CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201000870

Electronic Tuning of a Carbene Center via Remote Chemical Induction, and Relevant Effects in Catalysis

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Abstract: The present report develops the idea that an N-heterocyclic carbene incorporating a remote anionic functionality—here, a malonate group—as a backbone component of its heterocyclic framework, can be "post-functionalized" directly from its transition-metal complexes, upon simple addition of a variety of electrophiles interacting directly with the malonate group in the outer coordination sphere. From a palette of selected electrophilic reagents, it was thus possible to modulate the electronic donor properties of the carbene center over a rather broad range. Both the zwitterionic complex [Rh{*malo*-NHC}(cod)] and the cationic derivatives $[Rh\{malo\text{-}NHC^{E}\}(cod)]^{+}$ (where "*malo*-NHC^{E}" represents the ligand modified by a selected electrophile "E") were used as pre-catalysts in two types of catalytic reactions, namely, the polymerization of phenylacetylene and the hydroboration of styrene. The results indicate that, in both cases, the zwitterionic species is by far the best catalyst, whereas a decrease in the ligand donicity induced by the added electrophile results in a concomitant reduction of catalytic activity. Apparent deviations to such a trend in the case of the hydroboration of styrene were rationalized in terms of an interaction between the reactive catecholborane substrate and the remote functionality of the N-heterocyclic carbene leading to an in situ modification of the nature of the active species. These observations serve as a useful basis to define the scope and limitations of the present conceptual approach in catalysis.

Keywords: carbenes · heterocyclic compounds · hydroboration · polymerization · rhodium

Introduction

The development of transition-metal complexes, the catalytic performance of which can be remotely controlled by an external stimulus, represents a challenging conceptual advance in modern organometallic chemistry. To date, known examples of such complexes include a few homogeneous phosphine- and nitrogen-based catalysts incorporating either a redox-active ligand[1,2] or a "chemo-active" one possessing either a basic binding site susceptible to be attacked by a Lewis acid,[3] or an acidic site susceptible to be deprotonated.[4]

Now if we consider N-heterocyclic carbenes,[5,6] (NHCs), which have blossomed into a class of powerful ligands for organometallic catalysis,[7–9] it would be highly beneficial to apply them to the same concept, and we effectively see a number of successful preliminary approaches pursuing such a goal (see below).

In pioneering studies on the use of N-heterocyclic carbenes as ancillary ligands, substantial efforts were first directed toward the control and quantification of their steric and electronic properties. The steric shielding of an NHC was accurately quantified by Nolan et al.[10] as the percentage of "occupied volume" ($\%V_{bur}$), and the consequences of its variation on the catalytic performances were examined in detail by Glorius and co-workers.[11] On another hand, the electron-donating properties of NHCs were quantified by measuring the infrared ν_{CO} stretching frequencies of two kinds of complexes, namely, $[(NHC)Ni(CO)_3]$, and $[(NHC)MCl(CO)_2]$ (M = Rh, Ir) which were independently proposed as standard references.[12] The corresponding independent scales established from such complexes can be correlated with the Tolman electronic parameter (TEP),[13,14] which enables a direct comparison with the case of phosphine ligands. To date, attempts to modulate the electronic donor properties of NHCs have followed three main strategies (Scheme 1) including i) attachment of a pendant electron-donating or -withdrawing group at the periphery of the

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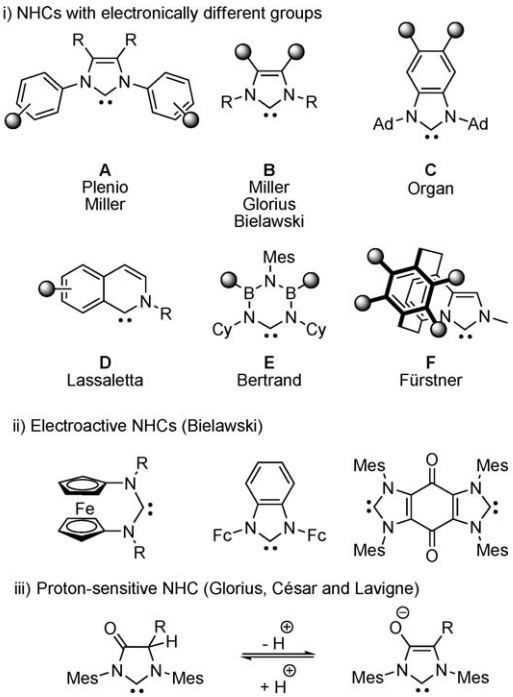
nitrogen substituents (type **A**),[15] or directly onto the backbone atoms of the NHC (types **B**–**F**),[12d,16] ii) incorporation of a redox active group such as a ferrocene or a quinone into the structure of the NHC,[17] or iii) incorporation of an easily deprotonable keto unit in close proximity to the carbenic center.[18] The latter two strategies allow a significant modulation of the electronic properties of the carbene, albeit only over two fixed values corresponding, for the former, to the ligand's reduced and oxidized states, respectively, and for the latter, to the ligand's protonated and deprotonated forms.

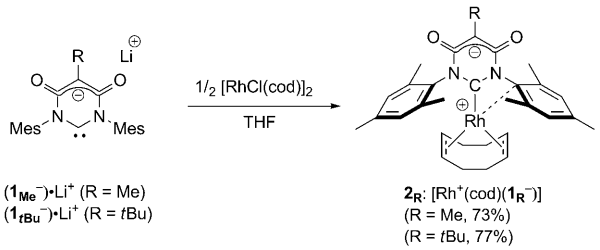


Scheme 1. Selected examples of previously reported means to modulate the electronic properties of an NHC ligand. The grey spheres indicate the locations where the influencial substituents are introduced.

To date, the consequences of an electronic tuning of the carbene center on the catalytic performances of relevant complexes have been examined only in few cases.[16a,d] Interestingly, very recently, Fürstner provided experimental evidence that a modulation of the π-acceptor properties of the carbene center of an NHC is also prone to influence its catalytic behavior.[19]

In a preliminary communication of part of the present work, we disclosed the modular synthesis of a new NHC ligand family, a six-membered anionic N-heterocyclic carbene, "*malo*-NHC" ($\mathbf{1}^-$) incorporating a malonate backbone synthetically accessible with different R groups (see below).[20]

Due to its anionic nature, $\mathbf{1_R}^-$ was found to react with numerous transition-metal complexes to give unsaturated zwitterionic species, exemplified here by the 14 e^- prototype [Rh(cod)($\mathbf{1_R}^-$)] ($\mathbf{2_R}$). Such a zwitterionic metal/ligand system



represents a favorable case where the steric and electronic properties are under control of totally independent parameters. Indeed, whereas the shape of the metal's cavity is controlled only by the ligand's steric parameters, determined by the size of the ring and the nature of the nitrogen substituents, an interesting feature is that the remote malonate group emerges in the outer coordination sphere, where it becomes directly accessible to an external chemical stimulus, possibly represented by external incoming electrophiles. With these observations in mind, we anticipated that simple addition of a range of electrophilic reagents exhibiting different electron-withdrawing properties might allow a rapid and effective fine-tuning of the electronic properties of the carbene center whithout change in the ligand's steric properties. Beyond, we also intended to examine the effects of such a modulation on the catalytic behavior of our complex. The attractive possibility to incorporate the electrophile after complexation appeared as a beneficial advantage in view of a rapid catalyst screening, particularly relative to most concurrent systems where the modulation has to be carried out on the ligand precursor (Scheme 1, types **A**–**F**).[15,16]

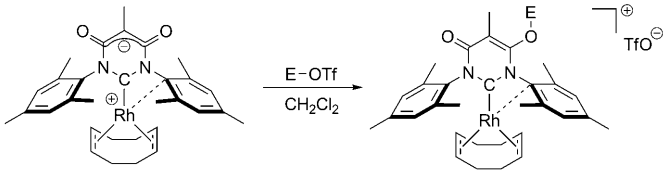
Results and Discussion

Synthesis of the pre-catalysts: The pyrimidinium betaïnes ($\mathbf{1_{Me}}$)·H and ($\mathbf{1_{tBu}}$)·H, incorporating two classical mesityl (2,4,6-trimethyphenyl) groups as the nitrogen substituents, were selected as the precursors of a series of target ligands all exhibiting the same steric hindrance. In the first part of the present investigation, we mainly considered the case where a methyl group is installed as R substituent of the malonate group. Later on, we found that in specific cases, varying the nature of this group can affect the steric accessibility of the oxygens.

The starting compound of the present investigation, the zwitterionic 14 e^- species [Rh^+(cod)($\mathbf{1_R}^-$)], $\mathbf{2_R}$, (see above) was originally obtained in high yields by trapping the free carbene ($\mathbf{1_R}^-$)·Li^+ with $^1/_2$ equivalent of $[RhCl(1,5\text{-cod})]_2$.[20] An X-ray structure analysis of $\mathbf{2_{Me}}$ revealed the existence of a labile bonding interaction between the C_{ipso} of one of the mesityl arms and the Rh center. In solution, a dynamic process, corresponding to the shuttling of the Rhodium center between the two mesityl arms was found to occur even at −80 °C thus resulting in an averaging of the ^{1}H and

^{13}C NMR spectra of compounds $\mathbf{2_R}$ to a formal C_{2v} symmetry.

The addition of electrophiles E-OTf (E = Me,Tf, H) to the zwitterionic complex $\mathbf{2_{Me}}$ yielded the corresponding ionic complexes [Rh(cod)($\mathbf{1_{Me}}^{\mathbf{E}}$)][TfO] ($\mathbf{3_{Me}}^{\mathbf{E}}$) in excellent yields (>90%) (Scheme 2).



$\mathbf{2_{Me}}$: [Rh$^+$(cod)($\mathbf{1_{Me}}^-$)]

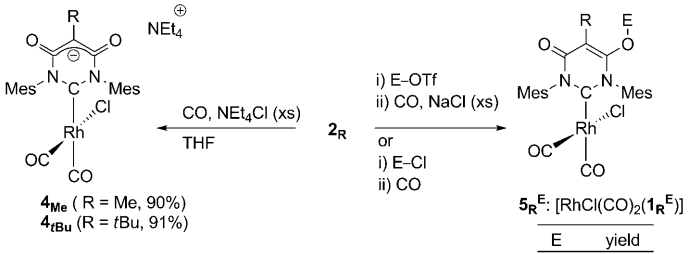
$\mathbf{3_{Me}}^{\mathbf{E}}$: [Rh(cod)($\mathbf{1_{Me}}^{\mathbf{E}}$)]$^+$[TfO]$^-$

E	yield
Me	quant.
Tf	90 %
H	97 %

Scheme 2. Reaction of the zwitterionic complexes $\mathbf{2_{Me}}$ with various electrophiles leading to the ionic complexes $\mathbf{3_{Me}}^{\mathbf{E}}$.

All of them were obtained in spectroscopically and analytically pure form by evaporation of volatiles and a simple washing with pentane. Analysis of the ^{1}H NMR spectra of complexes $\mathbf{3_{Me}}^{\mathbf{E}}$ recorded at 25°C, clearly revealed that the characteristic swing of the unsaturated Rh center between the mesityl groups, already observed for $\mathbf{2_R}$, is still operative here (as also the case for other cationic derivatives of closely related NHCs).[21] Again, this dynamic chemical exchange could not be frozen by lowering the temperature down to −80°C, and is thus responsible for the observed averaging of ^{1}H and ^{13}C NMR spectra of the two isomeric forms. In principle, the strong attachment of an electrophile to one of the remote oxygens should reduce the symmetry of the ligand from C_{2v} to C_s point group. This is effectively observed in the ^{1}H and ^{13}C NMR spectra of complexes $\mathbf{3_{Me}}^{\mathbf{Me}}$ and $\mathbf{3_{Me}}^{\mathbf{Tf}}$, where two sets of signals are indeed observed for the two mesityl arms. On the contrary, in the case of $\mathbf{3_{Me}}^{\mathbf{H}}$, the signals of the mesityl protons are averaged in the ^{1}H NMR spectra at 25°C, which can be rationalized in terms of a fast exchange of the proton between the two available oxygen sites of the malonate backbone. This dynamic process could not be frozen by lowering the temperature down to −80°C, indicating a very low activation energy barrier.

Evaluation of the donor properties of the ligands $\mathbf{1_R}^-$ and $\mathbf{1_R}^{\mathbf{E}}$: According to the literature, the donor properties of a given NHC ligand can be accurately evaluated by measuring the IR ν(CO) stretching frequencies of complexes like [(NHC)Ni(CO)$_3$], or [(NHC)MCl(CO)$_2$] (M = Rh, Ir) taken as standard references.[12] For the present investigation, the Rh scale was naturally selected. In view of evaluating the donor properties of our anionic NHC $\mathbf{1_R}^-$, it was first necessary to prepare a standard anionic chloro-carbonyl Rh^I derivative incorporating such a ligand. This was done simply by bubbling CO into a solution of the zwitterionic Rh complex $\mathbf{2_R}$ in the presence of a halide source (Scheme 3, left equation), a reaction which produced the new anionic complex [RhCl(CO)$_2$($\mathbf{1_R}^-$)](NEt$_4$)$^+$ ($\mathbf{4_R}$).



$\mathbf{4_{Me}}$ (R = Me, 90%)
$\mathbf{4_{tBu}}$ (R = *t*Bu, 91%)

$\mathbf{5_R}^{\mathbf{E}}$: [RhCl(CO)$_2$($\mathbf{1_R}^{\mathbf{E}}$)]

E	yield
Me	91%
Tf	87 %
H	93 %

Scheme 3. Formation of standard chloro-carbonyl Rh complexes RhCl(CO)$_2$(NHC) to be used for the evaluation of the ligand's donor properties.

The outcome of the conversion of $\mathbf{2_R}$ into $\mathbf{4_R}$ proved to be highly dependent on the nature of the chloride salt since it was observed that the counter-ion has a crucial role on the solubility of the final ionic complex $\mathbf{4_R}$. Our first attempts based on chloride salts known for giving good results in the solubilization of anionic metal complexes, such as bis(triphenylphosphine)iminium chloride ([PPN]Cl)[22] or (5-azoniaspiro[4.4]nonane)chloride ([ASN]Cl)[23] remained unsuccessful due to a poor solubility of the final products. Fortunately, the use of tetraethylammonium chloride ([NEt$_4$]Cl) furnished high yields of complexes $\mathbf{4_R}$ exhibiting high solubility in common organic solvents (alcohols, THF, CH$_3$CN, chlorinated solvents).

For the neutral N-heterocyclic carbenes $\mathbf{1_{Me}}^{\mathbf{E}}$ resulting from the addition of electrophiles to the parent zwitterionic complex $\mathbf{2_{Me}}$, the corresponding standard chloro-carbonyl complexes $\mathbf{5_{Me}}^{\mathbf{E}}$ were obtained by bubbling CO gas into a solution of in situ generated complexes $\mathbf{3_{Me}}^{\mathbf{E}}$ in the presence of a large excess of sodium chloride as the chloride source. For $\mathbf{5_{Me}}^{\mathbf{H}}$, the direct use of anhydrous HCl led to the transient formation of a neutral complex [RhCl(cod)($\mathbf{1_{Me}}^{\mathbf{H}}$)] which ultimately produced the complex [RhCl(CO)$_2$($\mathbf{1_{Me}}^{\mathbf{H}}$)] ($\mathbf{5_{Me}}^{\mathbf{H}}$) via displacement of the COD ligand by carbon monoxide.

Two representative complexes of the above series, namely, $\mathbf{4_{Me}}$ and $\mathbf{5_{Me}}^{\mathbf{Me}}$, were characterized by X-ray diffraction, and their molecular structures are depicted in Figure 1.

Both complexes possess distorted square-planar coordination geometries with the *malo*-NHC ligand being almost orthogonal to the mean coordination plane (N1-C3-Rh1-Cl1 torsion angle: 81.1° in $\mathbf{4_{Me}}$, 85.4° in $\mathbf{5_{Me}}^{\mathbf{Me}}$). Very characteristically, examination of geometrical parameters within the malonate backbone O3-C4-C5-C6-O4 of $\mathbf{4_{Me}}$ reveals that the corresponding C–O and C–C bond lengths are all intermediate between single and double bond values, reflecting the expected electron delocalization over the whole malonate group. By contrast, examination of the same structural parameters in $\mathbf{5_{Me}}^{\mathbf{Me}}$ reveals that attachment of the electro-

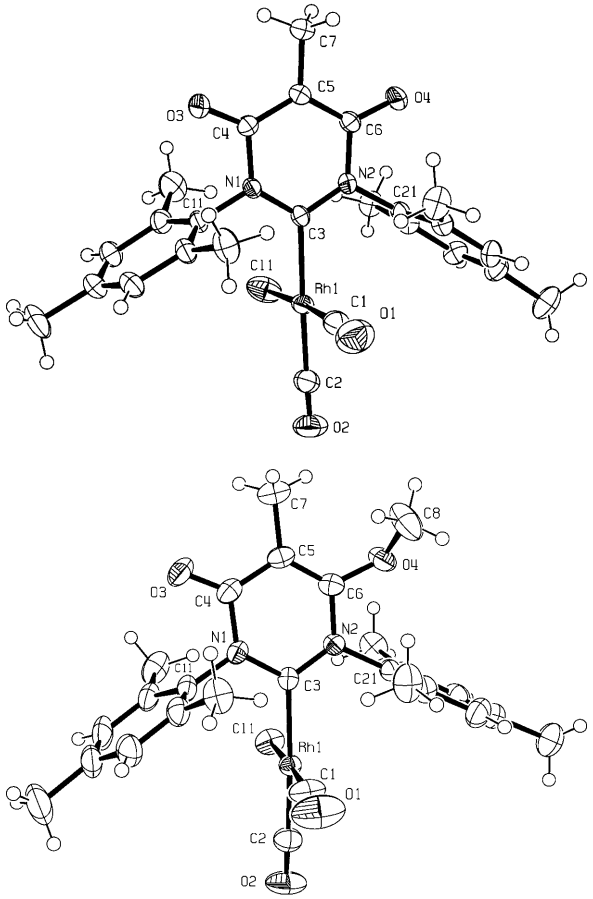
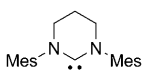


Figure 1. Top: Molecular structure of the anionic unit of complex $\mathbf{4_{Me}}$. Selected bond lengths [Å] and angles [°]: Rh1−C3 2.088(2), C3−N1 1.338(3), C3−N2 1.335(3), N1−C4 1.448(3), N2−C6 1.437(3), O3−C4 1.224(3), C4−C5 1.397(3), C5−C6 1.387(4), C6−O4 1.235(3); N1-C3-N2 116.1(2), N1-C3-Rh1-Cl1 81.1. Lower drawing: Molecular structure of complex $\mathbf{5_{Me}}^{\mathbf{Me}}$. Selected bond lengths [Å] and angles [°]: Rh1−C3 2.092(2), C3−N1 1.357(3), C3−N2 1.345(3), N1−C4 1.437(3), N2−C6 1.405(3), O3−C4 1.217(3), C4−C5 1.438(4), C5−C6 1.348(3), C6−O4 1.346(3); N1-C3-N2 116.04(19); N1-C3-Rh1-Cl1 85.4.

phile to the oxygen atom O4 restores the normal occurrence of alternating single and double bonds along the same chain. Besides, it is noteworthy that the NCN structural parameters are only slightly affected by the introduction of an electrophile onto the backbone oxygen, as illustrated by the small non significant changes of the C3−N1 and C3−N2 bond lengths and of the N1-C3-N2 bond angle. The N1−C4 ($\mathbf{4_{Me}}$: 1.448(3), $\mathbf{5_{Me}}^{\mathbf{Me}}$: 1.437(3) Å) and N2−C6 ($\mathbf{4_{Me}}$: 1.437(3), $\mathbf{5_{Me}}^{\mathbf{Me}}$: 1.405(3) Å) are indeed consistent with single bonds, reflecting a lack of conjugation between the malonate and the diaminocarbene moieties. Such a behavior was already observed in the case of the substitution of quinoidal-type zwitterions.[24] The influence of the addition of the electrophile onto the malonate backbone can be quantified by calculating the buried volume using the web application "SambVca" developed by Cavallo and co-workers.[10b] The anionic NHC in complex $\mathbf{4_{Me}}$ exhibits a buried volume of 39.6%, whereas the $\%V_{bur}$ of the methyl-substituted NHC in compound $\mathbf{5_{Me}}^{\mathbf{Me}}$ is found to be 38.8%,[25] which confirms that the O-substitution has only little or no influence on the steric properties of the *malo*-NHC ligand.[26] In the ^{1}H NMR spectra of $\mathbf{4_R}$, two sets of two singlets are observed for the four aromatic C*H* protons and for the four *ortho*-methyl groups of the mesityl rings, indicating a blocked or reduced ligand rotation around the Rh-carbene bond (on the NMR time scale). Such a symmetry break in the NMR spectra is found in all complexes $\mathbf{5_R}^{\mathbf{E}}$ and $\mathbf{4_R}$. In addition, the two sides of the NHC are well differentiated in complexes $\mathbf{5_{Me}}^{\mathbf{Me}}$ and $\mathbf{5_{Me}}^{\mathbf{Tf}}$ by adjunction of the electrophile leading to a total loss of symmetry. Just like the cationic rhodium–COD complex $\mathbf{3_{Me}}^{\mathbf{H}}$, the complex $\mathbf{5_{Me}}^{\mathbf{H}}$ experiences a fast exchange of the hydrogen atom between the two oxygens of the malonate group, a fluxional process which could not be frozen, even at a temperature as low as −80 °C in CD_2Cl_2.

In order to gain further insight into the electronic properties of the newly formed NHCs and to compare them with those of known derivatives, the IR spectra of the complexes $\mathbf{4_R}$ and $\mathbf{5_R}^{\mathbf{E}}$ were recorded in CH_2Cl_2 and the results are summarized in Table 1. In the same Table, we also report the values measured on two additional complexes incorporating ligands which are of specific interest for comparative purposes. One is 1,3-dimesityltetrahydropyrimidin-2-ylidene (**6**), representing the closest comparable case of saturated six-membered NHC ligand (IR ν_{CO} values recorded on the complex [RhCl(**6**)$(CO)_2$] in CH_2Cl_2). The other, referred to as **7**, is formally derived from the anionic NHC $\mathbf{1_{Me}}^-$ by a C-methylation (IR ν_{CO} values recorded on the complex [RhCl(**7**)$(CO)_2$] in CH_2Cl_2).[27]

Table 1. Comparison of ν_{CO} values for $RhCl(CO)_2${NHC} complexes.



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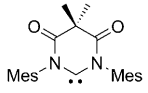


7

Entry	NHC ligand	ν_{CO} [cm^{-1}][a]	ν_{CO}^{av} [cm^{-1}]
1	**7**[b]	2086, 2005	2045
2	$\mathbf{1_{Me}}^{\mathbf{Tf}}$ in $\mathbf{5_{Me}}^{\mathbf{Tf}}$	2085, 2003	2044
3	$\mathbf{1_{Me}}^{\mathbf{H}}$ in $\mathbf{5_{Me}}^{\mathbf{H}}$	2082, 2000	2041
4	$\mathbf{1_{Me}}^{\mathbf{Me}}$ in $\mathbf{5_{Me}}^{\mathbf{Me}}$	2081, 1998	2039
5	**6**[c]	2076, 1988	2032
6	$\mathbf{1_{Me}}^-$ in $\mathbf{4_{Me}}$	2069, 1987	2028
7	$\mathbf{1_{tBu}}^-$ in $\mathbf{4_{tBu}}$	2068, 1986	2027

[a] IR spectra recorded in CH_2Cl_2. [b] **7**: 1,3-Dimesityl-5,5-dimethyl-4,6-dioxotetrahydropyrimidin-2-ylidene. [c] **6**: 1, 3-Dimesityltetrahydropyrimidin-2-ylidene.

A comparison of these spectroscopic data leads to the following conclusions:

The anionic NHC ligands $\mathbf{1_R}^-$ (Table 1, entries 6–7) are more electron-rich than all known six-membered NHCs reported so far (ν_{CO}^{av} ranging from 2029 to 2038 cm^{-1}).[28]

The nature of the apical R group attached to the central carbon atom of the malonate group has little or no influence on the electron-richness of the ligand (Table 1, entries 6–7).

The attachment of an electrophile to one oxygen of the malonate backbone of the NHC leads to a significant reduction of its electron-donor properties (entries 2–4), following the order Me < H < Tf, where the highest electron-withdrawing group, Tf, leads to the poorest electron-donor ligand within the present series of O-functionalized derivatives. Noticeably, all the neutral ligands $\mathbf{1_{Me}}^{\mathbf{E}}$ resulting from the addition of an electrophile to $\mathbf{1_{Me}}^{-}$ appear to be poorer electron donors than the previously reported six-membered ring NHCs.

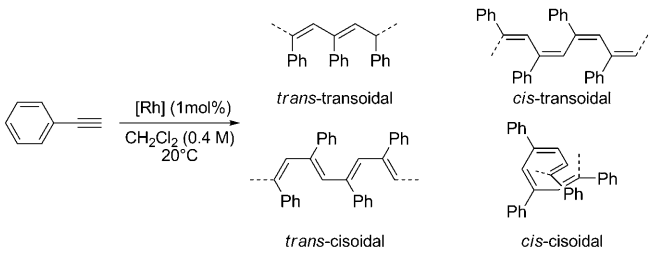
The diamidocarbene **7**, formally derived from the anionic NHC $\mathbf{1_{Me}}^{-}$ by a C-methylation, appears as the poorest electron donor of the whole series, a point already discussed in previous communications.[27] Thus, it clearly appears that the electronic properties of this class of ligands can be finely tuned over a range of ν_{CO} values covering about 18 cm^{-1}.

In line with these observations, we were prompted to examine the consequences of such a modulation on the catalytic performances of a series of comparable complexes incorporating these ligands. These included both the zwitterionic complex $\mathbf{2_R}$ and the cationic adducts $\mathbf{3_{Me}}^{\mathbf{E}}$ generated by addition of an electrophile associated with a non-coordinating anion. The catalytic assays were done on the two following reactions.

Polymerization of phenylacetylene: The rhodium-catalyzed polymerization of phenylacetylene was chosen as a first reference reaction for a comparative evaluation of the catalytic activity of our new series of NHC ligands, firstly because the reaction was known to be catalyzed by the complex [Rh(cod)(**6**)]$^+$ incorporating the closest comparable NHC, **6**,[21b] and, secondly, because such a reaction represents a simple elementary case where only one substrate, phenylacetylene, and a molecular catalyst are involved.

In these assays, our objective was not to optimize the catalytic system, but to work at the mildest possible conditions in such a way to detect differences in the catalytic behavior of our complexes. So, all catalytic runs were carried out in a bath thermostated at 20 °C, on 1 mmol of phenylacetylene to which 1 mol % of the rhodium catalyst was added (Scheme 4).

The range of pre-catalysts considered in the present screening included the zwitterionic species **2**, the cationic complexes $\mathbf{3_{Me}}^{\mathbf{E}}$, and complex [Rh(cod)(**7**)](OTf) (**8**) generated in situ upon reaction of [RhCl(cod)(**7**)], with AgOTf.



Scheme 4. Rhodium-catalyzed polymerization of phenylacetylene leading to configurationally different poly(phenylacetylene) (PPA).

Figure 2 displays the kinetic curves obtained for the above complexes under these standardized reaction conditions, whereas the characteristics of the resulting poly(phenylacetylene) (PPA) are summarized in Table 2.

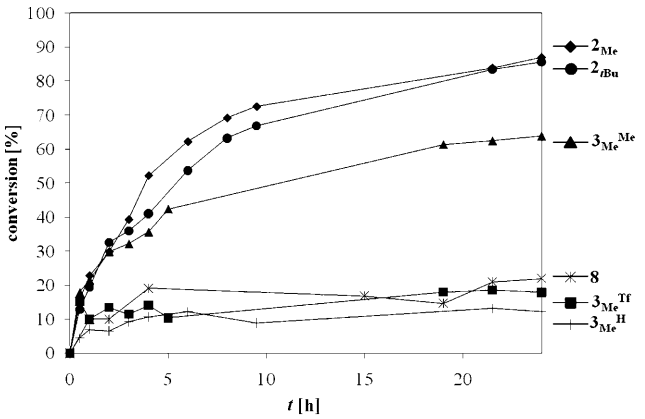


Figure 2. Kinetic profiles for the conversion of phenylacetylene as a function of time using complexes $\mathbf{2_R}$, $\mathbf{3_{Me}}^{\mathbf{E}}$ and **8**.

Table 2. Characteristics of the poly(phenylacetylene) (PPA).

Entry	Catalyst	% *cis*[a]	M_n [g mol^{-1}][b]	PDI (M_w/M_n)[b]
1	$\mathbf{2_{Me}}$	78	28500	2.18
2	$\mathbf{2_{tBu}}$	81	28600	2.33
3	$\mathbf{3_{Me}}^{\mathbf{Me}}$	39	23600	2.57
4	$\mathbf{3_{Me}}^{\mathbf{Tf}}$	40	11700	4.65
5	$\mathbf{3_{Me}}^{\mathbf{H}}$	40	12800	6.11
6	**8**	39	17900	3.39

[a] % *cis* corresponds to the percentage of the major *cis-transoid* structure of PPA and was measured by ^{1}H NMR using the formula %-*cis* = $100 \times (6 \times A_{5.84\ ppm}/A_{total})$.[21b] [b] Measured by SEC.

Very characteristically, it appears that modifications of the malonate backbone leading to a modification of the ligand's donicity are dramatically influencing the catalyst's activity. The most significant aspects and trends are the following:

The most active catalysts of the series are those bearing the two anionic NHC ligands (complexes $\mathbf{2_{Me}}$ and $\mathbf{2_{tBu}}$). Given that they display about the same activity and that the characteristics of the resulting PPA are the same, we can conclude that, at least in the present case, the nature of the substituent on the position 5 of the heterocyclic carbene has no significant influence on the catalytic performances.

Although the activity of the O-methylated complex $\mathbf{3_{Me}}^{\mathbf{Me}}$ is not negligible, only 64 % of conversion was obtained after 24 h of reaction, whereas the selectivity in the *cis*-transoidal form is only half the value recorded with catalysts $\mathbf{2_{Me}}$ and $\mathbf{2_{tBu}}$, indicating that an electron-rich metal center is required for the achievement and control of the reaction. Effectively, all other complexes exhibiting lower electron donor properties gave very low conversions (10–20 % after 24 h) with very high polydispersities.

Clearly, the above tendency illustrates the requirement of a strong electron-donor ligand to achieve the polymerization of phenylacetylene. It is worth noting, however, that complex $\mathbf{3_{Me}}^{\mathbf{H}}$ bearing the protonated ligand $\mathbf{1_{Me}}^{\mathbf{H}}$ was shown to be the least efficient catalyst, despite its relative electronic richness. Here, our interpretation of such a discrepancy is that the acidity of the ligand is inappropriate for the polymerization of phenylacetylene, a reaction which is known to be quenched by addition of acids.[21b]

Hydroboration of styrene: The rhodium-catalyzed hydroboration[29] of styrene with pinacol or catecholborane has been extensively studied with phosphine ligands,[30] but, to our knowledge, only once with NHC ligands.[16a]

The hydroboration was selected as a second test reaction with the aim to examine the scope and limitations of the present ligand types. Indeed, given that the borane reagent contains both a hydride and a Lewis acidic site, the possibility of an interaction with the potentially reactive backbone moiety of our NHC ligands could not be excluded. In order to maximize such a potential interaction, catecholborane was chosen as the hydride source since it is less sterically hindered than pinacolborane and more reactive toward nucleophiles.[31] In a typical standard catalytic procedure, the catalytic runs were conducted at 0 °C, using styrene as a substrate with a catalyst loading of 1 mol %. The crude mixture was analyzed by ^{1}H NMR spectroscopy after 90 min to determine the products yields and distribution (Table 3). The conversion curves were also monitored by gas chromatography in such a way to have a closer view to the reaction kinetics. A blank test (Table 3, entry 7) was carried out to verify that no hydroboration occurs in the absence of catalyst under the present reaction conditions.

The kinetic plots are particularly instructive, since, apart from the exceptions discussed below, the respective activities of the catalysts appear to be correlated with the electron-donor properties of the ligand $\mathbf{1_{Me}}^{\mathbf{E}}$ (Figure 3). Again, here, the zwitterionic catalysts $\mathbf{2_R}$ are, by far, the most efficient ones. In an apparent trend following the order $\mathbf{2_{Me}}$, $\mathbf{3_{Me}}^{\mathbf{Me}}$, $\mathbf{3_{Me}}^{\mathbf{Tf}}$, **8**, a progressive reduction of the donor properties of the carbene leads to a concomitant decrease of the observed catalytic activity. It is also noteworthy that in all cases examined here, the ratio between the linear anti-Markovnikov- and branched Markovnikov-type products is highly dependent on the activity of the catalyst, with the percentage of branched product being maximized for the more efficient complexes $\mathbf{2_R}$ (entries 1–2). However, as noted above, a close look at the kinetic plots reveals several deviations from the general trend, indicative of a more complex behavior. Firstly, the acidified complex $\mathbf{3_{Me}}^{\mathbf{H}}$ is not as active as one would have expected in account of the electron-donicity of its supporting ligand $\mathbf{1_{Me}}^{\mathbf{H}}$, since it experiences a rapid de-activation. Secondly, although catalysts $\mathbf{2_{Me}}$ and $\mathbf{2_{tBu}}$ exhibit a high activity in the early stages of the reaction, the activity of $\mathbf{2_{tBu}}$ is seen to be drastically reduced after 3 min of reaction. The latter observation suggests that the malonate backbone may exhibit a non-innocent behavior during the catalysis. In order to detect the occurrence of an adventitious side reaction between the NHC ligand backbone and the catecholborane reagent (HBCat), we were led to carry out a stoichiometric reaction between catecholborane and complexes $\mathbf{4_R}$ and $\mathbf{5_{Me}}^{\mathbf{E}}$ which both possess a saturated metal center being unlikely to react with such a substrate under the present reaction conditions. An additional advantage of using carbonyl derivatives in such an experiment was to allow a facile detection of any change in the NHC ligand structure by using IR ν_{CO} as a probe.

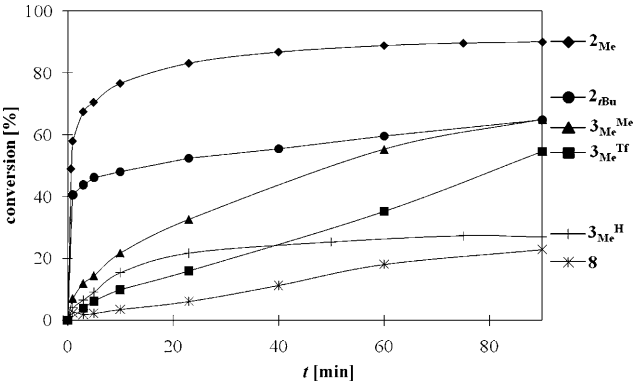
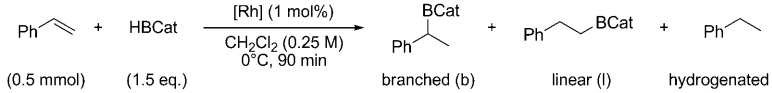


Figure 3. Kinetic curves of the catalytic hydroboration of styrene using complexes $\mathbf{2_R}$, $\mathbf{3_{Me}}^{\mathbf{E}}$ and **8** as pre-catalysts.

Table 3. Hydroboration of styrene with catecholborane (HBCat), using $\mathbf{2_R}$, $\mathbf{3_{Me}}^{\mathbf{E}}$ and **8** as catalyst precursors.

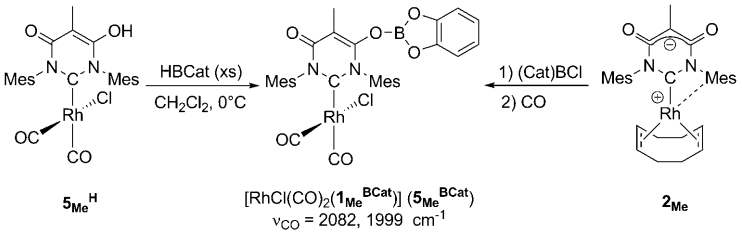


Entry	[Rh] catalyst	Conversion [%][a]	*b*/*lh* Yield [%][a]
1	$\mathbf{2_{Me}}$	91	44/37/10
2	$\mathbf{2_{tBu}}$	63	31/24/6
3	$\mathbf{3_{Me}}^{\mathbf{Me}}$	50	13/22/13
4	$\mathbf{3_{Me}}^{\mathbf{Tf}}$	48	3/39/6
5	$\mathbf{3_{Me}}^{\mathbf{H}}$	25	0/22/1
6	**8**	31	0/20/10
7	none	0	–

[a] Measured by ^{1}H NMR, using mesitylene as internal standard.

The addition of an excess of HBCat (5 equiv) to $\mathbf{5_{Me}}^{\mathbf{H}}$ was accompanied by the immediate appearance (within less than 5 min) of a broad signal at $\delta =$ 23.0 ppm in the ^{11}B NMR of the crude mixture, indicative of the formation of a new compound tentatively formulated as $[RhCl(CO)_2(\mathbf{1_{Me}}^{\mathbf{BCat}})]$ ($\mathbf{5_{Me}}^{\mathbf{BCat}}$) (Scheme 5, left equation), and resulting from a Brönstedt acid-base reaction between the acidic ligand $\mathbf{1_{Me}}^{\mathbf{H}}$ and the hy-

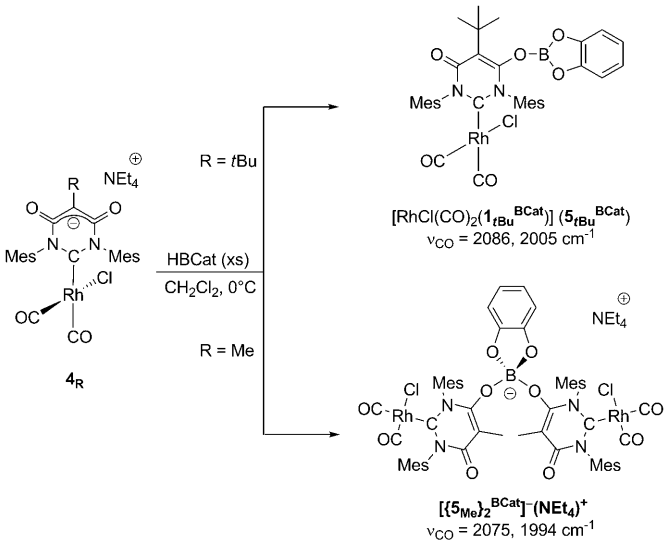
dride of catecholborane, followed by elimination of molecular hydrogen and concomitant formation of the borate ester. The formulation of the adduct $\mathbf{5_{Me}}^{\mathbf{BCat}}$ was confirmed by the direct reaction of $\mathbf{2_{Me}}$ with *B*-chlorocatecholborane and subsequent displacement of the COD ligand by CO (Scheme 5, right equation). Thus, the above experiment provides conclusive evidence that ligand $\mathbf{1_{Me}}^{\mathbf{BCat}}$ can be readily generated in situ from $\mathbf{3_{Me}}^{\mathbf{H}}$ under catalytic conditions. What we have here is an uncommon case where a reactive substrate is seen to interact with the ligand of the pre-catalyst, thereby modifying the nature of the active species.



Scheme 5. Parallel stoichiometric reactions between $\mathbf{5_{Me}}^{\mathbf{H}}$ and catecholborane and between $\mathbf{2_{Me}}$ and *B*-chlorocatecholborane.

The second critical point focusing our attention was the observation of a significant difference in activity between the two zwitterionic catalysts $\mathbf{2_{Me}}$ and $\mathbf{2_{tBu}}$ differing only in the nature of the apical group on the central carbon of the malonate group. We were thus led to check the respective stoichiometric reactivities of their chlorocarbonyl counterparts $\mathbf{4_{Me}}$ and $\mathbf{4_{tBu}}$ toward catecholborane, which proved to be different, as shown in Scheme 6.

Whereas the anionic complex $\mathbf{4_{tBu}}$ leads to adduct $\mathbf{5_{tBu}}^{\mathbf{Bcat}}$ as the major product along with some decomposition (Scheme 6, upper reaction), the reaction of $\mathbf{4_{Me}}$ with catecholborane is very clean and gives the anionic bimetallic adduct $[\{\mathbf{5_{Me}}\}_2^{\mathbf{BCat}}]^-$, which most probably results from an intermolecular nucleophilic attack of the remote anionic oxygen of a second molecular unit of $\mathbf{4_{Me}}$ at the trigonal boron center of the adduct $\mathbf{5_{Me}}^{\mathbf{BCat}}$. The inability of $\mathbf{4_{tBu}}$ to generate the analogous bimetallic borate-type adduct can be reasonably ascribed to the steric bulk of the *tert*-butyl group preventing further intermolecular nucleophilic attack. This hypothesis was corroborated by a stoichiometric reaction between isolated complexes $\mathbf{4_R}$ and $\mathbf{5_R}^{\mathbf{BCat}}$, in which a full conversion to $\mathbf{[\{5_{Me}\}_2^{BCat}]^-(NEt_4)^+}$ was observed with the methyl derivatives, wheras $\mathbf{4_{tBu}}$ and $\mathbf{5_{tBu}}^{\mathbf{BCat}}$ did not react together. By comparing the IR ν_{CO} spectra of the two types of adducts observed here ($\mathbf{5_{tBu}}^{\mathbf{Bcat}}$: $\nu_{CO}{}^{av} = 2045\ cm^{-1}$, $[\{\mathbf{5_{Me}}\}_2^{\mathbf{BCat}}]^-$: $\nu_{CO}{}^{av} = 2034\ cm^{-1}$), it is clear that the lower electron-withdrawing properties of the anionic borate-type adduct will lead to a carbene with enhanced electron-donor properties. The formation of two different types of boron substituted adducts, each modifying differently the nucleophilicity of the carbene, can therefore satisfactorily explain the observed differences between the behavior of the pre-catalysts $\mathbf{2_{Me}}$ and $\mathbf{2_{tBu}}$ under catalytic conditions.



Scheme 6. Divergent reactivities of $\mathbf{4_{Me}}$ and $\mathbf{4_{tBu}}$ toward catecholborane.

Conclusion

Whereas our previous report[20] drew attention on the remarkable synthetic accessibility of a family of anionic N-heterocyclic carbenes incorporating a malonate group as backbone functionality, the present account not only demonstrates the ability of these ligands to generate catalytically active zwitterionic complexes, but also reveals new facets of their reactivity. The most beneficial one in view of a rapid catalyst screening rests on the possibility to achieve a "real-time" tuning of the donor properties of their carbene center in a very simple way, and even after their coordination to a transition metal. Indeed, given that the nucleophilic oxygen atom of the malonate group emerges in the outer coordination sphere of the complex, its interaction with a selected incoming electrophilic reagent will modify the electron distribution through the heterocycle, thereby affecting the donor properties of the carbene center in the inner coordination sphere. From a palette of electrophilic reagents exhibiting different electron-withdrawing abilities, we were thus able to generate a series of "modulated" cationic Rh^I complexes whose catalytic activities were compared on the basis of two test reactions. For the polymerization of phenylacetylene, the experimental data revealed an apparent correlation between the activity of the complexes and the donicity of the carbene center, thus placing the unmodified zwitterionic

complex as the most efficient pre-catalyst. The specific case of the hydroboration of styrene was useful to determine the scope of the present conceptual approach and its possible limitations when it comes to highly reactive substrates. Indeed, stoichiometric reactions are seen to take place between catecholborane and the malonate group, leading to the rapid formation of boron-substituted derivatives which interfere in the catalytic system by modifying the nature of the initial active species. Finally, whereas the two specific examples reported here provide convincing evidence for an apparent correlation between the nucleophilicity of the carbene and its catalytic performances, this may not be systematically the case, and it seems obvious that the present approach giving a simple access to weakly nucleophilic N-heterocyclic carbenes, will find its full justification in the future as one will find specific transition metal-catalyzed reactions requiring weakly nucleophilic ancillary ligands. By the way, one of them was just discovered in a very recent report by Fürstner, quoted above.[19] Furthermore, weakly nucleophilic carbenes related to those accessed here were recently shown by Bertrand[32] and Bielawski,[27b–c] to be of high intrinsic interest in their own right for metal free activation of industrially important small molecules.

Experimental Section

General methods: 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 before use. THF and diethyl ether were freshly distilled from sodium/benzophenone, toluene from molten sodium, prior to use. Pentane and dichloromethane were dried over CaH_2 and subsequently distilled. NMR spectra were recorded on a Bruker ARX250, AV300 or AV400 spectrometer, in the solvents indicated; chemical shifts are reported in ppm (δ) compared to TMS using the residual peak of deuterated solvent as internal standard; coupling constants (J) in Hz. Infrared spectra were obtained 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 the Paul Sabatier University. Melting points were obtained with a Stuart Scientific Melting Point apparatus SMP1 and were not corrected. Complexes $\mathbf{2_{Me}}$ and $\mathbf{2_{tBu}}$ were synthesized according to our previously reported procedure.[20]

(η^4-1,5-Cyclooctadiene)(1,3-dimesityl-4-oxo-4*H*-5-methyl-6-methoxypyrimidin-2-ylidene)rhodium(I) trifluoromethanesulfonate ($\mathbf{3_{Me}^{Me}}$): To a solution of $\mathbf{2_{Me}}$ (49 mg, 85.6 μmol) in CH_2Cl_2 (5 mL) was added methyl trifluoromethanesulfonate (10 μL, 90 μmol, 1.05 equiv) at room temperature. After 3 h of reaction, the volatiles were removed by evaporation under vacuum. The solid residue was washed with pentane (2 mL) and dried in vacuo leading to an orange powder (62 mg, quant.). M.p. 106–108 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.13 (s, 2H, CH_{Mes}), 7.12 (s, 2H, CH_{Mes}), 4.26–4.24 (m, 2H, CH_{COD}), 3.80 (s, 3H, OCH_3), 3.10–3.07 (m, 2H, CH_{COD}), 2.42 (s, 3H, CH_{3para}), 2.41 (s, 3H, CH_{3para}), 2.26 (s, 6H, CH_{3ortho}), 2.17 (s, 6H, CH_{3ortho}), 2.08 (s, 3H, C$H_{3apical}$), 1.79–1.65 (m, 2H, CH_{2COD}), 1.65–1.54 (m, 2H, CH_{2COD}), 1.47–1.41 ppm (m, 4H, CH_{2COD}); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.3, 158.5 (*C*=O, *C*-OMe), 140.4, 140.4, 140.1, 140.1, 136.0, 129.8 (C_{Mes}), 129.8, 129.7 (*C*H$_{Mes}$), 105.6 (C_{apical}), 100.4 (br, *C*H$_{COD}$), 69.3 (br, *C*H$_{COD}$), 69.1 (br, *C*H$_{COD}$), 62.5 (O*C*H$_3$), 32.1 (*C*H$_{2COD}$), 26.7 (*C*H$_{2\ COD}$), 21.2, 21.1 (*C*H$_{3para}$), 18.9, 18.8 (*C*H$_{3ortho}$), 9.4 ppm (*C*H$_{3apical}$); IR (ATR): $\tilde{\nu}$ = 2917, 1662, 1613, 1476, 1450, 1384, 1359, 1302, 1272, 1064, 1034, 994, 959, 866, 853, 759 cm^{-1}; MS (ESI): *m*/*z* (%): 587 (100) [*M*−TfO]$^+$; elemental analysis calcd (%) for $C_{33}H_{40}F_3N_2O_5RhS{\cdot}0.25\,CH_2Cl_2$: C 52.69, H 5.39, N 3.70; found: C 52.65, H 5.57, N 3.55.

(η^4-1,5-Cyclooctadiene)(1,3-dimesityl-4-oxo-4*H*-5-methyl-6-(trifluoromethanesulfonato)pyrimidin-2-ylidene)rhodium(I) trifluoromethanesulfonate ($\mathbf{3_{Me}^{Tf}}$): To a solution of $\mathbf{2_{Me}}$ (58.7 mg, 0.102 mmol) in CH_2Cl_2 (5 mL) was added trifluoromethanesulfonic anhydride (18 μL, 0.11 mmol, 1.05 equiv) at 0 °C. After 15 min of reaction, the volatiles were removed by evaporation under vacuum. The solid residue was washed with pentane (2 mL) and dried in vacuo leading to an orange powder (78 mg, 90 %.). M.p. 98–100 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.17 (s, 2H, CH_{Mes}), 7.16 (s, 2H, CH_{Mes}), 4.62–4.58 (m, 2H, CH_{COD}), 3.17–3.14 (m, 2H, CH_{COD}), 2.43 (s, 3H, CH_{3para}), 2.42 (s, 3H, CH_{3para}), 2.27 (s, 6H, CH_{3ortho}), 2.22 (s, 3H, C$H_{3apical}$), 2.20 (s, 6H, CH_{3ortho}), 1.80–1.74 (m, 2H, CH_{2COD}), 1.65–1.60 (m, 2H, CH_{2COD}), 1.48–1.43 ppm (m, 4H, CH_{2COD}); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 212.0 (br, N_2C), 159.5, 146.8 (*C*=O, *C*-OTf), 141.6, 140.5, 136.8, 135.8 (C_{Mes}), 130.2, 129.9 (*C*H$_{Mes}$), 119.5 (q, $^1J_{CF}$ = 319 Hz, *C*F$_3$), 117.8 (q, $^1J_{CF}$ = 322 Hz, *C*F$_3$), 111.9 (C_{apical}), 101.2 (br, *C*H$_{COD}$), 69.1 (br, *C*H$_{COD}$), 32.0 (*C*H$_{2COD}$), 26.7 (*C*H$_{2COD}$), 21.1, 21.0 (*C*H$_{3para}$), 18.8, 18.7 (*C*H$_{3ortho}$), 10.7 ppm (*C*H$_{3apical}$); IR (ATR): $\tilde{\nu}$ = 2923, 2881, 1701, 1678, 1650, 1611, 1426, 1405, 1331, 1267, 1219, 1165, 1127, 1027, 966, 816, 766, 677 cm^{-1}; MS (ESI): *m*/*z* (%): 705 (46) [*M*−TfO]$^+$, 595 (37) [*M*−OTf−COD]$^+$, 573 (100) [*M*−2OTf]$^+$.

(η^4-1,5-Cyclooctadiene)(1,3-dimesityl-4-oxo-4*H*-5-methyl-6-hydroxypyrimidin-2-ylidene)rhodium(I) trifluoromethanesulfonate ($\mathbf{3_{Me}^{H}}$): To a solution of $\mathbf{2_{Me}}$ (34.6 mg, 60.4 μmol) in CH_2Cl_2 (2 mL) was added trifluoromethanesulfonic acid (5.5 μL, 62 μmol, 1.05 equiv) at 0 °C. After 20 min, the solution was concentrated to about 1 mL and the complex was precipitated by adding pentane (5 mL). The overlaying solution was evacuated and the solid was dried in vacuo to give an orange powder (42 mg, 96 %). M.p. 103–106 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.36 (br, 1H, O*H*), 7.07 (s, 4H, CH_{Mes}), 3.53 (br, 2H, CH_{COD}), 3.37 (br, 2H, CH_{COD}), 2.34 (s, 6H, CH_{3para}), 2.31 (s, 12H, CH_{3para}), 2.07 (s, 3H, C$H_{3apical}$), 2.07–1.98 (m, 4H, CH_{2COD}), 1.72–1.68 ppm (m, 4H, CH_{2COD}); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.6 (d, $^1J_{RhC}$ = 58 Hz, N_2C), 158.4 (*C*=O, *C*-OH), 142.9, 135.9 (C_{Mes}), 130.3 (*C*H$_{Mes}$), 120.3 (C_{Mes}), 105.8 (d, $^1J_{RhC}$ = 8 Hz, *C*H$_{COD}$), 99.0 (C_{apical}), 75.2 (d, $^1J_{RhC}$ = 19 Hz, *C*H$_{COD}$), 32.7 (*C*H$_{2COD}$), 26.7 (*C*H$_{2\ COD}$), 21.2 (*C*H$_{3\,para}$), 18.4 (*C*H$_{3ortho}$), 8.7 ppm (*C*H$_{3apical}$); IR (ATR): $\tilde{\nu}$ = 3363, 2921, 2884, 1684, 1653, 1611, 1449, 1380, 1281, 1223, 1163, 1068, 1025, 966, 854, 762 cm^{-1}; MS (ESI): *m*/*z* (%): 573 (100) [*M*−TfO]$^+$, 363 (70) [*M*−Rh(COD)OTf]$^+$; HR-MS (ESI): *m*/*z*: calcd for $C_{31}H_{38}N_2O_2Rh$: 573.1988, found: 573.1992.

Tetraethylammonium chloro(dicarbonyl)(1,3-dimesityl-5-methyl-6(4)-oxo-6*H*(4*H*)-pyrimidin-2-ylidene-4(6)-olate)rhodium(I) ($\mathbf{4_{Me}}$): Complex $\mathbf{2_{Me}}$ (315 mg, 0.55 mmol) and $NEt_4Cl{\cdot}xH_2O$ (200 mg, x ~2, 1.21 mmol, 2.2 equiv) were placed in a Schlenk tube and THF was syringed into (15 mL). CO gas was bubbled into the solution for 5 min during which time solution became light orange. After 1 h, volatiles were evacuated in vacuo and the residue was purified by flash chromatography (Al_2O_3 type III, CH_2Cl_2/MeOH 95:5, R_f = 0.38) to furnish the title compound as a yellow compound (338 mg, 90 %). Recrystallization from CH_2Cl_2/Et_2O gave yellow crystals suitable for an X-ray diffraction experiment; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.87 (s, 2H, CH_{Mes}), 6.83 (s, 2H, CH_{Mes}), 3.03 (q, J = 7.3 Hz, 8H, C$H_{2ammonium}$), 2.27 (s, 6H, CH_{3ortho}), 2.23 (s, 6H, CH_{3ortho}), 2.15 (s, 6H, CH_{3para}), 1.87 (s, 3H, C$H_{3apical}$), 1.09 ppm (t, J = 7.3 Hz, 12H, C$H_{3ammonium}$); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 198.1 (d, J_{RhC} = 41.9 Hz, N_2C), 186.2 (d, J_{RhC} = 53.2 Hz, Rh-*C*O), 183.4 (d, J_{RhC} = 77.8 Hz, Rh-*C*O), 161.8 (*C*4=O, *C*6-O), 138.4, 137.3, 136.9, 134.9 (C_{Mes}), 128.6, 128.1 (*C*H$_{Mes}$), 89.5 (C_{apical}), 52.1 (*C*H$_{2ammonium}$), 21.1, 19.6, 18.3 (*C*H$_{3Mes}$), 9.3 (*C*H$_{3apical}$), 7.4 ppm (*C*H$_{3ammonium}$); IR (ATR): $\tilde{\nu}$ = 2986, 2920, 2859, 2059 (CO$_{sym}$), 1974 (CO$_{asym}$), 1663, 1609, 1480, 1458, 1390, 1355, 1308, 1299, 1260, 1182, 1170, 1065, 1031, 1002, 919, 849, 783, 766, 728 cm^{-1}; IR (CH_2Cl_2): $\tilde{\nu}$ = 2069 (CO$_{sym}$), 1987 cm^{-1} (CO$_{asym}$); MS (ESI, negative mode): *m*/*z* (%): 555 (69) [*M*−H]$^-$, 527 (100) [*M*−H−CO]$^-$, 255 (27); elemental analysis calcd (%) for $C_{33}H_{45}ClN_3O_4Rh$: C 57.77, H 6.61, N 6.12; found: C 57.52, H 6.93, N 5.97.

Tetraethylammonium chloro(dicarbonyl)(1,3-dimesityl-5-*tert*-butyl-6(4)-oxo-6*H*(4*H*)-pyrimidin-2-ylidene-4(6)-olate)rhodium(I) ($\mathbf{4_{tBu}}$): Complex $\mathbf{2_{tBu}}$ (62 mg, 0.10 mmol) and $NEt_4Cl{\cdot}xH_2O$ (40 mg, x ~2, 0.24 mmol,

2.4 equiv) were placed in a Schlenk tube. THF was syringed into (5 mL) and CO gas was bubbled into the solution for 5 min during which time solution color changed from orange to light yellow. After 1 hour, volatiles were evacuated in vacuo and the residue was purified by flash chromatography (Al_2O_3 type III, CH_2Cl_2/MeOH 95:5) to yield an orange powder (66 mg, 91%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.86 (s, 2H, CH_{Mes}), 6.83 (s, 2H, CH_{Mes}), 2.97 (q, J=7.1 Hz, 8H, C$H_{2\,ammonium}$), 2.27 (s, 6H, CH_{3Mes}), 2.26 (s, 6H, CH_{3Mes}), 2.17 (s, 6H, CH_{3Mes}), 1.37 (s, 9H, CH_{3tBu}), 1.08 ppm (t, J=7.1 Hz, 12H, C$H_{3\,ammonium}$); ^{13}C NMR (63 MHz, $CDCl_3$): δ=196.7 (d, J_{RhC}=41.5 Hz, N$_2$*C*), 186.4 (d, J_{RhC}=53.0 Hz, Rh-*C*O), 183.5 (d, J_{RhC}=78.2 Hz, Rh-*C*O), 160.9 (*C*4=O, *C*6-O), 139.3, 137.5, 136.6, 135.2 (C_{Mes}), 128.5, 128.0 (*C*H$_{Mes}$), 99.5 (C_{apical}), 51.9 (*C*H$_{2\,ammonium}$), 33.8 (*C*(CH$_3$)$_3$), 30.5 (C(*C*H$_3$)$_3$), 21.2, 19.6, 18.4 (*C*H$_{3Mes}$), 7.4 ppm (*C*H$_{3\,ammonium}$); IR (ATR): $\tilde{\nu}$ = 2975, 2956, 2921, 2857, 2058, 1969, 1654, 1591, 1482, 1451, 1370, 1333, 1254, 1171, 1023, 999, 887, 856, 778, 754 cm^{-1}; IR (CH_2Cl_2): $\tilde{\nu}$ = 2068 (CO_{sym}), 1986 cm^{-1} (CO_{asym}); MS (ESI): *m*/*z* (%): 597 (77) [*M*−NEt$_4$−2H]$^+$, 569 (100) [*M*−NEt$_4$−H−CO]$^+$; elemental analysis calcd (%) for $C_{36}H_{53}ClN_3O_4Rh$: C 59.22, H 7.32, N 5.75; found: C 59.72, H 7.40, N 5.43.

Chloro(dicarbonyl)(1,3-dimesityl-4-oxo-4*H*-5-methyl-6-methoxypyrimidin-2-ylidene)rhodium(I) (5_{Me}^{Me}): Complex 2_{Me} (45.3 mg, 79.1 μmol) was dissolved in CH_2Cl_2 (5 mL) and methyl triflate (9 μL, 83 μmol, 1.05 equiv) was added at room temperature. After 3 h, an excess of dry NaCl was added and CO was bubbled into the solution for 10 min. The light yellow reaction mixture was filtered through a plug of celite and volatiles were removed in vacuo. The residue was washed with pentane (2×2 mL) and dried to give a pale yellow powder (41 mg, 91%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.99 (br, 4H, CH_{Mes}), 3.78 (s, 3H, OCH_3), 2.37 (s, 3H, CH_{3Mes}), 2.34 (s, 3H, CH_{3Mes}), 2.31 (s, 3H, CH_{3Mes}), 2.23 (s, 3H, CH_{3Mes}), 2.20 (s, 3H, CH_{3Mes}), 2.16 (s, 3H, C$H_{3\,apical}$), 2.14 ppm (s, 3H, CH_{3Mes}); ^{13}C NMR (75 MHz, $CDCl_3$): δ=208.8 (d, J_{RhC}=44.2 Hz, N$_2$*C*), 184.6 (d, J_{RhC}=54.6 Hz, Rh-*C*O), 182.6 (d, J_{RhC}=75.5 Hz, Rh-*C*O), 161.5, 158.7 (2C, *C*4=O, *C*6-OMe), 139.7, 139.2, 136.7, 136.3, 135.8, 135.6, 133.5, 133.2 (C_{Mes}), 130.0, 129.9, 129.0 (*C*H$_{Mes}$), 105.9 (C_{apical}), 62.3 (O-*C*H$_3$), 21.2, 19.8, 19.3, 18.5, 18.2 (*C*H$_{3Mes}$), 9.7 ppm (*C*H$_{3\,apical}$); IR (ATR): $\tilde{\nu}$ = 2923, 2856, 2076 (CO_{sym}), 1985 (CO_{asym}), 1674, 1640, 1610, 1455, 1429, 1380, 1355, 1277, 1230, 1070, 997, 920, 909, 856, 849, 772, 727 cm^{-1}; IR (CH_2Cl_2): $\tilde{\nu}$ = 2081 (CO_{sym}), 1998 cm^{-1} (CO_{asym}); MS (ESI): *m*/*z* (%): 548 (77) [*M*−CO]$^+$, 507 (100) [*M*−CO−Cl]$^+$; elemental analysis calcd (%) for $C_{26}H_{30}ClN_2O_4Rh$, 0.1CH_2Cl_2: C 53.92, H 5.24, N 4.82; found: C 53.78, H 5.61, N 4.90.

Chloro(dicarbonyl)(1,3-dimesityl-4-oxo-4*H*-5-methyl-6-(trifluoromethanesulfonato)pyrimidin-2-ylidene)rhodium(I) (5_{Me}^{Tf}): To a solution of 2_{Me} (40.0 mg, 69.8 μmol) in CH_2Cl_2 (5 mL) was added trifluoromethanesulfonyl anhydride (12 μL, 73.3 μmol, 1.05 equiv) at room temperature. After 30 min, a large excess of sodium chloride (>10 equiv) was added to the solution as a solid and CO gas was bubbled into the solution for 20 min. After 1 hour of reaction, the solution was filtered through celite to remove the remaining solids and evaporated. The residue was washed with pentane (2×2 mL) and dried in vacuo to furnish a yellow solid (42 mg, 87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.03 (s, 4H, CH_{Mes}), 7.02 (s, 4H, CH_{Mes}), 2.37 (s, 3H, CH_{3Mes}), 2.36 (s, 3H, CH_{3Mes}), 2.31 (s, 3H, C$H_{3\,apical}$), 2.30 (s, 3H, CH_{3Mes}), 2.24 (s, 3H, CH_{3Mes}), 2.23 (s, 3H, CH_{3Mes}), 2.15 ppm (s, 3H, CH_{3Mes}); ^{13}C NMR (75 MHz, $CDCl_3$): δ=213.1 (d, J_{RhC}=45.5 Hz, N$_2$*C*), 184.2 (d, J_{RhC}=55.2 Hz, Rh-*C*O), 182.4 (d, J_{RhC}=74.9 Hz, Rh-*C*O), 159.5, 146.8 (2C, *C*4=O, *C*6-OTf), 141.0, 139.8, 137.1, 135.7, 135.5, 134.6, 134.2 (C_{Mes}), 130.4, 130.2, 129.7, 129.3 (*C*H$_{Mes}$), 113.1 (C_{apical}), 21.1, 19.8, 19.1, 18.7, 18.2 (*C*H$_{3Mes}$), 1.0 ppm (*C*H$_{3\,apical}$); IR (ATR): $\tilde{\nu}$ = 2962, 2925, 2089 (CO_{sym}), 2001 (CO_{asym}), 1718, 1658, 1418, 1358, 1262, 1224, 1123, 1087, 1028, 852, 820, 764, 735, 680 cm^{-1}; IR (CH_2Cl_2): $\tilde{\nu}$ = 2085 (CO_{sym}), 2003 cm^{-1} (CO_{asym}); MS (ESI): *m*/*z* (%): 711 (34) [*M*−Cl+Na]$^+$, 683 (34), 653 [*M*−Cl]$^+$; elemental analysis calcd (%) for $C_{26}H_{25}ClF_3N_2O_6RhS$: C 45.33, H 3.66, N 4.07; found: C 45.76, H 4.16, N 3.80.

Chloro(dicarbonyl)(1,3-dimesityl-4(6)-hydroxy-5-methyl-6(4)-oxo-6*H*(4*H*)-pyrimidin-2-ylidene)rhodium(I) (5_{Me}^{H}): To a solution of 2_{Me} (62.3 mg, 0.109 mmol) in CH_2Cl_2 (4 mL), a solution of HCl (1 M in Et_2O, 120 μL, 0.120 mmol, 1.1 eq) was added and after 5 min, CO was bubbled into the solution for 10 min. After 1 h, all volatiles were evacuated under vacuum and the residue was washed with pentane (2×3 mL) to leave a yellow solid (56.2 mg, 93%). M.p. 210 °C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.95 (s, 2H, CH_{Mes}), 6.93 (s, 2H, CH_{Mes}), 5.25 (br, 1H, O*H*), 2.34 (s, 6H, CH_{3Mes}), 2.17 (s, 6H, CH_{3Mes}), 2.08 (s, 6H, CH_{3Mes}), 1.92 ppm (s, 3H, C$H_{3\,apical}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ=207.1 (d, J_{RhC}=39.9 Hz, N$_2$*C*), 184.6 (d, J_{RhC}=54.3 Hz, Rh-*C*O), 182.4 (d, J_{RhC}=75.7 Hz, Rh-*C*O), 159.0 (*C*4=O, *C*6-OH), 139.6, 136.6, 135.2, 133.8 (C_{Mes}), 129.9, 129.1 (*C*H$_{Mes}$), 97.1 (C_{apical}), 21.2, 19.2, 18.1 (*C*H$_{3Mes}$), 8.5 ppm (*C*H$_{3\,apical}$); IR (ATR): $\tilde{\nu}$ = 2922, 2073 (CO_{sym}), 1988 (CO_{asym}), 1686, 1610, 1437, 1376, 1309, 1276, 1206, 1165, 1061, 1033, 850, 771 cm^{-1}; IR (CH_2Cl_2): $\tilde{\nu}$ = 2082 (CO_{sym}), 2000 cm^{-1} (CO_{asym}); MS (ESI): *m*/*z* (%): 556 (100) [*M*]$^+$, 534 (98), 521 (20) [*M*−Cl]$^+$, 515 (65), 493 (54) [*M*−Cl−CO]$^+$; elemental analysis calcd (%) for $C_{25}H_{28}ClN_2O_4Rh$: C 53.73, H 5.05, N 5.01; found: C 52.95, H 4.68, N 5.03.

Complex 5_{Me}^{BCat}: Complex 2_{Me} (55.6 mg, 97 μmol) and *B*-chlorocatecholborane (16.5 mg, 0.106 mmol, 1.1 equiv) were weighed in a Schlenk tube. CH_2Cl_2 (5 mL) was added and after 10 min, CO gas was bubbled into the solution for 20 min. The solution color changed from orange to pale yellow. After 2 h, all volatiles were evacuated under vacuum and the residue was washed twice with pentane (3 mL) to give, after drying, a yellow powder (59 mg, 90%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ=6.99 (brs, 2H, CH_{Mes}), 6.97 (brs, 2H, CH_{Mes}), 6.79 (br, 2H, CH_{Cat}), 6.22 (br, 2H, CH_{Cat}), 2.35 (s, 6H, C$H_{3\,para}$), 2.17 (brs, 6H, C$H_{3\,ortho}$), 2.10 (brs, 6H, C$H_{3\,ortho}$), 1.91 ppm (s, 3H, C$H_{3\,apical}$); ^{13}C NMR (100 MHz, CD_2Cl_2): δ=206.8 (d, J_{RhC}=43.8 Hz, N$_2$*C*), 185.0 (d, J_{RhC}=54.1 Hz, Rh-*C*O), 182.5 (d, J_{RhC}=74.8 Hz, Rh-*C*O), 158.9 (*C*4=O, *C*6-OBCat), 140.3, 139.9, 136.9, 135.6, 135.4, 135.1, 134.2, (C_{Ar}, *C*H$_{Ar}$), 129.7, 129.2 (*C*H$_{Mes}$), 97.3 (C_{apical}), 20.9, 19.0, 18.3, 18.1, 18.0 (*C*H$_{3Mes}$), 8.3 ppm (*C*H$_{3\,apical}$); ^{11}B NMR (128.4 MHz, CD_2Cl_2): δ=23.06 ppm (br); IR (ATR): $\tilde{\nu}$ = 2958, 2923, 2857, 2075 (CO_{sym}), 1990 (CO_{asym}), 1689, 1609, 1466, 1377, 1335, 1309, 1274, 1204, 1165, 1031, 851, 771, 742 cm^{-1}; IR (CH_2Cl_2): $\tilde{\nu}$ = 2082 (CO_{sym}), 1999 cm^{-1} (CO_{asym}).

Complex [(5_{Me})$_2^{BCat}$](NEt$_4$): To a solution of complex 5_{Me}^{BCat} (7.1 mg, 10.5 μmol) in CH_2Cl_2 (1 mL) was added complex 4_{Me} (7.2 mg, 10.5 μmol, 1.0 equiv) at room temperature. After 10 min, an aliquot was analyzed by IR spectroscopy which indicated a full conversion ($\tilde{\nu}$ = 2075.0 (CO_{sym}), 1993.6 cm^{-1} (CO_{asym}). Evaporation of the solvent gave the title complex as an orange foam. ^{1}H NMR (300 MHz, CD_2Cl_2): δ=6.94 (s, 4H, CH_{Mes}), 6.91 (s, 4H, CH_{Mes}), 6.57 (s, 4H, CH_{Cat}), 3.07 (q, J=7.3 Hz, 8H, C$H_{2\,ammonium}$), 2.33 (s, 12H, C$H_{3\,para}$), 2.14 (s, 12H, C$H_{3\,ortho}$), 2.07 (s, 12H, C$H_{3\,ortho}$), 1.76 (s, 6H, C$H_{3\,apical}$), 1.20 ppm (t, J=7.3 Hz, 12H, C$H_{3\,ammonium}$); ^{13}C NMR (75 MHz, CD_2Cl_2): δ=203.1 (d, J_{RhC}=43.9 Hz, N$_2$*C*), 185.8 (d, J_{RhC}=53.9 Hz, Rh-*C*O), 183.0 (d, J_{RhC}=76.0 Hz, Rh-*C*O), 160.6 (*C*4=O, *C*6-OB), 138.4, 137.0, 134.4 (C_{Mes}), 129.0, 128.6 (*C*H$_{Mes}$), 118.0, 108.3 (*C*H$_{Cat}$), 95.2 (C_{apical}), 52.5 (*C*H$_{2\,ammonium}$), 20.9 (*C*H$_{3\,para}$), 19.1, 18.0 (*C*H$_{ortho}$), 8.6 (*C*H$_{3\,apical}$), 7.3 ppm (*C*H$_{3\,ammonium}$); ^{11}B NMR (96.2 MHz, CD_2Cl_2): 14.16 ppm (s); IR (ATR): $\tilde{\nu}$ = 2983, 2922, 2859, 2066 (CO_{sym}), 1983 (CO_{asym}), 1662, 1610, 1482, 1458, 1426, 1395, 1376, 1309, 1276, 1264, 1233, 1205, 1170, 1057, 1032, 1001, 851, 770, 735 cm^{-1}; IR (CH_2Cl_2): $\tilde{\nu}$ = 2075 (CO_{sym}), 1994 cm^{-1} (CO_{asym}).

Complex 5_{tBu}^{BCat}: Complex 2_{tBu} (65 mg, 0.106 mmol) and *B*-chlorocatecholborane (18 mg, 0.116 mmol, 1.1 equiv) were weighed and placed in a Schlenk tube and CH_2Cl_2 (6 mL) was added. The solution became almost immediately dark red. After 10 min, CO gas was bubbled into the solution for 20 min. The solution color changed to orange. The reaction was left running overnight. The solution was filtered through a plug of celite to remove a brown precipitate and the volatiles were evacuated under vacuum. The residue was washed twice with pentane (3 mL) to give, after drying, an orange-brown powder (55 mg, 72%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ=7.01 (brs, 4H, CH_{Mes}), 6.80–6.76 (br, 4H, CH_{Cat}), 2.39 (s, 6H, C$H_{3\,ortho}$), 2.35 (s, 6H, C$H_{3\,ortho}$), 2.15 (brs, 6H, C$H_{3\,para}$), 1.32 ppm (s, 9H, CH_3*t*$_{Bu}$); ^{13}C NMR (75 MHz, CD_2Cl_2): δ=232.6 (d, J_{RhC}=46.2 Hz, N$_2$*C*), 185.3 (d, J_{RhC}=51.1 Hz, Rh-*C*O), 182.2 (d, J_{RhC}=74.4 Hz, Rh-*C*O), 165.8 (*C*4=O, *C*6-OBCat), 140.1, 140.0, 136.0, 134.8 (C_{Ar}), 130.2, 129.5 (*C*H$_{Mes}$), 121.0 (*C*H$_{Cat}$), 115.3 (*C*H$_{Cat}$), 92.3 (C_{apical}), 40.4 (*C*(CH$_3$)$_3$), 28.7 (C(*C*H$_3$)$_3$), 20.8, 20.7, 18.7 ppm (*C*H$_{3Mes}$); ^{11}B NMR (96 MHz, CD_2Cl_2): δ= 23.6 ppm (br); IR (ATR): $\tilde{\nu}$ = 2966, 2922, 2079 (CO_{sym}), 1996

(CO_{asym}), 1752, 1728, 1666, 1606, 1511, 1468, 1410, 1374, 1297, 1274, 1252, 1186, 1143, 1123, 1094, 1029, 851, 744, 654 cm^{-1}; IR (CH_2Cl_2): $\tilde{\nu}$ = 2086 (CO_{sym}), 2005 cm^{-1} (CO_{asym}).

Stoichiometric reaction between 4_R, $5_{Me}{}^H$ and catecholborane: For the IR monitoring, complex 4_R or $5_{Me}{}^H$ (10–30 μmol) was solubilized in CH_2Cl_2 (1 mL) and the solution was cooled to 0°C. Catecholborane (5 equiv) was added and the IR spectra were recorded. For the NMR experiments, the reaction was carried out directly in a NMR tube using CD_2Cl_2 as the solvent.

General procedure for the hydroboration of styrene: The rhodium catalyst (0.005 mmol, 1 mol%) was weighed, placed in a 10 mL Schlenk tube and solubilized in CH_2Cl_2 (2 mL). Mesitylene (70 μL, 0.50 mmol, internal standard) and styrene (58 μL, 0.50 mmol) were then syringed into the Schlenk, and the solution was cooled to 0°C using an ice/water bath. Freshly distilled catecholborane (80 μL, 0.75 mmol, 1.5 eq) was added within 5 s and the conversion was monitored by GC. For the GC samples, an aliquot of the reaction mixture was diluted with CH_2Cl_2 and filtered through a small silica plug. For the determination of products distribution, the reaction was carried out in CD_2Cl_2 (on 0.25 mmol scale of styrene), and the yields of products were measured by ^1H NMR spectroscopy after 90 min.

General procedure for the polymerization of phenylacetylene: The rhodium catalyst (0.01 mmol, 1 mol%) was solubilized in CH_2Cl_2 (2.5 mL) and the solution was placed in a temperature-controlled bath at 20°C. Mesitylene (139 μL, 1.0 mmol, internal standard) and phenylacetylene (110 μL, 1.0 mmol) were then successively syringed into the reaction mixture. The conversion was measured by passing an aliquot of the solution through a plug of silica gel using pentane as eluant and monitoring the decrease of the peak of phenylacetylene in the GC chromatogram. % *cis* values were determined by ^1H NMR spectroscopy using CD_2Cl_2 as the deuterated solvent. The isolated polymer samples were dissolved in THF and the THF solution was filtered (pore size = 0.45 μm) before chromatographic analysis. Size-exclusion chromatography (SEC) of poly(phenylacetylene) was carried out in filtered THF (flow rate: 1 mL min^{-1}) on a 300 × 7.5 μm PLgel 5 μm mixed-D column (Polymer Laboratories), equipped with a multiangle light-scattering (miniDawn Tristar, Wyatt Technology Corporation) and a refractive index (R12000, Sopares) detectors. The column was calibrated against linear polystyrene standards (Polymer Laboratories).

X-ray diffraction studies: Crystals of 4_{Me} and $5_{Me}{}^{Me}$ suitable for X-ray diffraction were obtained through recrystallization from CH_2Cl_2/Et_2O (4_{Me}) or EtOAc/pentane ($5_{Me}{}^{Me}$) solutions. Data were collected on Oxford Diffraction Xclaibur (4_{Me}) or Bruker D8 APEX II ($5_{Me}{}^{Me}$) diffractometers. All calculations were performed on a PC-compatible computer using the-WinGX system.[33] The structures were solved by using the SIR92 program,[34] 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.[35] For $5_{Me}{}^{Me}$, after completing the initial structure solution, it was found that 26% of the total cell volume was filled with disordered solvent, which could not be modelled in terms of atomic sites. From this point on, residual peaks were removed and the solvent region was refined as a diffuse contribution without specific atom positions by using the PLATON[36] module SQUEEZE,[37] which subtracts electron density from the void regions by appropriately modifying the diffraction intensities of the overall structure. An electron count over the solvent region provides an estimate for the number of solvent molecules removed from the cell. The number of electrons thus located was 240 per unit cell. This residual electron density was assigned to 1.5 molecules of pentane per molecule of complex (240/4 = 60 electrons per molecule; 1.5 molecules of pentane would give 63 electrons), which were included in the formula, formula weight, calculated density, absorption coefficient, and $F(000)$. Applying this procedure led to a dramatic improvement in all refinement parameters and a minimization of residuals. Atomic scattering factors were taken from the usual tabulations. Anomalous dispersion terms for Rh and Cl atoms were included in Fc. All non-hydrogen atoms were allowed to vibrate anisotropically. All the hydrogen atoms;except hydrogen atoms attached to C8 and C9 in the structure of $5_{Me}{}^{Me}$ 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 times greater than the Ueq of the carbon atom to which the hydrogen atom is attached), and their positions were refined as "riding" atoms.

CCDC 772339 (4_{Me}), 772340 ($5_{Me}{}^{Me}$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Acknowledgements

Support from the CNRS and from the ANR (programme blanc ANR-08-BLAN-0137-01) is gratefully acknowledged.

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Received: April 7, 2010
Revised: June 8, 2010
Published online: September 6, 2010

