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# Reactivity of an Oxalamide-Based N-Heterocyclic Carbene

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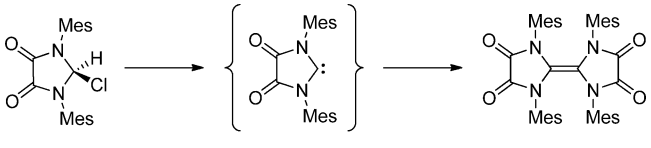
Supporting Information

**ABSTRACT:** The reactivity of the oxalamide-based carbene **2** was investigated. Treatment with styrene or methylacrylate proceeded under carbene addition to yield the respective cyclopropanation products **6a**,**b**. With elemental selenium the selenide **7** was obtained, which was characterized by X-ray diffraction. The Rh complex [(COD)RhCl(**2**)] (**10**) was also structurally characterized. From the IR spectrum of the dicarbonyl derivative [$(CO)_2$RhCl(**2**)] (**11**) a Tolman electronic parameter of 2068 $cm^{-1}$ was calculated for the diamidocarbene **2**, which characterizes this ligand as the least electron donating NHC known so far. The dimerization product of carbene **2**, the intensly fluorescing tetraamido ethylene **3**, showed an unexpected chemical stability. Treatment of the chloro compound **1a** with methanol afforded the methoxide **5a**, whose structure was determined by X-ray diffraction.

## INTRODUCTION

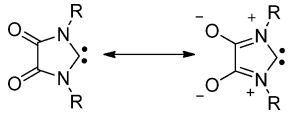
Since their isolation by Arduengo in 1991,[1] N-heterocyclic carbenes (NHCs) have found widespread and spectacular use as ligands in transition-metal catalysis[2] and as organocatalysts.[3] Apart from having widespread applications, NHCs are fascinating molecules in their own right and continue to stimulate various aspects of research. Today, their properties and reactivity are well investigated, and it is known that they are strong $\sigma$-donors and act as Lewis bases like phosphines. These concepts have been delineated in a number of excellent reviews.[4] However, in contrast to the strong $\sigma$-donor properties, potential $\pi$-acceptor contributions exerted by NHCs have been neglected for a long time. Meanwhile, theoretical[5] as well as experimental work indicates clearly that the $\pi$-acceptor character of NHCs can significantly contribute to the metal−NHC bonding interaction. Attempts to enforce $\pi$-back-bonding interactions included the attachment of electron-withdrawing groups to either the N-aryl groups or the heterocyclic carbene skeleton itself.[6] In a previous communication we reported the synthesis of the diamidocarbene **2**, which was obtained straightforwardly from the neutral oxalamide precursor **1a** (Scheme 1).[6e]

**Scheme 1. Preparation and Dimerization of Diamidocarbene 2**




NHC **2** was supposed to be a poorer electron donor compared to diaminocarbenes due to the amide resonance structures, which lead to a reduced stabilization of the empty $p_\pi$-orbital centered at the carbene carbon atom, which in turn should enforce stabilization through the metal center (Chart 1).

**Chart 1. Effect of the Amide Resonance on Carbene Stabilization**




The groups of César and Glorius reported the formation of a five-membered monoamidocarbene (MAC) independently,[7] followed by the reports of anionic and neutral six-membered diamidocarbenes (DACs) by César[8] and neutral six- and seven-membered DACs by the group of Bielawski.[9] Most recently, César described a six-membered diamidocarbene based on 4,5-dioxo-1,3,5-triazine and its behavior as an ambidentate Janus-type ligand system.[10]

In contrast to the analogous six- and seven-membered DACs, the five-membered derivative **2** is not stable as a monomeric species but dimerizes to the corresponding tetraamidoethylene **3** as a result of its small HOMO−LUMO gap[11] (Scheme 1). In this report we present the results of a comprehensive investigation of the reactivity of the oxalamide-based NHC **2** and the tetraamidoethylene **3**.

## RESULTS AND DISCUSSION

On the basis of the observation that the carbene **2** is not stable as a monomeric species, we tried to use more bulky groups attached to the nitrogen atoms to protect the carbene center and avoid the dimerization reaction. Like the mesityl compound **1a**,[12] the

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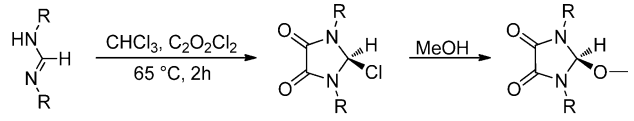
precursors **1b** and **1c** with sterically demanding Dipp and 1-adamantyl groups were obtained from the respective formamidines **4** and oxalylic chloride in good yield (Scheme 2). In

**Scheme 2. Syntheses and Reactivity of the Carbene Precursor**




**4a**, R = Mes
**4b**, R = Dipp
**4c**, R = Ad

**1a**, R = Mes
**1b**, R = Dipp
**1c**, R = Ad

**5a**, R = Mes
**5c**, R = Ad

the case of compound **4c** the addition of 1 equiv of triethylamine was necessary to capture the emerging hydrogen chloride. In the absence of triethylamine the *N*,*N*′-diadamantylformamidine **4c** will be protonated and the conversion to **1c** is limited to 50%. Unfortunately, the chloro compounds **1b**,**c** could not be deprotonated by NaHDMS, KO*t*Bu, LDA, or *n*BuLi to give the anticipated diamidocarbenes. For the 1-adamantyl derivative, addition of the base to a solution of **1c** in THF at −78 °C immediately initiated the formation of a white precipitate, which was insoluble in all common organic solvents including DMSO. No meaningful peaks could be detected in the EI-MS spectrum. When the Dipp derivative **1b** was subjected to deprotonation, a yellowish solid could be isolated after workup, which was identified to be neither the free NHC nor the dimer or the product of insertion of the intermediate carbene into the C−H unit of a Dipp-*i*Pr group, as was observed for a malonic diamido NHC by Bielawski and co-workers.[9a] Interestingly, the solubility of the precursors **1b** and **1c** was quite different. Like the mesityl compound **1a**, the Dipp derivative **1b** was soluble in all common solvents, while the 1-adamantyl compound **1c** was soluble only in THF. When methanol was added to a suspension of **1c** in chloroform, a colorless solution formed immediately due to the formation of the methoxy product **5c**, which in turn showed good solubility in common organic solvents. Unfortunately, we were not able to obtain a correct elemental analysis for this compound. The preparation of the related methoxide derivative with Dipp substituents attached to the N atoms has not been attempted. However, the analogous mesityl derivative **5a**, whose synthesis has been described before,[6e] could be crystallized from dichloromethane and hexane to give crystals suitable for an X-ray diffraction analysis. The molecular structure of the methoxide **5a** is shown in Figure 1 together with selected geometrical data. The structure is affected by a disorder of the molecule, which appears to be located on a crystallographic 2-fold axis, leading to disorder of the CHOMe unit (only one orientation is shown in Figure 1).

The observed bond lengths and angles are close to the values found for the derivative bearing 2,6-dimethylphenyl groups instead of mesityl[5d] and 2-methoxy-2-methylimidazolidine-4,5-dione[13] with trigonal-planar N atoms, shorter OC−N bonds, and longer N−CHOMe bonds as a consequence of the amide resonance. Accordingly, in the saturated derivative 2-methoxy-*N*,*N*′-dimesitylimidazolidine[14] the N−CHOMe bonds are shorter (average: 143.5 pm) than the N−$CH_2$ bonds (average: 146.3 pm) and the geometry around the N atoms is pyramidal.

We also investigated the reactivity of the air- and moisture-stable olefin **3**, which results from the dimerization of carbene **2** in the absence of trapping reagents. Olefin **3** does not react

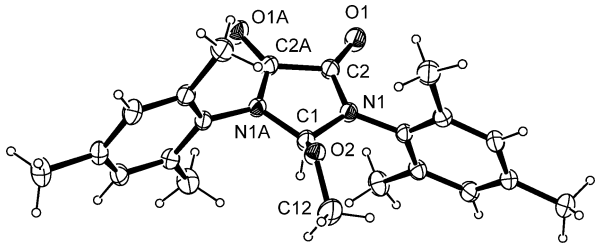



**Figure 1.** ORTEP representation of **5a** (ellipsoids drawn at the 40% probability level). Only one orientation of the disordered CHOMe group is shown. Selected distances (pm) and angles (deg): C1−O2 127.2(3), C12−O2 143.7(6), C1−N1 145.0(2), C2−O1 120.9(2), C2−C2A 153.3(4), C1−O2−C12 118.0(5), N1−C1−N1A 102.7(2), C1−N1−C2 112.78(16), O1−C2−C2A 126.37(12).

with $[(COD)RhCl]_2$ or with $CS_2$ to yield the corresponding rhodium-carbene complex or the NHC-dithiocarboxylate, respectively. Such reactions have been reported for electron-rich enetetramines by Lappert, Delaude, and Regitz.[15] Surprisingly, olefin **3** withstands the presence of 3-chloroperbenzoic acid or potassium permanganate without reaction. In each case the olefin **3** is recovered in almost quantitative yield after workup. The group of Beckert reported a photooxygenation reaction of 1,4,5,8-tetraazafulvalenes with singlet oxygen, leading to rupture of the C−C double bond and concomitant formation of the corresponding imidazolidine-2-one. In the case of **3**, however, no reaction with singlet oxygen was observed leading to *N*,*N*′-dimesitylimidazolidine-2,4,5-trione.[16]

An interesting feature of compound **3** is its strong yellow fluorescence. Figure 2 shows the UV−vis and fluorescence

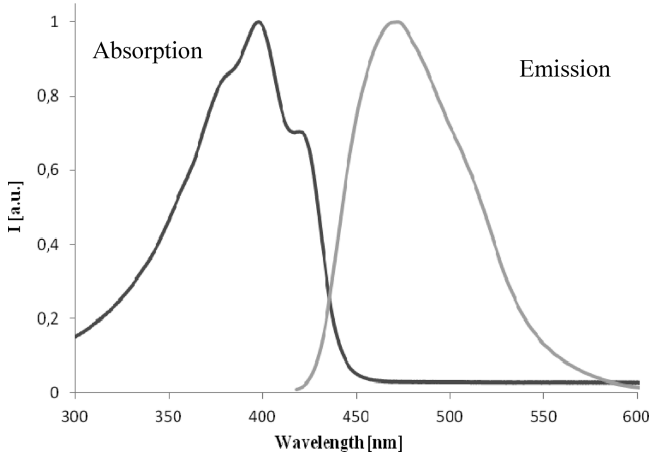



**Figure 2.** UV−vis and fluorescence spectra of **3** ($6.1 \times 10^{-2}$ mg/mL) in $CH_2Cl_2$ at room temperature.

spectra recorded in dichloromethane at room temperature. The absorption is characterized by a strong band at 398 nm with an extinction coefficient of $\varepsilon$ = 27 000 L/mol cm, whereas a Stokes shift of 75 nm (3984 $cm^{-1}$) is observed for the emission peak at 473 nm. Compared to a 1,4,5,8-tetraazafulvalene,[17] whose absorption was detected at 330 nm with an extinction of $\varepsilon$ = 8000 L/mol cm, the absorption of the tetraamidoethylene **3** is significantly shifted into the visible region and is also much more intense. Bielawski and co-workers reported a series of dibenzotetraazafulvalenes which showed absorption bands between 400 and 464 nm with extinctions ranging from 8000 to 10 000 L/mol cm.[18]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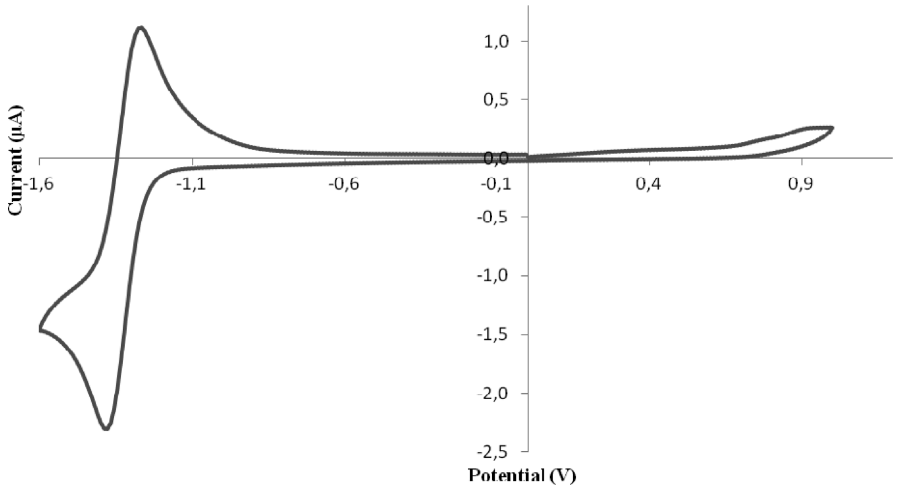
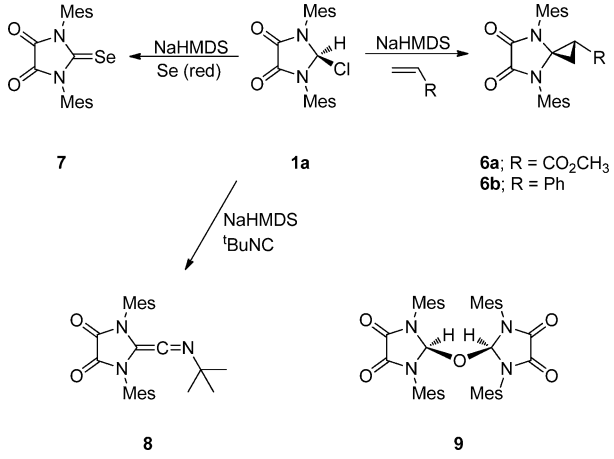



**Figure 3.** CV of **3** obtained in dry $CH_2Cl_2$ with 0.1 M $n$Bu$_4$NPF$_6$ electrolyte using a 100 mV s$^{-1}$ scan rate and referenced to Fc$^+$/Fc.

In addition, the redox properties of olefin **3** were evaluated by cyclic voltammetry (Figure 3). The CV shows a reversible redox step at a fairly low potential of $E_{1/2}$ = −1325 mV, attributed to the reduction of the carbonyl moiety of **3** in analogy with the findings reported by Bielawski and co-workers for a quinone annelated carbene system.[6b] No oxidation wave was detected up to 1000 mV.

The reactivity of carbene **2** toward electron-rich as well as electron-poor olefinic double bonds was also evaluated. Thus, the carbene was prepared *in situ* and treated with styrene and methyl acrylate, respectively, leading to the formation of the cyclopropanes **6a,b** in moderate to good yield (Scheme 3).

**Scheme 3. Reactivity toward Several Substituted Olefins and Trapping with Selenium or Isonitriles**




Cyclopropanation reactions with electron-poor acrylates have already been reported for (phosphanyl)(silyl)carbenes,[19] (alkyl)(amino)carbenes,[20] and a ferrocene-derived diaminocarbene.[21] Interestingly, the electron-poor carbene **2** reacted preferentially with the electron-poor methyl acrylate, affording the product in higher yield and without formation of dimer **3** as a side product, whereas carbene dimerization competed significantly with the cyclopropanation in the case of styrene. Olefin **3** could not be removed completely by column chromatography and thus prevented the isolation of **6b** in analytically pure form. When **6a** was recrystallized from dichloromethane and hexane, colorless crystals were obtained, which were identified by X-ray diffraction to consist of *N,N*′-dimesityloxaldiamide, whose structure was already reported by Połoński and co-workers in 2007.[22] The formation of this compound is unclear. Remarkably, a solution of **6a** in $CDCl_3$ in the presence of water showed no degradation over a period of several days in the $^1$H NMR spectrum.

Similar to the formation of a thione, carbene **2** could also be trapped by reaction with elemental selenium in good yield. Dark red crystals suitable for an X-ray diffraction analysis were grown by slow diffusion of hexane into a solution of **7** in dichloromethane. The molecular structure of selenide **7** is shown in Figure 4 together with some representative geometric parameters.

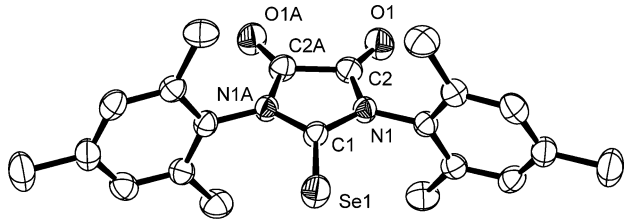



**Figure 4.** ORTEP representation of **7** (ellipsoids drawn at 30% probability; H atoms are omitted for clarity). Selected distances (pm) and angles (deg): C1−Se1 177.7(4), C1−N1 137.6(3), N1−C2 137.4(4), C2−O1 119.2(3), C2−C2A 153.6(6), Se1−C1−N1 125.98(15), C1−N1−C2 111.4(2), N1−C2−O1 127.9(3), O1−C2−C2A 127.55(18).

Compared to the large number of structurally characterized carbene sulfur adducts, only a couple of related selenium compounds have been described.[23] Interestingly, among these derivatives, the closely related *N,N*′-diethylimidazolidine-2-selenone-4,5-dione[24] features almost identical geometric parameters.

The reaction of **2** with *tert*-butyl isonitrile leading to the formation of keteneimine **8** has been described in our previous report.[6e] While various attempts to obtain X-ray quality crystals of ketenimine **8** failed, a degradation product (**9**) was identified by X-ray diffraction in one case (Figure 5). Formally, the ether **9** is derived by addition of the two O−H bonds of a water molecule to the carbene C atoms of two molecules of **2**. However, when *in situ* generated DAC **2** was reacted with water, the formation of **9** was not observed. Instead, olefin **3** was isolated under these conditions in moderate yield as the only identifiable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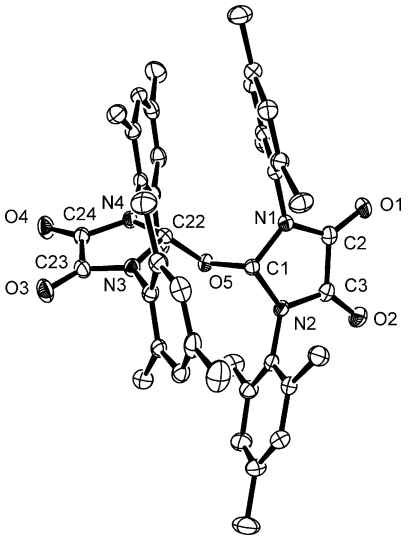
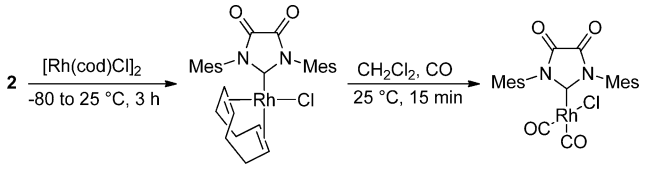



**Figure 5.** ORTEP representation of **9** (ellipsoids drawn at 30% probability; H atoms are omitted for clarity). Selected distances (pm) and angles (deg): C1−O5 142.2(4), C22−O5 141.6(4), C1−N2 145.5(4), C3−O2 120.2(4), C2−C3 152.2(6), C22−N3 145.9(5), N3−C23 135.5(5), C23−O3 120.5(5), C23−C24 152.9(6), C1−O5−C22 116.2(3), O5−C1−N2 108.2(3), N1−C1−O5 113.7(3), O5−C22−N3 114.2(3), O5−C22−N4 109.3(3).

product. The structural parameters of the two heterocyclic components of compound **9** are close to the values observed for the methoxide **5a** (*vide supra*). In order to avoid steric repulsion between the bulky mesityl groups, the ring planes of the heterocycles form an angle of 74.5°.

The propensity of **2** to coordinate to metal fragments has already been demonstrated in our previous communication by the preparation of the rhodium complexes **10** and **11** according to Scheme 4.[6e] In extension of this report, we were now able

**Scheme 4. Generation of the Carbene Metal Complex and Conversion into the Dicarbonyl Complex**




10 11

to determine the crystal structure of the (COD)Rh complex **10**, which is depicted in Figure 6 together with some relevant geometrical data.

The Rh atom is coordinated in a slightly distorted square-planar environment with an exceptionally short Rh1−C1 distance of 194.2(3) pm. This distance is fairly short compared to other Rh−C(NHC) distances for MACs, DACs, or NHCs derived from the imidazole core,[6a,g,8a,b,9b,25] which are typically found in the range from 200 to 205 pm. As is commonly observed, the Rh−C(COD) bonds *trans* to chlorine are shorter (213.3(3) and 214.7(3) pm) than those *trans* to the NHC ligand (225.5(3) and 228.6(3) pm) compared with other (NHC)Rh(COD)Cl complexes. Overall, the geometrical features observed for the Rh complex **10** are very close to the data found for the analogous Ir compound.[6e]

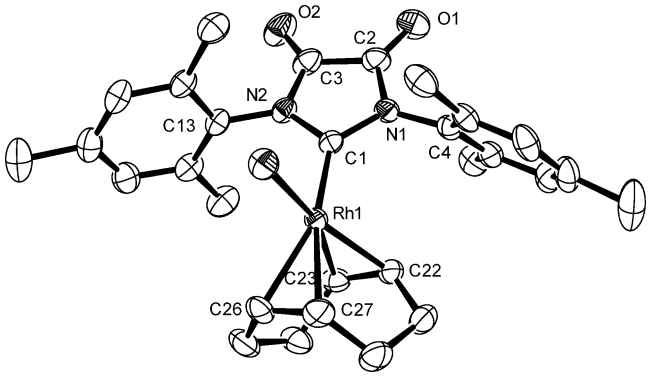



**Figure 6.** ORTEP representation of **10** (ellipsoids drawn at the 30% probability level; H atoms are omitted for clarity). Selected distances (pm) and angles (deg): Rh1−Cl1 236.93(9), Rh1−C1 194.2(3), Rh1−C22 213.3(3), Rh1−C23 214.7(3), Rh1−C26 225.5(3), Rh1−C27 228.6(3), N1−C1−N2 105.9(2), C1−Rh1−Cl1 94.69(9).

The IR spectrum of the dicarbonyl complex **11** shows two strong CO stretching vibrations at 2017 and 2103 $cm^{-1}$ ($\nu_{av}$ = 2060 $cm^{-1}$), which were converted to a Tolman electronic parameter (TEP) value of 2068 $cm^{-1}$ using a relation established by Nolan and Plenio.[6f,26]

TEP values are a common measure for the donor properties of Lewis bases including a large number of NHCs. Selected values are compiled in Table 1 together with the corresponding Rh−C(NHC) distances derived from X-ray diffraction analyses. The parent saturated and unsaturated system (entries 5 and 6) feature TEP values of ca. 2053 $cm^{-1}$. The presence of an anionic alcoholate (entry 2) or alkoxy group (entry 4) leads to an enhanced donor capability and hence to a significant decline of TEP values. In contrast, the introduction of keto groups to the backbone—leading to amido functional groups—is accompanied by a reduced donor strength due to the involvement of the nitrogen lone pair in the amide resonance (see Chart 1), which in turn leads to a reduced stabilization of the carbenic center. Accordingly, TEP values shifted to higher wavenumbers are expected and indeed observed, as can be seen from the values in Table 1: introduction of one carbonyl group results in a moderately shifted TEP (entry 9), while the diamido derivative **2** is characterized by one of the highest TEP values reported so far for a NHC (entry 12), being on the same order as the dicyano compound in entry 11. Interestingly, the TEP of the malonic diamide (entry 7) is on the same order as that of the five-membered monoamide (entry 9), while the anionic malonic diamide derivative features a much lower TEP, as expected (entry 1). It is noteworthy that the neutral seven-membered DAC derived from phthalic diamide (entry 3) features a lower TEP than the diamino derivatives in entries 5 and 6. Collectively, the two neighboring carbonyl groups in the oxalamide NHC **2** exert a strong electron-withdrawing effect of comparable strength to the two cyano groups in the backbone (entry 11). Just as anionic charge leads to enhanced donor strength, the opposite effect is expected for cationic derivatives. Indeed, we recently reported a benzimidazole-based NHC with a cationic $Cp^*Ru^+$ fragment attached to the six-membered ring (entry 10), which shows a fairly high TEP value. It is tempting to correlate the observed TEP values with the corresponding Rh−C distances. At first glance, for the five-membered diamino, monoamido, and diamido derivatives (entries 6, 9, and 12) an increase of the TEP is paralleled by a shortening of the Rh−C bond. This is in accord with theoretical results that especially the DAC **2** is


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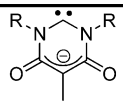
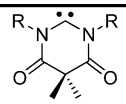
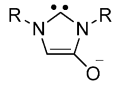
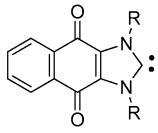
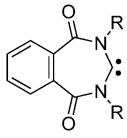
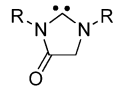
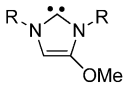
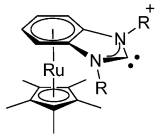
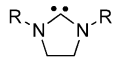
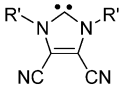
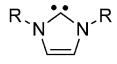
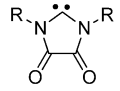
**Table 1. Comparison of Several NHC Ligands Regarding Their Metal Carbene Distances and TEP Values**

| entry | ligand | Rh-C(NHC)[a] | TEP[b] | entry | ligand | Rh-C(NHC)[a] | TEP[b] |
|---|---|---|---|---|---|---|---|
| 1[8c] |  | 203.6(2) | 2043[c] | 7[8b] |  | 201.07(19) | 2057[c] |
| 2[27] |  | - | 2044[c] | 8[6b] |  | 203.2(8) | 2057[d] |
| 3[9b] |  | 205.1(6) | 2049[f] | 9[27] |  | 202.0(3) | 2058[e] |
| 4[27] |  | 204.4(4) | 2050[c] | 10[28] |  | 199.8(10) | 2061[c] |
| 5[6f] |  | - | 2053[c] | 11[6a] |  | 200.6(6) | 2066[e] |
| 6[6f] |  | 204.94(16) | 2053[c] | 12 |  | 194.2(3) | 2068[c] |

[a]Rh−C(NHC) distance in pm in (NHC)Rh(COD)Cl. [b]Tolman electronic parameter (TEP) in $cm^{-1}$. [c]Calculated from $\nu$(CO) in $CH_2Cl_2$. [d]Calculated from $\nu$(CO) in $CHCl_3$. [e]Calculated from $\nu$(CO) in $CDCl_3$. [f]Calculated from $\nu$(CO) in KBr.

capable of acting significantly in a metal-to-carbene $\pi$-back-bonding interaction, which leads to a short and strong Rh−C bond despite the fact that the donor strength of this ligand is reduced compared to diaminocarbenes, which are known to act as superb $\sigma$-donors. The same trend holds for the dicyano and the cationic derivatives (entries 11 and 10). However, steric effects can certainly not be ignored. Thus, increasing NHC ring size (six- and seven-membered, entries 7, 1, and 3) is expected to push the nitrogen substituents toward the coordination site, which should result in elongated Rh−C bonds compared to the smaller five-membered systems. Moreover, care has to be taken when comparing TEP values from different studies, as the positions of IR bands are known to depend on the solvent used for the measurement. Nevertheless, the data provided in Table 1 can certainly be taken as a suitable guideline for the classification of NHCs according to their ligand properties.

## CONCLUSION

In conclusion, the diamidocarbene **2** displays a rich chemistry, including adduct formation with sulfur and selenium, cyclopropanation reactions, and the formation of transition-metal complexes. In these complexes, carbene **2** is the least electron donating NHC described so far, and a significant metal-to-ligand $\pi$-back-bonding is assumed to augment the metal−NHC bonding, in accord with the short Rh−C distance observed in complex **10**.

## EXPERIMENTAL SECTION

**Materials and Methods.** All manipulations were performed under an inert gas atmosphere of dry nitrogen by using standard vacuum line and Schlenk techniques. Glassware was dried at 120 °C in an oven for at least 12 h. THF and diethyl ether were distilled from sodium/benzophenone, hexane was distilled from sodium, and dichloromethane and chloroform were dried over $CaH_2$ and subsequently distilled. All solvents were stored under an atmosphere of nitrogen. NMR spectra were recorded on Bruker DRX200 or DRX500 spectrometers. Chemical shifts are reported in ppm ($\delta$) compared to TMS ($^1$H and $^{13}$C) using the residual peak of deuterated solvents as internal standard ($^1$H: $CDCl_3$ 7.26 ppm; THF-$d_8$ 3.58 ppm; $^{13}$C: $CDCl_3$ 77.0 ppm; THF-$d_8$ 67.21 ppm). Coupling constants ($J$) are quoted in Hz. Infrared spectra were obtained on a Shimadzu IRAffinity-1 spectrometer. Elemental analyses were recorded on a Perkin CHN 2400 series II. For MS data a Thermo Finnigan Trace DSQ (EI) and a Bruker Ultrafelx I TOF (MALDI) were used. UV−vis measurements were performed on a Hewlett-Packard 84252 diode array spectrophotometer, and the fluorescence measurements were performed on a Perkin-Elmer LS55.

Cyclovoltametric measurements were performed on a Metrohm $\mu$-Autolab Type III using an Ag/AgCl electrode in dry $CH_2Cl_2$ with 0.1 M $n$-$Bu_4NPF_6$ electrolyte using a 100 mV $s^{-1}$ scan rate and referenced to $Fc^+$/Fc.

*N*,*N*′-Dimesitylformamidine[29] and *N*,*N*′-bis(2,6-diisopropylphenyl)-formamidine[29] were prepared according to literature procedures. Oxalyl chloride was purchased from Merck Chemicals; sodium bis(trimethylsilyl)-amide (NaHMDS) (2 M in THF), styrene, and methyl acrylate were purchased from Acros Organics. The commercially available chemicals were used without further purification. Column chromatography was performed on Merck silica gel 60 (0.040−0.063 mm), which was oven-dried for at least 24 h.

**4c.** Acetic acid (710 $\mu$L) was added to a round-bottom flask charged with 1.88 g (12.43 mmol) of 1-adamantylamine and 10 mL of triethyl orthoformate. The resulting suspension was refluxed for 4 h, and while cooling to ambient temperature a white solid started to settle. The precipitation was completed by adding 40 mL of hexane. The crude product was filtered and dissolved in dichloromethane, and 10 mL of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2 N NaOH was added. The phases were separated, and the aqueous phase was washed three times with 5 mL of dichloromethane. The combined organic phases were dried over sodium sulfate and dried *in vacuo* to obtain a white powder in 60% yield. $^1$H NMR (500 MHz in $CDCl_3$): $\delta$ 1.64−1.70 (m, 24H, $CH_2$), 2.07 (s, 6H, CH), 7.60 (s, 1H, C2−H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz in $CDCl_3$): $\delta$ 29.66 (s, $\underline{C}H_{2\ adamantyl}$), 36.43 (s, $\underline{C}H_{adamantyl}$), 44.50 (s, $\underline{C}_{adamantyl}$), 145.97 (s, NH-$\underline{C}$H=N) ppm. MS (EI): $m/z$ 312 ($M^+$, 90%). IR (ATR): $\nu$ 2898, 2844, 1653, 1088 $cm^{-1}$. Anal. Calcd (%) for $C_{21}H_{32}N_2$ (312.15): C 80.71, H 10.32, N 8.96. Found: C 80.07, H 9.33, N 8.93.

**1b.** To a chloroform solution (20 mL) of 1.49 g (11.74 mmol) of oxalyl chloride was added dropwise and with stirring a dilute chloroform solution (20 mL) of 4.0 g (10.97 mmol) of *N*,*N*′-bis(2,6-diisopropylphenyl)formamidine while the reaction temperature was maintained around 0 °C. The resulting colorless solution was heated to reflux for 2 h. After removing the solvent *in vacuo*, the crude product was washed with hexane (3 × 5 mL) and dried *in vacuo* to obtain a white powder in 98% yield. $^1$H NMR (200 MHz in $CDCl_3$): $\delta$ 1.24 (d, 6H, $^3J_{HH}$ = 6.8 Hz, $CH_{3\text{-}iPr}$), 1.29 (d, 6H, $^3J_{HH}$ = 6.8 Hz, $CH_{3\text{-}iPr}$), 1.32 (d, 6H, $^3J_{HH}$ = 6.8 Hz, $CH_{3\text{-}iPr}$), 1.34 (d, 6H, $^3J_{HH}$ = 6.8 Hz, $CH_{3\text{-}iPr}$), 2.80 (sept, 2H, $^3J_{HH}$ = 6.8 Hz, $H_{iPr}$), 3.10 (sept, 2H, $^3J_{HH}$ = 6.8 Hz, $H_{iPr}$), 6.93 (s, 1H, C2-H), 7.38−7.28 (m, 4H, $CH_{Ring}$), 7.50 (t, 2H, $^3J_{HH}$ = 7.8 Hz, $CH_{Ring}$) ppm. $^{13}C\{^1H\}$ NMR (126 MHz in $CDCl_3$): $\delta$ 23.40 (s, $\underline{C}H_{3\ iPr}$), 24.13 (s, $\underline{C}H_{3\ iPr}$), 24.99 (s, $\underline{C}H_{3\ iPr}$), 25.10 (s, $\underline{C}H_{3\ iPr}$), 29.53 (s, $\underline{C}(CH_3)_{2\ iPr}$), 29.57 (s, $\underline{C}(CH_3)_{2\ iPr}$), 86.44 (s, N$\underline{C}$N), 124.32 (s, $\underline{C}H_{Ring}$), 125.37 (s, $\underline{C}H_{Ring}$), 126.87 (s, $\underline{C}_{Ring}$), 130.89 (s, $\underline{C}H_{Ring}$), 145.71 (s, $\underline{C}C(CH_3)_{2\ Ring}$), 148.91 (s, $\underline{C}C(CH_3)_{2\ Ring}$), 156.45 (s, $\underline{C}$O) ppm. MS (EI, 70 eV): $m/z$ 455 ($M^+$, 3%), 420 ($[M - Cl]^+$, 28%). IR (ATR): $\nu$ 1758 (C=O) $cm^{-1}$. Anal. Calcd (%) for $C_{27}H_{35}ClN_2O_2$ (455.03): C 71.27, H 7.75, N 6.16. Found: C 71.50, H 8.40, N 5.78.

**1c.** To a chloroform solution (10 mL) of 503 mg (3.96 mmol) of oxalyl chloride was added dropwise and with stirring a dilute chloroform solution (10 mL) of 1.48 g (3.67 mmol) of *N*,*N*′-diadamantylformamidine and 510 $\mu$L (3.67 mmol) of triethylamine while the reaction temperature was maintained around 0 °C. The resulting yellow solution was heated to reflux for 2 h. After removing the solvent *in vacuo*, the crude product was suspended in THF and the insoluble triethylammonium chloride was removed over a thin pad of Celite. After removing the solvent *in vacuo*, the crude product was washed with hexane (2 × 5 mL) and dried *in vacuo* to obtain a yellow powder in 80% yield. $^1$H NMR (500 MHz in THF-$d_8$): $\delta$ 1.70−1.76 (m, 12H, $CH_2$), 2.10 (s, 6H, CH), 2.24−2.32 (m, 12H, $CH_2$), 6.10 (s, 1H, C2-H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz in THF-$d_8$): $\delta$ 30.57 (s, $\underline{C}H_{2\ adamantyl}$), 37.01 (s, $\underline{C}H_{2\ adamantyl}$), 39.93 (s, $\underline{C}H_{adamantyl}$). 56.65 (s, $\underline{C}_{adamantyl}$), 85.66 (s, N$\underline{C}$N), 158.05 (s, $\underline{C}$=O) ppm. MS (MALDI): $m/z$ 367.1 ($[M + Cl^-]$, 100%). IR (ATR): $\nu$ 1735 (C=O) $cm^{-1}$. Anal. Calcd (%) for $C_{23}H_{31}N_2ClO_2$ (402.96): C 68.56, H 7.75, N 6.95. Found: C 69.40, H 8.35, N 7.14.

**5c. 4c** (100 mg, 0.29 mmol) was suspended in chloroform (30 mL) before methanol (5 mL) was added. The resulting solution was heated to reflux for 1 h. After removing the solvent *in vacuo*, the crude product was washed with hexane (2 × 5 mL) and dried *in vacuo* to obtain a white powder in 99% yield. $^1$H NMR (500 MHz in $CDCl_3$): $\delta$ 1.67−1.74 (m, 12H, $CH_2$), 2.13 (s, 6H, CH), 2.21 (s, 12H, $CH_2$), 3.01 (s, 3H, $OCH_3$), 6.10 (s, 1H, C2-H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz in $CDCl_3$): $\delta$ 29.42 (s, $\underline{C}H_{2\ adamantyl}$), 36.03 (s, $\underline{C}H_{2\ adamantyl}$), 39.07 (s, $\underline{C}H_{adamantyl}$), 46.23 (s, $O\underline{C}H_3$), 57.42 (s, $\underline{C}_{adamantyl}$), 87.51 (s, N$\underline{C}$N), 158.31 (s, $\underline{C}$=O) ppm. MS (MALDI): $m/z$ 398 ($M^+$, 100%). IR (ATR): $\nu$ 1725 (C=O) $cm^{-1}$. Analysis Calcd (%) for $C_{24}H_{34}N_2O_3$ (398.54): C 72.33, H 8.60, N 7.03. Found: C 70.82, H 8.25, N 6.84.

**(7).** 2-Chloro-1,3-dimesitylimidazolidine-4,5-dione (500 mg, 1.348 mmol) was dissolved in THF (15 mL) and cooled to −80 °C. NaHMDS (750 $\mu$L, 2 M in THF, 1.05 equiv) was added dropwise. The red solution was stirred for 5 min, and elemental selenium (red) (300 mg, 3.800 mmol) was added. After 30 min of stirring, 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 ($SiO_2$; $CH_2Cl_2$) to yield **7** as a gray-brown solid (446 mg, 80%). Crystals suitable for an X-ray diffraction analysis were obtained by slow diffusion of hexane into a saturated solution of **7** in dichloromethane. $^1$H NMR (200 MHz in $CDCl_3$): $\delta$ 2.18 (s, 12H, $CH_{3\ Mes}$), 2.36 (s, 6H, $CH_{3\ Mes}$), 7.04 (s, 4H, $CH_{Mes}$) ppm. $^{13}C\{^1H\}$ NMR (126 MHz in $CDCl_3$): $\delta$ 17.75 (s, $\underline{C}H_{3\ Mes}$), 19.43 (s, $\underline{C}H_{3\ Mes}$), 128.32 (s, $\underline{C}_{Mes}$), 129.61 (s, $\underline{C}H_{Mes}$), 135.71 (s, $\underline{C}CH_{3\ Mes}$), 140.61 (s, $\underline{C}CH_{3\ Mes}$), 154.60 (s, $\underline{C}$O), 182.09 (s, $\underline{C}$=Se) ppm. MS (EI, 70 eV): $m/z$ 414 ($M^+$, 85%). IR (ATR): $\nu$ 1763 (C=O) $cm^{-1}$. Anal. Calcd (%) for $C_{21}H_{22}N_2O_2Se$ (413.37): C 61.02, H 5.36, N 6.78. Found: C 60.95, H 5.49, N 6.81.

**(6a).** 2-Chloro-1,3-dimesitylimidazolidine-4,5-dione (505 mg, 1.360 mmol) and 300 $\mu$L (3.31 mmol) of methyl acrylate were dissolved in THF (15 mL) and cooled to −80 °C. NaHMDS (750 $\mu$L, 2 M in THF, 1.05 equiv) was added dropwise, and the resulting yellow solution was stirred at −80 °C. After 45 min of stirring, the cooling bath was removed and the solution was allowed to warm to room temperature. After removing the solvent *in vacuo*, the crude product was purified by flash chromatography ($SiO_2$; diethyl ether) to yield **6a** as a white solid (397 mg, 70%). $^1$H NMR (500 MHz in $CDCl_3$): $\delta$ 1.44 (dd, 1H, $^3J_{HH}$ = 10.4 Hz, $^3J_{HH}$ = 7.6 Hz, CHCOOMe), 1.93 (dd, 2H, $^2J_{HH}$ = 9.1 Hz, $^3J_{HH}$ = 7.6 Hz, $CH_2$), 1.93 (dd, 2H, $^2J_{HH}$ = 9.1 Hz, $^3J_{HH}$ = 10.4 Hz, $CH_2$), 2.12 (s, 3H, $CH_{3\ Mes}$), 2.23 (s, 3H, $CH_{3\ Mes}$), 2.26 (s, 3H, $CH_{3\ Mes}$), 2.30 (s, 3H, $CH_{3\ Mes}$), 2.31 (s, 3H, $CH_{3\ Mes}$), 2.34 (s, 3H, $CH_{3\ Mes}$), 3.44 (s, 3H, $OCH_3$), 6.92−7.03 (s, 4H, $CH_{Mes}$) ppm. $^{13}C\{^1H\}$ NMR (50 MHz in $CDCl_3$): $\delta$ 10.07 (s, $\underline{C}H_2$), 17.87 (s, $\underline{C}H_{3\ Mes}$), 18.07 (s, $\underline{C}H_{3\ Mes}$), 18.31 (s, $\underline{C}H_{3\ Mes}$), 20.94 (s, $\underline{C}H_{3\ Mes}$), 21.07 (s, $\underline{C}H_{3\ Mes}$), 21.13 (s, $\underline{C}H_{3\ Mes}$), 21.58 (s, $\underline{C}HCOOCH_3$), 22.00 (s, $\underline{C}H_{3\ Mes}$), 52.56 (s, $O\underline{C}H_3$), 63.59 (s, N$\underline{C}$N), 125.75 (s, $\underline{C}_{ipso\ Mes}$), 127.76 (s, $\underline{C}_{ipso\ Mes}$), 129.32 (s, $\underline{C}H_{Mes}$), 129.84 (s, $\underline{C}H_{Mes}$), 130.03 (s, $\underline{C}H_{Mes}$), 130.24 (s, $\underline{C}H_{Mes}$), 135.27 (s, $\underline{C}CH_{3\ Mes}$), 136.83 (s, $\underline{C}CH_{3\ Mes}$), 137.29 (s, $\underline{C}CH_{3\ Mes}$), 137.61 (s, $\underline{C}CH_{3\ Mes}$), 139.80 (s, $\underline{C}CH_{3\ Mes}$), 140.52 (s, $\underline{C}CH_{3\ Mes}$), 156.63 (s, $\underline{C}$=O), 157.81 (s, $\underline{C}$=O), 166.73 (s, $O\underline{C}H_3$) ppm. MS (MALDI): $m/z$ 421 ($M^+$, 100%), 334 ($[M^+ - CH_2CHCOOCH_3]$, 20%). IR ($CDCl_3$): $\nu$ 1749 (C=O) $cm^{-1}$. Anal. Calcd (%) for $C_{15}H_{28}N_2O_4$ (420.50): C 71.74, H 6.71, N 6.66. Found: C 71.21, H 6.56, N 6.58.

**(6b).** 2-Chloro-1,3-dimesitylimidazolidine-4,5-dione (500 mg, 1.348 mmol) and 1.5 mL (13.11 mmol) of styrene were dissolved in THF (15 mL) and cooled to −80 °C. NaHMDS (750 $\mu$L, 2 M in THF, 1.05 equiv) was added dropwise, and the resulting yellow solution was stirred at −80 °C. After 35 min of stirring, the cooling bath was removed and the solution was allowed to warm to room temperature. After removing the solvent *in vacuo*, the crude product was purified by flash chromatography ($SiO_2$; diethyl ether) to yield **6b** as a white solid (266 mg, 45%). $^1$H NMR (500 MHz in $CDCl_3$): $\delta$ 1.29 (s, 3H, $CH_{3\ Mes}$), 1.55 (dd, 1H, $^3J_{HH}$ = 11.7 Hz, $^3J_{HH}$ = 7.8 Hz, CH-Ph), 1.93 (dd, 2H, $^2J_{HH}$ = 9.7 Hz, $^3J_{HH}$ = 7.8 Hz, $CH_2$), 2.24 (s, 3H, $CH_{3\ Mes}$), 2.29 (s, 3H, $CH_{3\ Mes}$), 2.30 (s, 3H, $CH_{3\ Mes}$), 2.33 (s, 3H, $CH_{3\ Mes}$), 2.48 (s, 3H, $CH_{3\ Mes}$), 2.37 (dd, 2H, $^2J_{HH}$ = 9.7 Hz, $^3J_{HH}$ = 11.7 Hz, $CH_2$), 6.44−6.64 (m, 4H, $CH_{Mes}$), 6.94−7.13 (m, 5H, Ph) ppm. $^{13}C\{^1H\}$ NMR (126 MHz in $CDCl_3$): $\delta$ 8.90 (s, $\underline{C}H_2$), 17.24 (s, $\underline{C}$H-Ph), 18.29 (s, $\underline{C}H_{3\ Mes}$), 18.47(s, $\underline{C}H_{3\ Mes}$), 18.55 (s, $\underline{C}H_{3\ Mes}$), 20.96 (s, $\underline{C}H_{3\ Mes}$), 21.10 (s, $\underline{C}H_{3\ Mes}$), 63.63 (s, N$\underline{C}$N), 126.38 (s, $\underline{C}_{ipso}$ Ph), 126.96 (s, $\underline{C}$H Ph), 127.99 (s, $\underline{C}$H Ph), 128.17 (s, $\underline{C}_{ipso\ Mes}$), 128.41 (s, $\underline{C}_{ipso\ Mes}$), 129.14 (s, $\underline{C}H_{Mes}$), 129.39 (s, $\underline{C}H_{Mes}$), 130.00 (s, $\underline{C}H_{Mes}$), 130.08 (s, $\underline{C}H_{Mes}$), 131.59 (s, $\underline{C}$H Ph), 134.90 (s, $\underline{C}CH_{3\ Mes}$), 136.89 (s, $\underline{C}CH_{3\ Mes}$), 136.98 (s, $\underline{C}CH_{3\ Mes}$), 139.14 (s, $\underline{C}CH_{3\ Mes}$), 134.41 (s, $\underline{C}CH_{3\ Mes}$),140.24 (s, $\underline{C}CH_{3\ Mes}$), 156.92 (s, $\underline{C}$=O), 157.84 (s, $\underline{C}$=O) ppm. MS (MALDI): $m/z$ 439 ($M^+$, 100%).

**Crystal Structure Determinations.** Crystals of compounds **5a**, **7**, **9**, and **10** suitable for X-ray study were selected by means of a polarization microscope and investigated with a STOE imaging plate diffraction system and an Oxford Diffraction Xcalibur diffractometer, respectively, using graphite-monochromatized Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å). Unit cell parameters were determined by least-squares refinements on the positions of 8000, 8000, 31 779, and 8000 reflections, respectively. Space groups no. 60, no. 43, no. 19, and no. 14 were uniquely determined for **5a**, **7**, **9**, and **10**, respectively. Corrections for Lorentz and polarization effects were applied. The structures were solved by direct methods[30] and subsequent $\Delta F$ syntheses.[31]

Table 2. Crystal Data and Structure Refinement for Compound 5a, 7, 9, and 10

| | 5a | 7 | 9 | 10 |
|---|---|---|---|---|
| CCDC no. | 855559 | 855560 | 855561 | 855562 |
| empirical formula | $C_{22}H_{26}N_2O_3$ | $C_{21}H_{22}N_2O_2Se$ | $C_{43}H_{48}Cl_2N_4O_5$ | $C_{29}H_{34}ClN_2O_2Rh$ |
| fw | 366.45 | 413.37 | 771.75 | 580.94 |
| temperature (K) | 291(2) | 291(2) | 291(2) | 291(2) |
| cryst syst | orthorhombic | orthorhombic | orthorhombic | monoclinic |
| space group | *Pbcn* | *Fdd*2 | $P2_12_12_1$ | $P2_1/n$ |
| unit cell dimensions (Å, deg) | $a$ = 15.3988(9) | $a$ = 11.2248(5) | $a$ = 13.0623(4) | $a$ = 11.3659(7) |
| | $b$ = 8.1980(4) | $b$ = 32.4746(18) | $b$ = 16.4429(5) | $b$ = 15.1471(6) |
| | $c$ = 16.2972(10) | $c$ = 11.1989(5) | $c$ = 19.0786(7) | $c$ = 15.9812(10) |
| | | | | $\beta$ = 98.205(7) |
| volume (Å$^3$) | 2057.3(2) | 4082.2(3) | 4097.7(2) | 2723.2(3) |
| $Z$ | 4 | 8 | 4 | 4 |
| density$_{calc}$ (Mg/m$^3$) | 1.183 | 1.345 | 1.251 | 1.417 |
| absorp coeff (mm$^{-1}$) | 0.079 | 1.856 | 0.207 | 0.753 |
| $F$(000) | 784 | 1696 | 1632 | 1200 |
| cryst size (mm$^3$) | 0.5 × 0.3 × 0.25 | 0.3 × 0.3 × 0.3 | 0.3 × 0.3 × 0.3 | 0.1 × 0.04 × 0.03 |
| theta range (deg) | 2.50 to 25.00 | 2.51 to 25.00 | 1.99 to 25.00 | 2.07 to 25.85 |
| reflns collected | 17 047 | 12 952 | 31 131 | 33 034 |
| indep reflns | 1807 [$R$(int) = 0.0567] | 1806 [$R$(int) = 0.0501] | 7203 [$R$(int) = 0.0941] | 5262 [$R$(int) = 0.0403] |
| completeness to theta = 25.85° | 99.7% | 99.9% | 99.9% | 99.9% |
| absorption corr | none | none | none | none |
| refinement method | full-matrix least-squares on $F^2$ | full-matrix least-squares on $F^2$ | full-matrix least-squares on $F^2$ | full-matrix least-squares on $F^2$ |
| data/restraints/params | 1807/0/136 | 1806/1/122 | 7203/0/499 | 5262/0/322 |
| goodness-of-fit on $F^2$ | 1.067 | 1.048 | 1.215 | 1.002 |
| final $R$ indices [$I > 2\sigma(I)$] | $R_1$ = 0.0482, $wR_2$ = 0.1543 | $R_1$ = 0.0296, $wR_2$ = 0.0632 | $R_1$ = 0.0691, $wR_2$ = 0.1297 | $R_1$ = 0.0338, $wR_2$ = 0.0785 |
| $R$ indices (all data) | $R_1$ = 0.0650, $wR_2$ = 0.1610 | $R_1$ = 0.0367, $wR_2$ = 0.0645 | $R_1$ = 0.0779, $wR_2$ = 0.1328 | $R_1$ = 0.0484, $wR_2$ = 0.0878 |
| largest diff peak and hole (e·Å$^{-3}$) | 0.148 and −0.155 | 0.345 and −0.146 | 0.170 and −0.449 | 0.480 and −0.406 |

Approximate positions of all but the hydrogen atoms of some methyl groups were found in different stages of converging refinements (max. shift/s.u. = 0.000 in all cases) by full-matrix least-squares calculations on $F^2$.[31] As explained in the Results and Discussion section, a 1:1 disorder of the methoxy group of **5a** was observed. Anisotropic displacement parameters were refined for all atoms heavier than hydrogen. With idealized bond lengths and angles assumed for all the CH, $CH_2$, and $CH_3$ groups, the riding model was applied for the corresponding H atoms, and their isotropic displacement parameters were constrained to 120%, 120%, and 150% of the equivalent isotropic displacement parameters of the parent carbon atoms, respectively. In addition, the H atoms of the $CH_3$ groups were allowed to rotate around the neighboring C−C bonds. The right choice of the polar axis for **7** and the enantiomorphic form for **9** is indicated by the Flack parameter[32] −0.016(11) and 0.11(12), respectively. Selected crystal data and refinement parameters are collected in Table 2. CCDC-855559 (**5a**), CCDC-855560 (**7**), CCDC-855561 (**9**), and CCDC-855562 (**10**) contain the supplementary crystallographic data (excluding structure factors) 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.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

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[†]X-ray structure determinations.


### Notes

The authors declare no competing financial interest.

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