 (C_{ipso}), 132.2 (C_{ipso}), 135.8 (=*C*), 136.0 (C_{ortho}), 139.1 (C_{para}), 139.5 (C_{para}), 161.4 (*C*=O), 183.2 (J_{RhC} = 86.4 Hz, *C*O), 213.5 (J_{RhC} = 59.8 Hz, N_2C); IR (ATR) $\tilde{\nu}$ 1988 (ν_{CO}) cm^{-1}; MS (ESI) m/z (%) 504 (100) [M/2 − Cl + CH_3CN]$^+$, 463 (69) [M/2 − Cl]$^+$, 435 (50) [M/2 − CO − Cl]$^+$.

X-ray Diffraction Studies. Single crystals of 7^{E2} and 7^{E4} suitable for X-ray diffraction were obtained by slow evaporation of a dichloromethane/pentane mixture, and the data were collected on a Bruker D8 APEX II diffractometer. Crystal and intensity data are summarized in Table 3. All calculations were performed on a PC-compatible computer using the WinGX system.[31] The structures were solved using the SIR92 program,[32] which revealed in each instance the position of most of the non-hydrogen atoms. All remaining non-hydrogen atoms were located by the usual combination of full matrix least-squares refinement and difference electron density syntheses by using the SHELXL97 program.[33] For 7^{E2}, carbon atoms C7 and C12 belonging to the cyclo-octadiene ring were found to be disordered over two positions. Concomitantly, the methoxy group attached to the NHC backbone was found to be distributed over two different sites, being attached to either C2 or C3. Each couple of atoms C7a and C7b, C12a and C12b, O1a and O1b, and C4a and C4b were refined with structure occupancy factors of 0.68 and 0.32, respectively. Atomic scattering factors were taken from the usual tabulations. Anomalous dispersion terms for Rh, Cl, and P atoms were included in F_c. All non-hydrogen atoms were allowed to vibrate anisotropically. All the hydrogen atoms were set in idealized position (R_3CH, C−H = 0.96 Å; R_2CH_2, C−H = 0.97 Å; RCH_3, C−H = 0.98 Å; C(sp^2)−H = 0.93 Å; U_{iso} 1.2 or 1.5 time greater than the U_{eq} of the carbon atom to which the

(31) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.
(32) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.
(33) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.

hydrogen atom is attached), and their positions were refined as "riding" atoms.

Acknowledgment. This research was supported by the CNRS. We thank the Ministère de l'Education Nationale for a Ph.D. Fellowship to L.B., the RDR2 network of the CNRS for additional funding, and the Agence Nationale de la Recherche (ANR) for financial support of the proposal ANR-08-BLAN-0137-01.

Supporting Information Available: CIF files giving crystallographic data and including a full list of interatomic bond lengths and angles for the reported complexes $\mathbf{7}^{\mathbf{E2}}$ and $\mathbf{7}^{\mathbf{E4}}$. This material is available free of charge via the Internet at http://pubs.acs.org