



HAL
open science

Reprogramming of a Malonic N-Heterocyclic Carbene: A Simple Backbone Modification with Dramatic Consequences on the Ligand's Donor Properties

Vincent César, Noël Lugan, Guy Lavigne

► **To cite this version:**

Vincent César, Noël Lugan, Guy Lavigne. Reprogramming of a Malonic N-Heterocyclic Carbene: A Simple Backbone Modification with Dramatic Consequences on the Ligand's Donor Properties. *European Journal of Inorganic Chemistry*, 2010, 2010 (3), pp.361-365. 10.1002/ejic.200901113 . hal-03710153

HAL Id: hal-03710153

<https://hal.science/hal-03710153v1>

Submitted on 30 Jun 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Reprogramming of a malonic N-heterocyclic carbene: a simple backbone modification with dramatic consequences on the ligand's donor properties

Vincent César,*^[a] Noël Lugan,^[a] and Guy Lavigne*^[a]

Keywords: Heterocyclic carbenes/diamidocarbene/organometallic chemistry/electronic properties/Rhodium

Reaction of N,N'-dimesitylformamidine with dimethylmalonyl dichloride in dichloromethane in the presence of an excess of triethylamine gives the 2-chloro-4,5-dioxo-hexahydropyrimidine **1**. The corresponding diamidocarbene **3** is generated *in situ* by further deprotonation with KHMDS at -40°C, and identified by trapping with S₈ giving the fully characterized sulphur adduct **4** (X-ray structure available). It also reacts with [RhCl(COD)]₂ to yield the NHC complex [RhCl{**3**}(COD)] (**5**) (X-ray structure available)

The donor properties of **3** were evaluated against the established IR (νCO) scale from the compound [RhCl{**3**}(CO)₂] (**6**). The average value of IR ν(CO) = 2045 cm⁻¹ indicates that the diamidocarbene **3** is much less nucleophilic than structurally relevant six-membered NHCs including the anionic diaminocarbenes previously reported in our group.

(© WILEY-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2009)

^[a] CNRS, LCC (Laboratoire de Chimie de Coordination), 205 route de Narbonne, 31077 Toulouse Cedex 4, France and Université de Toulouse, UPS, INPT, 31077 Toulouse Cedex 4, France
E-mail: vincent.cesar@lcc-toulouse.fr; guy.lavigne@lcc-toulouse.fr
Supporting information for this article is available on the WWW under <http://www.eurjic.org/> or from the author.

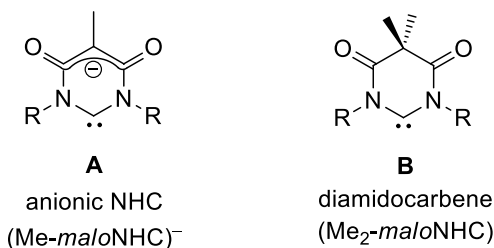


Figure 1. Anionic N heterocyclic carbene and diamidocarbene based on the same six-membered skeleton.

Introduction

N-heterocyclic carbenes (NHCs)^{[1][2]} have gained valuable significance over the past fifteen years, both as organocatalysts^[3] and as “universal” ligands for organometallic catalysis.^[4] Due to the presence of at least one amino-type nitrogen (two nitrogens directly connected to the carbene for the most studied cyclic diaminocarbenes) in the vicinity of the carbene centre, they are typically classified as *nucleophilic* carbenes and, by consequence, currently behave as strong electron-donor ligands, particularly in comparison with phosphines.^[5] So, whereas the successful design of highly nucleophilic NHCs has received considerable attention,^[6] the alternate possibility of reducing their donor properties has been only disclosed in a few cases.^[7]

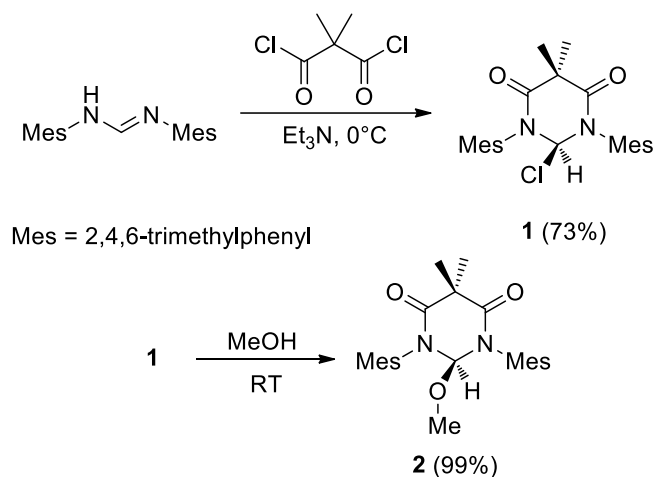
Our recent disclosure of a modulable synthetic strategy^[8] leading to the six-membered anionic NHC **A** incorporating a malonate backbone (figure 1) offered further possibilities to devise structurally related derivatives exhibiting different donor properties.^[8] Indeed, we reasoned that a slightly modified approach based on dimethyl malonyl chloride as a coupling partner (*vide infra*) would allow the introduction of a second substituent at the position 5 of the heterocycle, thereby blocking the electronic delocalisation through the malonate skeleton, ultimately producing the neutral type **B** carbene being much less nucleophilic due to the incorporation of nitrogens as amide groups.

During the course of this work, we became aware of the very recent independent publication by Bielawski and co-workers of a slightly different synthetic approach leading to the first diamidocarbene of type **B**.^[9] This prompted us to disclose our parallel results giving additional insight into the chemistry of this fascinating new type of N-heterocyclic carbene incorporating amide type nitrogens.^[10]

Results and Discussion

In a logical transposition of our synthesis of **A**,^[8] the precursor of **B** was prepared by coupling N,N'-dimesitylformamidine with dimethylmalonyl dichloride in dichloromethane in the presence of an excess of triethylamine as a base (scheme 1). Surprisingly, the product did not display any salt-like character but behaved as a neutral compound, with a relative good solubility in aromatic solvents (toluene or benzene) as well as in non polar mixtures usually unable to dissolve chloride salts. Such properties facilitated the isolation of the product by simple selective extraction from a CH₂Cl₂/Et₂O mixture (1/2: v/v). Considering that the attachment of two electron-withdrawing carbonyl functionalities on the nitrogen atoms renders the formamidinium unit sufficiently electrophilic to undergo a nucleophilic attack by the chloride counter-anion, a formulation of the compound as a 2-chloro-4,5-dioxo-

hexahydropyrimidine **1** - a “masked” form for a formamidinium -- was reasonably anticipated.^[11] Such a structure was confirmed by ¹H and ¹³C NMR spectra, where the proton and carbon resonances at the position 2 of the heterocycle appeared at $\delta = 6.93$ ppm (singlet) and $\delta = 90.5$ ppm, respectively. Such signals are in agreement with the chemical shifts reported for 4,6-dioxo-1,3-diazine with a sp^3 -hybridized at the position 2.^[12]



Scheme 1. Synthesis of compound **1** and its subsequent methanolysis.

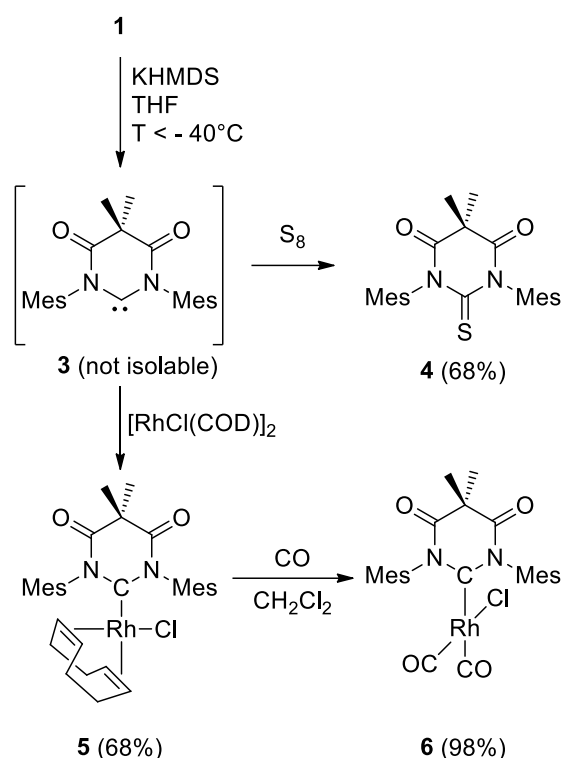
The chloride adduct **1** proved to be extremely moisture sensitive, thus requiring manipulation under inert atmosphere. Typically, the chlorine atom in position 2 of the heterocycle could be readily replaced by better nucleophiles, as exemplified by the reaction of **1** with methanol producing the air-stable, methoxy-substituted heterocycle **2** (Scheme 1), exhibiting a shift of the ¹H NMR signal at position 2 to $\delta = 5.28$ ppm, consistent with a reduced electrophilicity.

The free N,N'-diamidocarbene **3** could be generated by treatment of **1** with potassium bis(trimethylsilyl)amide (KHMDs) in THF at low temperature (-40°C) (Scheme 2).

Whereas **3** appears to be viable only at low temperature, its formulation as a carbene was established by its trapping with S_8 to form the thiourea **4**. The architecture of the new heterocycle was confirmed by the crystal structure of **4**, depicted in Figure 2. Very characteristically, the cycle exhibits boat conformation, with the sp^3 -hybridized carbon C3 lying out of the plane of the cycle in contrast to the previously reported case of planar pyrimidinium betaine.^[8] This clearly reflects the disappearance of the electron-delocalisation along the malonate unit, as also corroborated by a concomitant lengthening of interatomic distances C2-C3 and C3-C6, now appearing as single C-C bonds (1.514(3) Å and 1.516(3) Å, respectively).

The reaction between the *in situ* generated carbene **3** and $[\text{RhCl}(\text{COD})]_2$ (COD = 1,5-cyclooctadiene) led to the formation of the expected NHC complex $[\text{RhCl}(\mathbf{3})(\text{COD})]$ (**5**) in good yield (68%), confirming Bielawski's original observation (in the case of iridium) that the carbene **3** is still a suitable ligand for transition metal complexes in spite of its reduced nucleophilicity. The latter characteristics can be illustrated by the carbene's ¹³C NMR resonance appearing at 245.2 ppm (d, $J_{\text{RhC}} = 49\text{Hz}$), which is significantly downfield-shifted compared to those observed in related NHC-rhodium complexes reported in the literature (175-

225 ppm),^[13] and in particular the (4-oxoimidazolin-2-ylidene)-rhodium complex reported by us ($\delta = 229.7$ ppm).^[10a] Such a high chemical shift can be attributed to a decrease of the electron-density on the carbene centre due to the electron-withdrawing effect of the two carbonyl groups.



Scheme 2. Generation of diamidocarbene **3**, its trapping with S_8 and complexation on a rhodium(I) center.

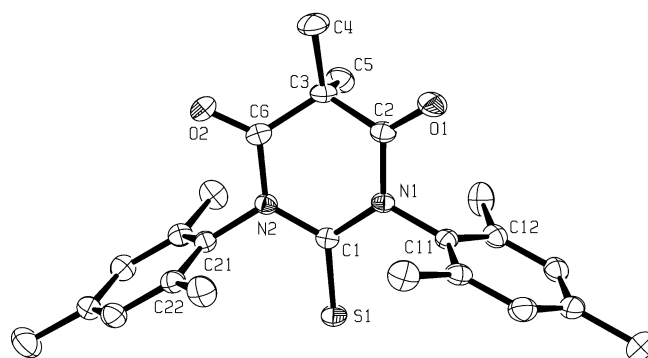


Figure 2. Perspective view of **4**. Anisotropic displacement parameter ellipsoids are shown at the 50% probability level, whereas hydrogen atoms were omitted for clarity. Selected bond lengths (Å): C1-S1: 1.640(2), C1-N1: 1.397(3), C1-N2: 1.391(3), C2-O1: 1.210(3), C6-O2: 1.205(3), C2-C3: 1.514(3), C3-C6: 1.516(3).

A perspective view of the molecular structure of complex **5** established by X-Ray diffraction is depicted in figure 3 along with the principal interatomic distances and bond angles. The complex exhibits a square-planar arrangement of ligands around the Rhodium centre, with the carbenic ring being orthogonal to the mean coordination plane [torsion angle: $\text{N1-C1-Rh1-C11} = 83.9(2)^\circ$]. Again, the heterocycle is not planar and exhibits a half chair conformation in which the sp^3 -hybridized carbon C3 is pointing towards the chloride atom, C3 being off the mean plane

defined by {C2-N1-C1-N2-C4} (average deviation from mean plane of 0.004 Å) by 0.486(2) Å. Most importantly, the Rh1-C1 bond distance of 2.0107(19) Å is considerably shorter than those reported for six-membered NHC-RhCl(COD) complexes (2.036(2) Å < Rh-C_{carbene} < 2.090(3) Å).^[14] This reflects a stronger interaction between the carbene and the rhodium center, probably due to a greater level of π -backdonation from the metal centre to the carbene ligand. Further studies are currently carried out in order to completely understand the real nature of the metal-carbene bonding.

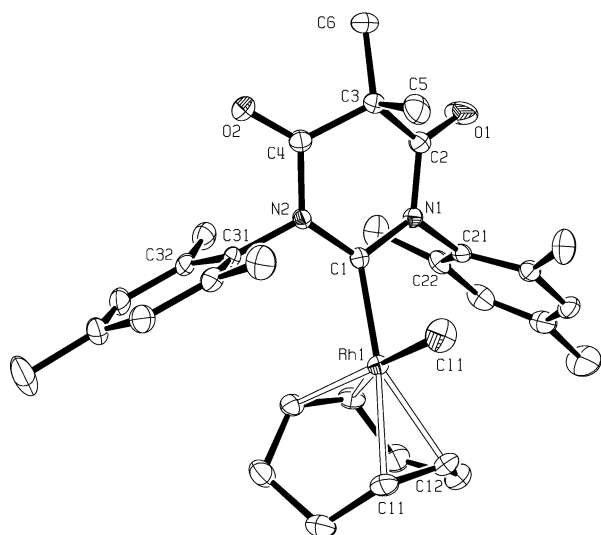


Figure 3. Perspective view of complex **5**. Anisotropic displacement parameter ellipsoids are shown at 50% probability level, whereas hydrogen atoms were omitted for clarity. Selected bond lengths (Å): Rh1-C1: 2.0107(19), C1-N1: 1.374(2), C1-N2: 1.380(3), N1-C2: 1.410(3), N2-C4: 1.416(3), C2-O1: 1.201(3), C4-O2: 1.204(3). Selected bond angles (°): Rh1-C1-N1: 117.71(13), Rh1-C1-N2: 125.77(14), N1-C1-N2: 115.49(16).

Due to the adjunction of the two carbonyl groups in its core, the electron-donating properties of the carbene **3** were also expected to be significantly reduced. In order to quantify this, complex **5** was converted into its dicarbonyl analogue [RhCl(**3**)(CO)₂] by bubbling CO gas into a solution of **5** in CH₂Cl₂. The outcome of the reaction was observable by a colour change of the solution from dark red to pale yellow. Complex **6** was obtained in excellent yields (99%) and was fully characterized.^[15] As for complex **5**, the ¹³C NMR carbene signal at $\delta = 230.8$ ppm is found at much higher field than those reported for known [RhCl(NHC)(CO)₂] complexes ($\delta < 219.6$ ppm).^[16] The electron-deficiency of the carbene **3** was confirmed by the IR spectra of complex **6** in CH₂Cl₂. Two strong bands at 2005.3 cm⁻¹ and 2086.1 cm⁻¹ were indeed observed, corresponding to the asymmetric and symmetric normal vibrations of the two CO ligands. The average value of $\nu_{av} = 2045.4$ cm⁻¹ is much higher than those reported for other six-membered NHC's, which are typically ranged within 2029 < ν_{av} < 2038 cm⁻¹. This result points out the critical role of the two carbonyl groups on the electronic structure of the carbene, which renders carbene ligand **3** much less of an electron donor than typical NHCs. Moreover, the Tolman electronic Parameter (TEP) of the carbene **3** could be calculated by the two linear regressions developed by Plenio and Nolan,^[17] and was found to be equal to 2055 cm⁻¹. Considering the approximations due to the linear regressions, this value confirms this obtained by Bielawski *et al.* of 2057 cm⁻¹.

Conclusion

In conclusion, it is hoped that this and earlier reports from several groups cited above will draw growing attention on the rich chemistry of functional six-membered N-heterocyclic carbenes. Indeed, with one more skeletal atom than for five-membered NHCs, they offer not only different sterical properties, but also a broader variability in the number and nature of the functionalities which can be introduced as integral parts of their heterocyclic backbone. This is particularly important, since we see growing evidence that such remote functionalities can very significantly modify the intrinsic properties of the carbene ligand.

Experimental Section

All manipulations were performed 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. Solvents were dried and distilled by classical methods. NMR spectra were recorded on Bruker ARX250 or AV300 spectrometers. Chemical shifts are reported in ppm (δ) compared to TMS (¹H and ¹³C) using the residual peak of deuterated solvent as internal standard. 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. N,N'-dimesitylformamidinium^[18] was synthesized according to literature procedure.

2-chloro-1,3-dimesityl-5,5-dimethyl-4,6-dioxo-hexahydropyrimidine (**1**)

Dimethylmalonyl dichloride (0.75 mL, 5.6 mmol, 1.05 eq.) was added dropwise to a well-stirred solution of N,N'-dimesitylformamidinium (1.5 g, 5.35 mmol) and Et₃N (1.1 mL, 8.0 mmol, 1.5 eq.) in CH₂Cl₂ (15 mL) at 0°C. After stirring for 1 h at this temperature, all volatiles were removed *in vacuo* and the residue was taken up in CH₂Cl₂/Et₂O (1/2 v/v, 18 mL) and filtered through a pad of Celite to remove triethylammonium chloride. After washing the solid a second time with CH₂Cl₂/Et₂O (1/2 v/v, 6 mL), solvents were evaporated which afforded the desired product as a white, fluffy solid (1.6 g, 73%); mp = 212-214°C (dec.); ¹H NMR (300 MHz, CDCl₃): $\delta = 6.96$ (s, 4H, CH_{Mes}), 6.93 (s, 1H, N₂CHCl), 2.30 (s, 12H, CH₃ortho), 2.29 (s, 6H, CH₃para), 1.79 (s, 6H, C(CH₃)₂); ¹³C{¹H} NMR (75.4 MHz, CDCl₃): $\delta = 170.8$ (C=O), 139.0 (C_{Mes}), 136.0 (C_{Mes}), 132.2 (C_{Mes}), 130.2 (CH_{Mes}), 90.5 (N₂CHCl), 48.2 (C(CH₃)₂), 23.6 (C(CH₃)₂), 20.9 (CH₃para), 19.2 (CH₃ortho); IR (ATR): $\nu = 2975, 2925, 1713, 1682, 1665, 1608, 1459, 1401, 1356, 1261, 1249, 1189, 1167, 1103, 1034, 974, 910, 856, 763, 739, 720$ cm⁻¹; MS (ESI) : m/z (%) 412 (100) [M]⁺, 395 (98) [M - Cl + H₂O]⁺.

2-methoxy-1,3-dimesityl-5,5-dimethyl-4,6-dioxo-hexahydropyrimidine (**2**)

To a solution of N,N'-dimesitylformamidinium (373 mg, 1.33 mmol) and Et₃N (0.28 mL, 2.0 mmol, 1.5 eq.) in CH₂Cl₂ (5 mL) was added dimethylmalonyl dichloride (186 μ L, 1.39 mmol, 1.05 eq.) at 0°C. The resulting solution was then stirred for 1 h before MeOH (1 mL) was added. After 5 min., all volatiles were removed *in vacuo* and the residue was purified by flash chromatography (SiO₂, CH₂Cl₂/MeOH : 95/5) to afford the expected product as a white solid (540 mg, 99%); mp = 185°C; ¹H NMR (300 MHz, CDCl₃): $\delta = 6.94$ (s, 4H, CH_{Mes}), 5.28 (s, 1H, N₂CH(OMe)), 2.83 (s, 3H, OCH₃), 2.28 (s, 12H, CH₃ortho), 2.27 (s, 6H, CH₃para), 1.83 (s, 3H, C(CH₃)₂), 1.58 (s, 3H, C(CH₃)₂); ¹³C{¹H} NMR (75.4 MHz, CDCl₃): $\delta = 170.8$ (C=O), 138.3, 138.0, 134.5, 133.4 (C_{Mes}), 129.9, 129.5 (CH_{Mes}), 98.5 (N₂CH(OMe)), 59.6 (OCH₃), 47.0 (C(CH₃)₂), 28.1 (C(CH₃)₂), 21.2 (C(CH₃)₂), 20.9 (CH₃para), 18.5 (CH₃ortho), 18.3 (CH₃ortho); IR (ATR): $\nu = 2984, 2918, 2859, 1696$ (C=O), 1666, 1606, 1484, 1456, 1422, 1366, 1353, 1238, 1167, 1108, 1059, 957, 862, 776, 725, 684 cm⁻¹; MS (ESI) : m/z (%) 431 (100) [M + Na]⁺, 281 (26) [HC(NHMe)₂]⁺; elemental analysis *calcd*

(%) for C₂₅H₃₂N₂O₃ (408.53): C 73.50, H 7.90, N 6.86; *found*: C 73.39, H 8.00, N 6.79.

1,3-dimesityl-5,5-dimethyl-hexahydropyrimidin-4,6-dione-2-thione (4)

A solution of **1** (856 mg, 2.07 mmol) in THF (15 mL) was cooled to -80°C and KHMDS (0.5 M in toluene, 4.6 mL, 1.1 eq.) was added dropwise. The very pale yellow solution was stirred for 30 min and S₈ (139 mg, 4.35 mmol) was added all at once as a solid. After 1 h of stirring at -80°C, the cooling bath was removed and the solution was allowed to warm to room temperature. After evaporation of all volatiles, the crude product was purified by flash chromatography (SiO₂, hexane/CH₂Cl₂: 1/1 then 1/2) to yield **4** as a bright orange crystalline solid (573 mg, 68%); mp = 282°C (dec.); ¹H NMR (300 MHz, CDCl₃): δ = 6.97 (s, 4H, CH_{Mes}), 2.32 (s, 6H, CH_{3 para}), 2.13 (s, 12H, CH_{3 ortho}), 1.79 (s, 6H, C(CH₃)₂); ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ = 177.4 (C=S), 170.3 (C=O), 138.7, 134.4, 134.3 (C_{Mes}), 129.6 (CH_{Mes}), 48.6 (C(CH₃)₂), 25.0 (C(CH₃)₂), 21.2 (CH_{3 para}), 17.5 (CH_{3 ortho}); IR (ATR): ν = 2971, 2916, 1855, 1731, 1701, 1671, 1658, 1608, 1480, 1459, 1382, 1330, 1305, 1263, 1222, 1144, 1121, 1034, 1011, 963, 856, 818, 762 cm⁻¹; MS (ESI): m/z (%) 431 (100) [M + Na]⁺, 409 (18) [M + H]⁺; elemental analysis *calcd* (%) for C₂₄H₂₈N₂O₂S (408.56): C 70.55, H 6.91, N 6.86; *found*: C 70.53, H 6.96, N 6.78.

Chloro(1,5-cyclooctadiene)(1,3-dimesityl-5,5-dimethyl-4,6-dioxo-tetrahydropyrimidin-2-ylidene)rhodium(I) (5)

Compound **1** (143 mg, 0.346 mmol) was dissolved in THF (6 mL) and the solution was cooled at -40°C. A solution of KHMDS in toluene (0.5M, 0.73 mL, 0.36 mmol, 1.05 eq.) was then added dropwise and after 30 minutes of stirring, [RhCl(COD)]₂ (85 mg, 0.17 mmol, 0.5 eq.) was added all at once as a solid. After 15 min. at that temperature, the cooling bath was removed and the reaction mixture allowed to warm up to room temperature, time during which the solution gradually turned from yellow to dark red. After 30 min at room temperature, all volatiles were evaporated *in vacuo* and the crude product was directly purified by flash chromatography (neutral Al₂O₃ type III, CH₂Cl₂) to leave the desired complex as a red powder (147 mg, 68%). Single crystals suitable for an X-Ray diffraction experiment were obtained by slow diffusion of pentane into a solution of **5** in THF. mp: 197°C; ¹H NMR (300 MHz, CDCl₃): δ = 7.11 (s, 2H, CH_{Mes}), 6.98 (s, 2H, CH_{Mes}), 4.71 (br, 2H, CH_{COD}), 3.23 (br, 2H, CH_{COD}), 2.54 (s, 6H, CH_{3 Mes}), 2.39 (s, 6H, CH_{3 Mes}), 1.99 (s, 3H, C(CH₃)₂), 1.98 (s, 6H, CH_{3 Mes}), 1.58-1.44 (m, 8H, CH_{2 COD}), 1.55 (s, 3H, C(CH₃)₂); ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ = 245.2 (d, ¹J_{RhC} = 49.1 Hz, N₂C), 169.1 (d, ³J_{RhC} = 2.2 Hz, C=O), 139.0, 137.4, 135.8, 135.1 (C_{Mes}), 130.5 (CH_{Mes}), 128.4 (CH_{Mes}), 101.3 (d, J_{RhC} = 6.3 Hz, CH_{COD}), 72.7 (d, J_{RhC} = 13.9 Hz, CH_{COD}), 50.8 (C(CH₃)₂), 31.8 (CH_{2 COD}), 29.8 (C(CH₃)₂), 27.2 (CH_{2 COD}), 21.0 (CH_{3 Mes}), 20.1 (CH_{3 Mes}), 19.6 (CH_{3 Mes}), 18.8 (C(CH₃)₂); IR (ATR): ν = 2919, 2877, 1738, 1711, 1697, 1668, 1460, 1429, 1384, 1365, 1351, 1322, 1306, 1226, 1104, 1071, 1053, 1037, 1016, 957, 941, 848, 783, 767 cm⁻¹; MS (ESI): m/z (%) 769 (39), 683 (69), 624 (22) [M + H]⁺, 587 (100) [M - Cl]⁺, 566 (30), 413 (18), 286 (28); elemental analysis *calcd* (%) for C₃₂H₄₀ClN₂O₂Rh (623.03): C 61.69, H 6.47, N 4.50; *found*: C 61.78, H 6.57, N 4.44.

Chloro-dicarbonyl-(1,3-dimesityl-5,5-dimethyl-4,6-dioxo-tetrahydropyrimidin-2-ylidene)rhodium(I) (6)

CO was bubbled into a solution of **5** (43 mg, 69 mmol) in CH₂Cl₂ (3 mL) for 10 min. From dark red, the solution gradually turned pale yellow. After 1 hour of stirring, all volatiles were removed *in vacuo*. In order to remove thoroughly free (ou the freed) cyclooctadiene, pentane (2 x 3 mL) was added to the crude product, the mixture was sonicated and evaporated again. This procedure gave pure **6** as a pale yellow powder (39 mg, 98%); mp: 235°C (dec.); ¹H NMR (250 MHz, CDCl₃): δ = 7.00 (s, 4H, CH_{Mes}), 2.36 (s, 6H, CH_{3 Mes}), 2.34 (s, 6H, CH_{3 Mes}), 2.20 (s, 6H, CH_{3 Mes}), 1.92 (s, 3H, C(CH₃)₂), 1.69 (s, 3H, C(CH₃)₂); ¹³C{¹H} NMR (63 MHz, CDCl₃): δ = 230.8 (d, ¹J_{RhC} = 43.4 Hz, N₂C), 184.6 (d, J_{RhC} = 53.9 Hz, Rh-CO), 182.4 (d,

J_{RhC} = 75.7 Hz, Rh-CO), 169.9 (C=O), 139.8, 136.1, 134.9, 134.1 (C_{Mes}), 130.4 (CH_{Mes}), 129.4 (CH_{Mes}), 51.5 (C(CH₃)₂), 28.7 (C(CH₃)₂), 21.1 (CH_{3 Mes}), 20.4 (CH_{3 Mes}), 19.5 (CH_{3 Mes}), 18.5 (C(CH₃)₂); IR (ATR): ν = 2923, 2077, 1994, 1768, 1736, 1697, 1667, 1469, 1411, 1389, 1315, 1289, 1243, 1172, 1096, 1036, 1008, 870, 848, 782, 767, 678 cm⁻¹; IR (CH₂Cl₂): ν = 2086.1 (CO), 2005.3 (CO), 1764.5, 1735.2 cm⁻¹; MS (ESI): m/z (%) 611 (43) [M - 2 CO + 2 CH₃CN + H]⁺, 507 (65) [M - Cl - CO]⁺, 415 (100) [M - Cl - Mes]⁺; elemental analysis *calcd* (%) for C₂₆H₂₈ClN₂O₄Rh (570.87): C 54.70, H 4.94, N 4.91; *found*: C 55.13, H 4.99, N 4.75.

X-ray Diffraction Studies. Crystals of **4**, and **5** suitable for X-ray diffraction were obtained through crystallization from CH₂Cl₂/pentane and THF/pentane, respectively. Data were collected at 180 K on a Bruker D8 Apex II diffractometer, and on a Oxford Diffraction Xcalibur diffractometer, respectively. All calculations were performed on a PC-compatible computer using the WinGX system.^[19] The structures were solved using the SIR92 program,^[20] 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.^[21] Atomic scattering factors were taken from the usual tabulations. Anomalous dispersion terms for Rh, S, and Cl atoms were included in Fc. All non-hydrogen atoms were allowed to vibrate anisotropically. All the hydrogen atoms - except olefinic H atoms of the COD ligand in **5** - were set in idealized position (R₂CH, C-H = 0.96 Å; R₂CH₂, C-H = 0.97 Å; RCH₃, C-H = 0.98 Å; C(sp²)-H = 0.93 Å; U_{iso} 1.2 or 1.5 time greater than the U_{eq} of the carbon atom to which the hydrogen atom is attached) and their position were refined as "riding" atoms. The olefinic H atoms of the COD ligand in **5** were located from a difference electron density synthesis; their position and isotropic thermal parameters (arbitrary set to 0.05 Å²) were held fixed during the final refinement. CCDC-755193 (**4**) and CCDC-755194 (**5**) contains 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.

Acknowledgments

Support from the "Centre National de la Recherche Scientifique" (CNRS) and from the "Agence nationale de la Recherche" (ANR: programme blanc ANR-08-BLAN-0137-01) is gratefully acknowledged.

- [1] For monographs, see: a) *N-Heterocyclic Carbenes in Transition Metal Catalysis* (Ed. F. Glorius), *Top. Organomet. Chem.*, **2007**, *21*, Springer, Berlin, **2007**; b) *N-Heterocyclic Carbenes in synthesis* (Ed. S. P. Nolan), Wiley-VCH, Weinheim, **2006**.
- [2] General reviews: a) O. Schuster, L. Yang, H. G. Raubenheimer, M. Albrecht, *Chem. Rev.* **2009**, *109*, 3445-3478; b) F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3122-3172; c) D. Bourissou, O. Guerret, F. Gabbai, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39-91.
- [3] a) D. Enders, O. Niemeier, A. Henseler, *Chem. Rev.* **2007**, *107*, 5606-5655; b) N. Marion, S. Díez-González, S. P. Nolan, *Angew. Chem. Int. Ed.* **2007**, *46*, 2-15.
- [4] a) S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612-3676; b) C. Samojłowicz, M. Bieniek, K. Grela, *Chem. Rev.* **2009**, *109*, 3708-3742; c) M. Poyatos, J. A. Mata, E. Peris, *Chem. Rev.* **2009**, *109*, 3677-3707; d) E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, *Angew. Chem. Int. Ed.* **2007**, *46*, 2768-2813; e) V. César, S. Bellemin-Laponnaz, L. H. Gade, *Chem. Soc. Rev.* **2004**, *33*, 619-636; f) C. M. Crudden, D. P. Allen, *Coord. Chem. Rev.* **2004**, *248*, 2247-2273; g) W. A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1290-1309.
- [5] a) S. Díez-González, S. P. Nolan, *Coord. Chem. Rev.* **2007**, *251*, 874-883; b) A. Fürstner, M. Alcarazo, H. Krause, C.W. Lehmann, *J. Am. Chem. Soc.* **2007**, *129*, 12676-12678.

- [6] a) A. Fürstner, M. Alcarazo, K. Radkowski, C. W. Lehmann, *Angew. Chem. Int. Ed.* **2008**, *47*, 8302-8306; b) S. Nakafuji, J. Kobayashi, T. Kawashima, *Angew. Chem. Int. Ed.* **2008**, *47*, 1141-1144; c) V. Lavallo, Y. Canac, C. Präsang, B. Donnadiou, G. Bertrand, *Angew. Chem. Int. Ed.* **2005**, *44*, 5705-5709; d) M. Mayr, K. Wurst, K.-H. Ongania, M. R. Buchmeiser, *Chem. Eur. J.* **2004**, *10*, 1256-1266; e) P. Bazinet, G. P. A. Yap, D. S. Richeson, *J. Am. Chem. Soc.* **2003**, *125*, 13314-13315.
- [7] a) U. Siemeling, C. Färber, C. Bruhn, *Chem. Commun.* **2009**, 98-100; b) D. M. Khramov, E. L. Rosen, V. M. Lynch, C. W. Bielawski, *Angew. Chem. Int. Ed.* **2008**, *47*, 2267-2270; c) D. M. Khramov, E. L. Rosen, J. A. V. Er, P. D. Vu, V. M. Lynch, C. W. Bielawski, *Tetrahedron* **2008**, *64*, 6853-6862; d) M. Alcarazo, R. Fernández, E. Alvarez, J. M. Lassaletta, *J. Organomet. Chem.* **2005**, *690*, 5979-5988; e) M. Viciano, E. Mas-Marza, M. Sanau, E. Peris, *Organometallics* **2006**, *25*, 3063-3069.
- [8] V. César, N. Lukan, G. Lavigne, *J. Am. Chem. Soc.* **2008**, *130*, 11286-11287.
- [9] T. W. Hudnall, C. W. Bielawski, *J. Am. Chem. Soc.* **2009**, *131*, 16039-16041.
- [10] We and others have also disclosed very recently a mixed aminoamidocarbene, see: a) L. Benhamou, V. César, H. Gornitzka, N. Lukan, G. Lavigne, *Chem. Commun.* **2009**, 4720-4722; b) A. T. Biju, K. Hirano, R. Fröhlich, F. Glorius, *Chem. Asian J.* **2009**, DOI: 10.1002/asia.200900410.
- [11] Such an attack was already reported leading to a similar structure, see: E. A. Barsa, R. Richter, *J. Org. Chem.* **1986**, *51*, 4483-4485.
- [12] a) K.-U. Fulda, E. Maassen, H. Ritter, R. Sperber, B. Tieke, *Langmuir* **1996**, *12*, 854-856; b) H. Gotthardt, M. Riegels, *Chem. Ber.* **1987**, *120*, 445-447; c) H. Gotthardt, J. Blum, *Chem. Ber.* **1987**, *120*, 109-114.
- [13] For a compilation, see: a) D. Tapu, D. A. Dixon, C. Roe, *Chem. Rev.* **2009**, *109*, 3385-3407.
- [14] a) reference 8; b) M. Mayr, K. Wurst, K.-H. Ongania, M. R. Buchmeiser, *Chem. Eur. J.* **2004**, *10*, 1256-1266; c) C. Präsang, B. Donnadiou, G. Bertrand, *J. Am. Chem. Soc.* **2005**, *127*, 10182-10183; d) P. Bazinet, T.-G. Ong, J. S. O'Brien, N. Lavoie, E. Bell, G. P. A. Yap, I. Korobkov, D. S. Richeson, *Organometallics* **2007**, *26*, 2885-2895; e) H. Arslan, D. VanDerveer, I. Ozdemir, S. Demir, B. Cetinkaya, *Acta Crystallogr.* **2007**, *E63*, m770-m771.
- [15] In particular, no decomposition and no loss of carbon monoxide were observed during the work-up of the reaction, on contrary to other reports dealing with poor-donating NHC systems, see: a) M. D. Sanderson, J. W. Kamplain, C. W. Bielawski, *J. Am. Chem. Soc.* **2007**, *128*, 16514-16515; b) S. Wolf, H. Plenio, *J. Organomet. Chem.* **2009**, *694*, 1487-1492.
- [16] The most downfield carbene ¹³C chemical shift in [RhCl(NHC)(CO)₂] was found in reference 14c.
- [17] For Plenio's linear regression, see reference 15b; For Nolan's method, see: R. A. I. Kelly, H. Clavier, S. Giudice, N. M. Scott, E. D. Stevens, J. Bordner, I. Samardjiev, C. D. Hoff, L. Cavallo, S. P. Nolan, *Organometallics* **2008**, *27*, 202-210.
- [18] K. E. Krahulic, G. D. Enright, M. Parvez, R. Roesler, *J. Am. Chem. Soc.* **2005**, *127*, 4142-4143.
- [19] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837-838.
- [20] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343-350.
- [21] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112-122.

Received: ((will be filled in by the editorial staff))
 Published online: ((will be filled in by the editorial staff))

