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

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Reaction of *N*,*N*′-dimesitylformamidine with dimethylmalonyl dichloride in dichloromethane in the presence of an excess of triethylamine gives the 2-chloro-4,5-dioxohexahydropyrimidine **1**. The corresponding diamidocarbene **3** is generated in situ by further deprotonation with KHMDS at –40 °C and identified by trapping with S_8 to give the fully characterized (including X-ray structure) sulfur adduct **4**. It also reacts with $[RhCl(cod)]_2$ to yield the NHC complex [RhCl(**3**)(cod)] (**5**) (characterized also by X-ray structure). The donor properties of **3** were evaluated against the established IR [ν(CO)] scale from [RhCl(**3**)$(CO)_2$] (**6**). The average value of 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.

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 atom (two nitrogen atoms directly connected to the carbene atom for the most studied cyclic diaminocarbenes) in the vicinity of the carbene centre, they are typically classified as *nucleophilic* carbenes and, by consequence, behave as strong electron-donor ligands, particularly in comparison with phosphanes.[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 reported 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 dimethylmalonyl 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 carbene of type **B**, being much less nucleophilic due to the incorporation of nitrogen atoms as amide groups.

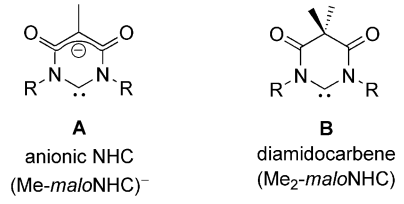

Figure 1. Anionic N-heterocyclic carbene and diamidocarbene based on the same six-membered skeleton.

During the course of this work, we became aware of the very recent independent publication by Bielawski and coworkers 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 nitrogen atoms.[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 nonpolar mixtures usually unable to dissolve chloride salts. Such properties facilitated the isolation of the product by simple selective extraction from a CH_2Cl_2/Et_2O mixture (1:2, v/v). Considering that the attachment of two electron-withdrawing carbonyl functionalities on the nitrogen atoms renders the formamid-

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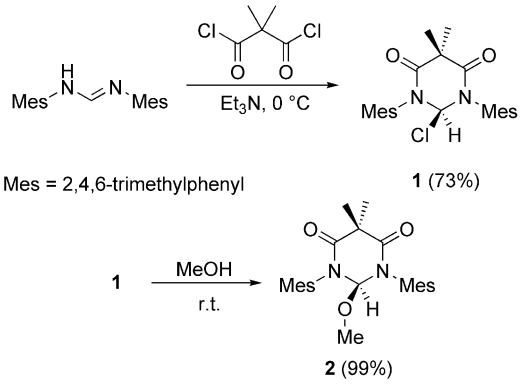
inium unit sufficiently electrophilic to undergo a nucleophilic attack by the chloride counteranion, a formulation of the compound as a 2-chloro-4,5-dioxohexahydropyrimidine **1** – a "masked" form for a formamidinium – was reasonably anticipated.[11] Such a structure was confirmed by ^{1}H and ^{13}C NMR spectra, where the proton and carbon resonances at the position 2 of the heterocycle appeared at δ = 6.93 ppm (singlet) and δ = 90.5 ppm, respectively. Such signals are in agreement with the chemical shifts reported for 4,6-dioxo-1,3-diazine with an sp^3-hybridized carbon atom at the position 2.[12]



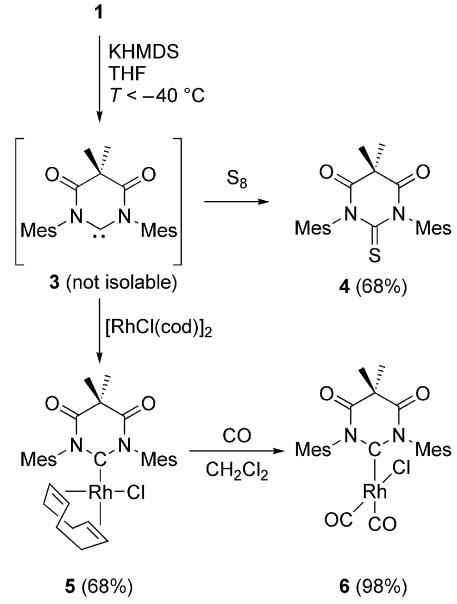
Scheme 1. Synthesis of compound **1** and its subsequent methanolysis.

The chloride adduct **1** proved to be extremely moisture-sensitive, thus requiring manipulation under an inert gas. 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 to produce the air-stable, methoxy-substituted heterocycle **2** (Scheme 1), exhibiting a shift of the ^{1}H NMR signal at position 2 to δ = 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-hydridized carbon atom C3 lying out of the plane of the cycle in contrast to the previously reported case of a 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 C–C single bonds [1.514(3) Å and 1.516(3) Å, respectively].

The reaction between the in situ generated carbene **3** and $[RhCl(cod)]_2$ (cod = 1,5-cyclooctadiene) led to the formation of the expected NHC complex [RhCl(**3**)(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 ^{13}C NMR resonance appearing at δ = 245.2 ppm (d, J_{RhC} = 49 Hz), which is significantly downfield-shifted compared to those observed in related (NHC)rhodium complexes reported in the literature (δ = 175–225 ppm),[13] and in particular the (4-oxoimidazolin-2-ylidene)rhodium complex reported by us (δ = 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 with a rhodium(I) center.

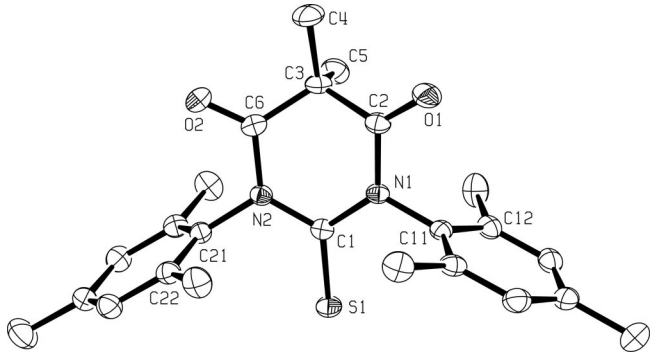


Figure 2. Perspective view of **4**. Anisotropic displacement parameter ellipsoids are shown at the 50% probability level, whereas hydrogen atoms were omitted for clarity. Selected bond lengths [Å]: C1–S1 1.640(2), C1–N1 1.397(3), C1–N2 1.391(3), C2–O1 1.210(3), C6–02 1.205(3), C2–C3 1.514(3), C3–C6 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 carbene ring being orthogonal to the mean coordination plane [torsion

angle: N1–C1–Rh1–Cl1 83.9(2)°]. Again, the heterocycle is not planar and exhibits a half-chair conformation in which the sp^3-hybridized carbon atom 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 0.004 Å) by 0.486(2) Å. Most importantly, the Rh1–C1 bond [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.

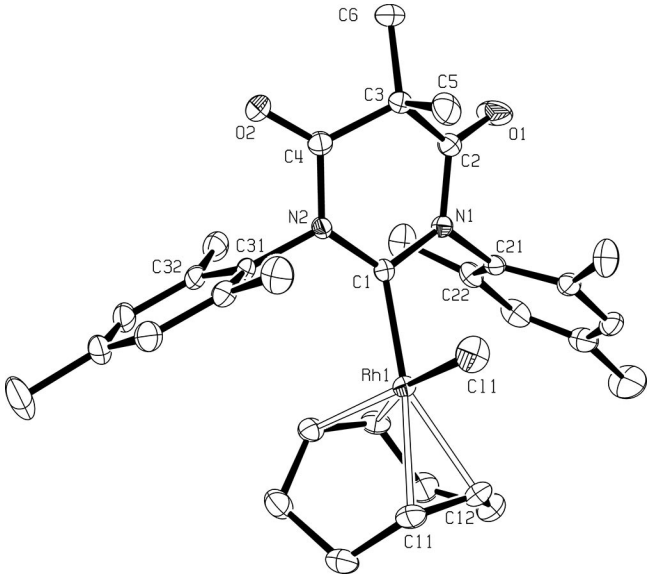


Figure 3. Perspective view of complex **5**. Anisotropic displacement parameter ellipsoids are shown at 50% probability level, whereas hydrogen atoms were omitted for clarity. Selected bond lengths [Å]: Rh1–C1 2.0107(19), C1–N1 1.374(2), C1–N2 1.380(3), N1–C2 1.410(3), N2–C4 1.416(3), C2–O1 1.201(3), 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 CH_2Cl_2. 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 ^{13}C NMR carbene signal at δ = 230.8 ppm is found at much higher field than those reported for known [RhCl(NHC)$(CO)_2$] complexes (δ < 219.6 ppm).[16] The electron deficiency of the carbene **3** was confirmed by the IR spectra of complex **6** in CH_2Cl_2. Two strong bands at 2005.3 and 2086.1 cm^{-1} were indeed observed, corresponding to the asymmetric and symmetric normal vibrations of the two CO ligands, respectively. The average value of ν_{av} = 2045.4 cm^{-1} is much higher than those reported for other six-membered NHCs, which typically are in the range 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 that of 2057 cm^{-1} obtained by Bielawski et al.

Conclusions

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 steric properties, but also a broader variability in the number and nature of the functionalities that 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

General: All manipulations were performed under dry nitrogen by using standard vacuum-line and Schlenk-tube techniques. Glassware was dried at 120 °C in an oven for at least 3 h. Solvents were dried and distilled by classical methods. NMR spectra were recorded with Bruker ARX250 or AV300 spectrometers. Chemical shifts are reported in ppm (δ) compared to TMS (^1H and ^{13}C) by using the residual peak of the deuterated solvent as internal standard. IR spectra were obtained with a Perkin–Elmer Spectrum 100 FT-IR spectrometer. Microanalyses were performed by the Laboratoire de Chimie de Coordination Microanalytical Service, and mass spectra were obtained from the Mass Spectrometry Service of the Paul Sabatier University. *N*,*N*′-dimesitylformamidine[18] was synthesized according to a literature procedure.

2-Chloro-1,3-dimesityl-5,5-dimethyl-4,6-dioxohexahydropyrimidine (1): Dimethylmalonyl dichloride (0.75 mL, 5.6 mmol, 1.05 equiv.) was added dropwise to a well-stirred solution of *N*,*N*′-dimesitylformamidine (1.5 g, 5.35 mmol) and Et_3N (1.1 mL, 8.0 mmol, 1.5 equiv.) in CH_2Cl_2 (15 mL) at 0 °C. After stirring at this temperature for 1 h, all volatiles were removed in vacuo, and the residue was taken up in CH_2Cl_2/Et_2O (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 CH_2Cl_2/Et_2O (1:2, v/v; 6 mL), the solvents were evaporated, which afforded the desired product as a white, fluffy solid (1.6 g, 73%); m.p. 212–214 °C (dec.). ^1H NMR (300 MHz, $CDCl_3$): δ = 6.96 (s, 4 H, CH_{Mes}), 6.93 (s, 1 H, N_2CHCl), 2.30 (s, 12 H, $CH_{3\ ortho}$), 2.29 (s, 6 H, $CH_{3\ para}$), 1.79 [s, 6 H, $C(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ = 170.8 (*C*=O), 139.0 (C_{Mes}), 136.0 (C_{Mes}), 132.2 (C_{Mes}), 130.2 (CH_{Mes}), 90.5 (N_2CHCl), 48.2 [$C(CH_3)_2$], 23.6 [$C(CH_3)_2$], 20.9

($CH_{3\ para}$), 19.2 ($CH_{3\ ortho}$) ppm. IR (ATR): $\tilde{\nu}$ = 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) $[M - Cl + H_2O]^+$.

1,3-Dimesityl-2-methoxy-5,5-dimethyl-4,6-dioxohexahydropyrimidine (2): To a solution of *N*,*N*′-dimesitylformamidine (373 mg, 1.33 mmol) and Et_3N (0.28 mL, 2.0 mmol, 1.5 equiv.) in CH_2Cl_2 (5 mL) was added dimethylmalonyl dichloride (186 μL, 1.39 mmol, 1.05 equiv.) 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 (SiO_2; CH_2Cl_2/MeOH, 95:5) to afford the expected product as a white solid (540 mg, 99%); m.p. 185 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.94 (s, 4 H, CH_{Mes}), 5.28 [s, 1 H, N_2CH(OMe)], 2.83 (s, 3 H, OCH_3), 2.28 (s, 12 H, $CH_{3\ ortho}$), 2.27 (s, 6 H, $CH_{3\ para}$), 1.83 [s, 3 H, $C(CH_3)_2$], 1.58 [s, 3 H, $C(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ = 170.8 (*C*=O), 138.3, 138.0, 134.5, 133.4 (C_{Mes}), 129.9, 129.5 (CH_{Mes}), 98.5 [N_2CH(OMe)], 59.6 (OCH_3), 47.0 [$C(CH_3)_2$], 28.1 [$C(CH_3)_2$], 21.2 [$C(CH_3)_2$], 20.9 ($CH_{3\ para}$), 18.5 ($CH_{3\ ortho}$), 18.3 ($CH_{3\ ortho}$) ppm. IR (ATR): $\tilde{\nu}$ = 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) $[HC(NHMes)_2]^+$. $C_{25}H_{32}N_2O_3$ (408.53): calcd. C 73.50, H 7.90, N 6.86; found C 73.39, H 8.00, N 6.79.

1,3-Dimesityl-5,5-dimethylhexahydropyrimidin-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 equiv.) was added dropwise. The very pale yellow solution was stirred for 30 min, and S_8 (139 mg, 4.35 mmol) was added as a solid all at once. After 1 h of stirring at –80 °C, the cooling bath was removed, and the solution was warmed to room temperature. After evaporation of all volatiles, the crude product was purified by flash chromatography (SiO_2; hexane/CH_2Cl_2, 1:1 then 1:2) to yield **4** as a bright orange crystalline solid (573 mg, 68%); m.p. 282 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.97 (s, 4 H, CH_{Mes}), 2.32 (s, 6 H, $CH_{3\ para}$), 2.13 (s, 12 H, $CH_{3\ ortho}$), 1.79 [s, 6 H, $C(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ = 177.4 (*C*=S), 170.3 (*C*=O), 138.7, 134.4, 134.3 (C_{Mes}), 129.6 (CH_{Mes}), 48.6 [$C(CH_3)_2$], 25.0 [$C(CH_3)_2$], 21.2 ($CH_{3\ para}$), 17.5 ($CH_{3\ ortho}$) ppm. IR (ATR): $\tilde{\nu}$ = 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) $[M + H]^+$. $C_{24}H_{28}N_2O_2S$ (408.56): calcd. C 70.55, H 6.91, N 6.86; found C 70.53, H 6.96, N 6.78.

Chlorido(1,5-cyclooctadiene)(1,3-dimesityl-5,5-dimethyl-4,6-dioxotetrahydropyrimidin-2-ylidene)rhodium(I) (5): Compound **1** (143 mg, 0.346 mmol) was dissolved in thf (6 mL), and the solution was cooled to –40 °C. A solution of KHMDS in toluene (0.5 M, 0.73 mL, 0.36 mmol, 1.05 equiv.) was then added dropwise, and, after stirring for 30 min, $[RhCl(cod)]_2$ (85 mg, 0.17 mmol, 0.5 equiv.) was added as a solid all at once. After 15 min at that temperature, the cooling bath was removed and the reaction mixture warmed up to room temperature, during which time 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 Al_2O_3 type III; CH_2Cl_2) 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; m.p. 197 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.11 (s, 2 H, CH_{Mes}), 6.98 (s, 2 H, CH_{Mes}), 4.71 (br., 2 H, CH_{cod}), 3.23 (br., 2 H, CH_{cod}), 2.54 (s, 6 H, $CH_{3\ Mes}$), 2.39 (s, 6 H, $CH_{3\ Mes}$), 1.99 [s, 3 H, $C(CH_3)_2$], 1.98 (s, 6 H, $CH_{3\ Mes}$), 1.58–1.44 (m, 8 H, $CH_{2\ cod}$), 1.55 [s, 3 H, $C(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ = 245.2 (d, $^1J_{RhC}$ = 49.1 Hz, N_2C), 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 [$C(CH_3)_2$], 31.8 ($CH_{2\ cod}$), 29.8 [$C(CH_3)_2$], 27.2 ($CH_{2\ cod}$), 21.0 ($CH_{3\ Mes}$), 20.1 ($CH_{3\ Mes}$), 19.6 ($CH_{3\ Mes}$), 18.8 [$C(CH_3)_2$] ppm. IR (ATR): $\tilde{\nu}$ = 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). $C_{32}H_{40}ClN_2O_2Rh$ (623.03): calcd. C 61.69, H 6.47, N 4.50; found C 61.78, H 6.57, N 4.44.

Dicarbonyl(chlorido)(1,3-dimesityl-5,5-dimethyl-4,6-dioxotetrahydropyrimidin-2-ylidene)rhodium(I) (6): CO was bubbled into a solution of **5** (43 mg, 69 mmol) in CH_2Cl_2 (3 mL) for 10 min. From dark red, the solution gradually turned pale yellow. After 1 h of stirring, all volatiles were removed in vacuo. In order to thoroughly remove the liberated cyclooctadiene, pentane (2 × 3 mL) was added to the crude product, the mixture was sonicated and concentrated again. This procedure gave pure **6** as a pale yellow powder (39 mg, 98%); m.p. 235 °C (dec.). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.00 (s, 4 H, CH_{Mes}), 2.36 (s, 6 H, $CH_{3\ Mes}$), 2.34 (s, 6 H, $CH_{3\ Mes}$), 2.20 (s, 6 H, $CH_{3\ Mes}$), 1.92 [s, 3 H, $C(CH_3)_2$], 1.69 [s, 3 H, $C(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$): δ = 230.8 (d, $^1J_{RhC}$ = 43.4 Hz, N_2C), 184.6 (d, J_{RhC} = 53.9 Hz, Rh*C*O), 182.4 (d, J_{RhC} = 75.7 Hz, Rh*C*O), 169.9 (*C*=O), 139.8, 136.1, 134.9, 134.1 (C_{Mes}), 130.4 (CH_{Mes}), 129.4 (CH_{Mes}), 51.5 [$C(CH_3)_2$], 28.7 [$C(CH_3)_2$], 21.1 ($CH_{3\ Mes}$), 20.4 ($CH_{3\ Mes}$), 19.5 ($CH_{3\ Mes}$), 18.5 [$C(CH_3)_2$] ppm. IR (ATR): $\tilde{\nu}$ = 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 (CH_2Cl_2): $\tilde{\nu}$ = 2086.1 (CO), 2005.3 (CO), 1764.5, 1735.2 cm^{-1}. MS (ESI): *m*/*z* (%) = 611 (43) $[M - 2\ CO + 2\ CH_3CN + H]^+$, 507 (65) $[M - Cl - CO]^+$, 415 (100) $[M - Cl - Mes]^+$. $C_{26}H_{28}ClN_2O_4Rh$ (570.87): calcd. 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 CH_2Cl_2/pentane and thf/pentane, respectively. Data were collected at 180 K with a Bruker D8 Apex II diffractomer and an Oxford Diffraction Xcalibur diffractometer, respectiveley. All calculations were performed with a PC-compatible computer by using the WinGX system.[19] The structures were solved by 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 F_c. All non-hydrogen atoms were allowed to vibrate anisotropically. All the hydrogen atoms – except for olefinic H atoms of the cod ligand in **5** – were set in idealized positions [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 that of 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 positions and isotropic thermal parameters (arbitrarily set to 0.05 $Å^2$) were kept fixed during the final refinement. CCDC-755193 (**4**) and CCDC-755194 (**5**) contain the supplementary crystallographic data for this paper. These data can be ob-

tained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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