# Synthesis and Characterization of a Carbene·$SO_2$ Adduct − New Insights into the Structure and Bonding of Thiourea *S*,*S*-Dioxides[‡][‡‡]

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**Keywords:** Carbenes / Sulfenes / Density functional calculations / Thermochemistry / Sulfur ylides

The title compound 1,3-di-*tert*-butylimidazol-2-ylidene·$SO_2$ (**2**) was obtained from the respective stable carbene **1** and $SO_2$ in quantitative yield and investigated by single crystal X-ray crystallography and NMR spectroscopy. Quantum chemical calculations show that thiourea-*S*,*S*-dioxides like **2** are Lewis acid-base adducts of the respective diamino carbenes with $SO_2$ (CS bond energies $< 20$ kcal·mol$^{-1}$). They possess long CS bonds and a pyramidal sulfur atom and are thus structurally distinct from sulfur ylides or sulfenes.

## Introduction

Despite the frequent assumption of their involvement as reactive intermediates, sulfenes ($R_2C=SO_2$)[1] have remained elusive and are thus clearly distinct from the growing list of isolable compounds featuring carbon-sulfur double[1,2] and even triple bonds.[2]

Sulfenes can be generated in situ by the 1,2-elimination of HCl from sulfonyl chlorides ($R_2CH$-$SO_2Cl$) or by fluorodesilylation of 2-silylsulfochlorides.[1h] The reaction of carbenes with $SO_2$ can result in the formation of sulfenes but has found little synthetic use. While the formation of sulfene, $CH_2=SO_2$, from methylene and $SO_2$ was deduced from the formation of secondary products only,[3] diphenylsulfene has been isolated in a frozen matrix and characterized by its IR and Raman spectra at 100 K.[4]

Thiourea *S*,*S*-dioxide (**2**),[5−7] a stable, commercially available compound has been known since 1910[5] and is readily obtained by oxidation of thiourea (**1**) with peracids. It could be described as a donor-stabilized sulfene but the X-ray structure of **2** shows a long C-S bond (185 pm) and a pyramidal sulfur atom.[8] The C-S double bond of a sulfene would imply a short C-S bond and a planar or close to planar C-$SO_2$ fragment.

Using X-ray data[8c] and EHMO calculations,[8d] Chen and Wang[8d] have concluded that the C-S bond in **2** is essentially a single bond. Despite this attempt to clarify the bonding situation, **2** is still usually written with a C-S double bond.

In 1994, Skrypnik and Lyashchuk reported the isolation of the diamino ketene **4′**[9a,9c] and the stable sulfene **5′** (Scheme 1).[9b,9c] The existence of **4′** has since been refuted through high level ab initio calculations[10] which demonstrated that **4′** would only have the marginal stability of a van-der-Waals complex.[10] Two notes questioning the existence of **5′**[10b,10c] have appeared in the literature, but, in the absence of additional experimental or computational data, the issue remains unresolved. X-ray data reported for **5′**[9b] are limited to selected bond lengths and bond angles and have not been deposited in the Cambridge database.

Our interest in the subject was triggered by our previous investigations of stable diamino carbenes,[11] diamino silylenes[12] and related species and, in particular, by the question whether thiourea *S*,*S*-dioxides like **2** or **5′** could act as synthons for diamino carbenes. We now present experimental evidence (NMR spectroscopy, X-ray crystallographic data) and quantum chemical calculations which indicate that thiourea *S*,*S*-dioxides (including **5′**) are not sulfenes or sulfur ylides but Lewis acid-base adducts of diamino carbenes.

## Results and Discussion

Reaction of the stable carbene **3** or **3′** with $SO_2$ did not give any indication of the formation of **5** (previously unknown) or **5′** (ref.[9b]).

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[‡] Synthesis and Reactivity of Subvalent Compounds, 12. Part 11: Michael K. Denk, José M. Rodezno, Shilpi Gupta and Alan J. Lough, Oxidation, Hydrogenation and Hydrolysis of Stable Diamino Carbenes, *J. Organomet. Chem.* **2001**, *617/618*, 242−253.

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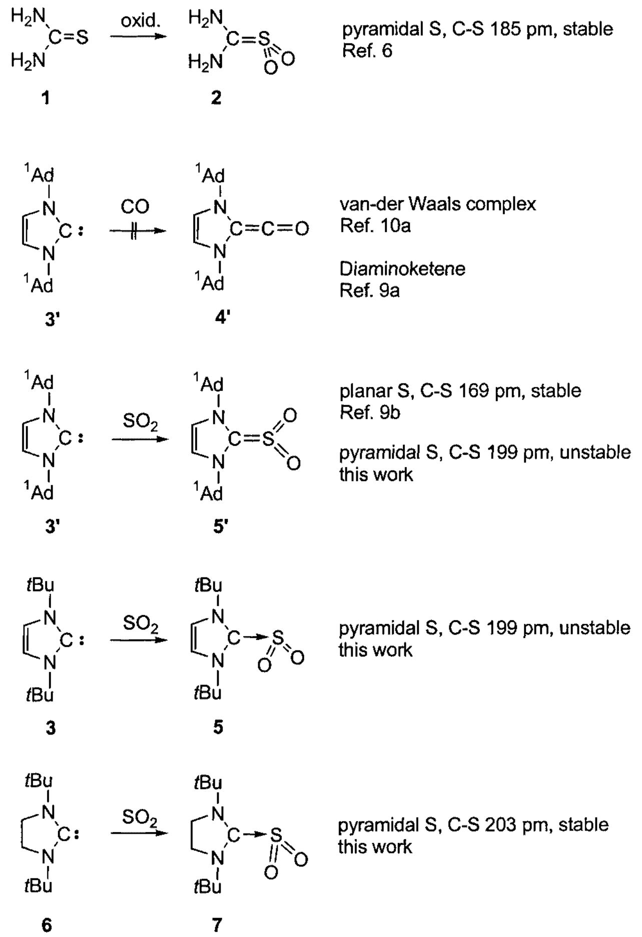


Scheme 1. Reactions of stable carbenes with CO and $SO_2$

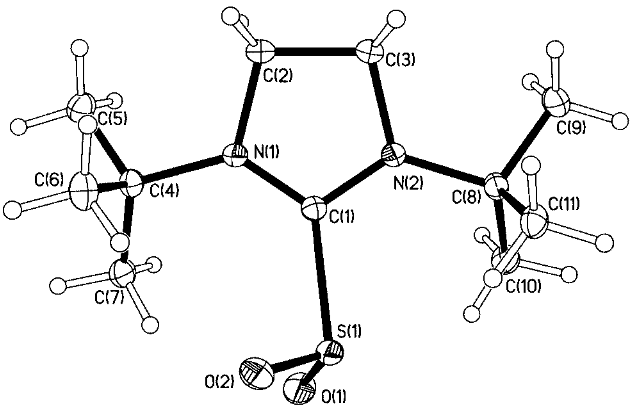


Figure 1. Molecular structure of **7**; selected bond lengths [pm] and angles [°]: C(1)−S(1) 203.0(2), S(1)−O(2) 146.85(13), S(1)−O(1) 146.93(13), C(1)−N(1) 132.9(2); C(1)−N(2) 133.9(2), O(1)−S(1)−O(2) 113.09(8), O(1)−S(1)−C(1) 104.04(7), O(2)−S(1)−C(1) 100.25(7), N(1)−C(1)−N(2) 111.61(3), N(1)−C(1)−S(1) 129.94(11), N(2)−C(1)−S(1) 117.33(11); selected torsional angles: O(1)−S(1)−C(1)−N(1) 77.93(15), O(2)−S(1)−C(1)−N(1), −39.20(15), C(2)−N(1)−C(1)−S(1) 162.89(11), C(4)−N(1)−C(1)−S(1) −12.20(23)

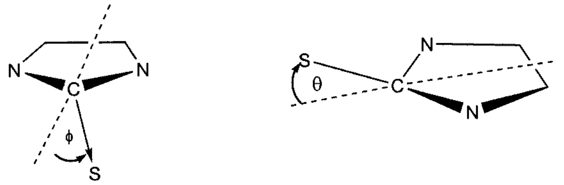


Figure 2. horizontal ($\varphi$) and vertical ($\theta$) tilt angles used in the description of **7**

Much to our surprise, reaction of the closely related but electronically less stabilized[12] carbene **6**[11a] with $SO_2$ led to the clean formation of **7**, which was characterized by single crystal X-ray crystallography (Figure 1),[14−17] multinuclear NMR spectroscopy, and computational methods.[18−22]

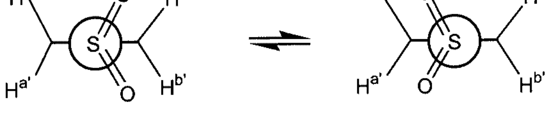
Compound **7** is poorly soluble in hydrocarbons such as hexane and toluene but dissolves well in THF and dichloromethane. These solutions are unreactive towards oxygen, pyridine and CsF but are sensitive to moisture.[13] Attempts to sublime **7** ($T \leq 110$ °C, 0.05 Torr) resulted in decomposition. The compound is undissociated in benzene solution ($^1$H NMR spectroscopy) and is unaffected by prolonged storage under vacuum. Samples heated to 100 °C for 24 h show no signs of decomposition ($^1$H NMR, IR spectroscopy) but decomposition occurs upon melting (123 °C).

The C-S bond length of 203.0(2) pm in **7** exceeds the sum of the covalent single-bond-radii of sulfur and carbon (187 pm).[23] The pyramidal $SO_2$ fragment is off-center from its idealized position (C-S bond axis bisecting the N−C−N angle) by $\varphi = 6.3°$ and is also tilted away from the N−C−N plane by $\theta = 10.8°$ (Figure 2).

The C-S bond length in **7** is also significantly longer than that reported for **2**, which may be related to the fact that **2**, unlike **7**, shows hydrogen bonding in the solid state (NH···OS 186 pm).[8] Hydrogen bonding can enhance the Lewis acidity of the $SO_2$ fragment by reducing its electron density. Despite the difference of the C-S bond lengths in **2** and **7**, the C-S bond energies (see below) are very similar so that fundamental differences in the bonding situation for **2** and **7** must be ruled out.

Preservation of the solid-state structure of **7** in solution would give rise to an AA′BB′ spin system for the ring protons. However, between −100 °C and 25 °C the VT $^1$H NMR spectrum of **7** shows only two singlets, one for the ethylene protons (4 H) and the one for the two *tert*-butyl groups (18 H).

A rapid equilibrium between the conformers **7a**/**7b** (Figure 3) can occur through rotation of the $SO_2$ group or inversion of the sulfur atom and can explain the observed be-



**7a** **7b**

Figure 3. Dynamic behavior of **7**

havior of **7**. The high configurational stability of the pseudo-tetrahedral sulfur geometry (e.g. in sulfoxides) seems incompatible with the observed dynamic behavior and the rotational mechanism is more likely.[27]

The $^1H$ and $^{13}C$ NMR shifts of **7** resemble that of the stable carbene **6**. Coordination of **6** to $SO_2$ leads to a moderate shielding of the carbene carbon atom [$\delta^{13}C = +238$ (**6**), +231 ppm (**7**)], a trend that is analogous to the shielding effect caused by protonation of **6** ($\delta^{13}C$, **[6H]$^+$SCN$^-$**, $CDCl_3$, $N_2\mathit{C}H$ +152.4 ppm).[11e]

The structural and spectroscopic data characterize **7** as a Lewis acid-base adduct of the carbene **6** and are inconsistent with those presented for **5′** which has been described as a stable sulfene (short C-S bond, planar $N_2CSO_2$ framework).[9b] This discrepancy and the doubts raised about the existence of **5′** elsewhere,[10b,10c] have prompted us to study the bonding situation through high level quantum chemical methods.[18−22]

## Computational Structures of Sulfene *S*,*S*-Dioxides

A method for the calculation of accurate structures of **7** was established by comparison of computational structures with the experimental structures. Computational structures[19] were obtained with Gaussian 98[18] at the HF and DFT[20,21] levels. The respective methyl-substituted compounds **5Me** and **7Me** were chosen as model compounds for **5** and **7**.

Table 1. Molecular structure of $SO_2$ at different levels of theory

| Method | Basis set | Gaussians | S−O [pm] | O−S−O [deg] | $E_o$ [a] |
|---|---|---|---|---|---|
| Exp.[b] | − | − | 143.08 | 119.33 | − |
| HF | 6-31G(d) | 108 | 141.40 | 118.82 | −547.169006 |
| B3LYP | 6-31G(d) | 108 | 146.40 | 119.13 | −548.587479 |
| MPW1PW91 | 6-31G(d) | 108 | 145.40 | 119.07 | −548.540504 |
| MPW1PW91 | 6-311G(d) | 110 | 144.72 | 118.81 | −548.604023 |
| MPW1PW91 | 6-31+G(d) | 120 | 145.52 | 118.70 | −548.550124 |
| MPW1PW91 | 6-311+G(d) | 122 | 144.83 | 118.73 | −548.611774 |
| HF | 6-31G(2d) | 126 | 140.18 | 118.74 | −548.563322 |
| MPW1PW91 | 6-31G(2d) | 126 | 143.92 | 119.10 | −547.184484 |
| B3LYP | 6-31G(2d) | 126 | 144.69 | 119.20 | −548.609993 |
| MPW1PW91 | 6-311G(2d) | 128 | 143.65 | 119.08 | −548.635021 |
| MPW1PW91 | 6-31G(df) | 138 | 145.01 | 118.94 | −548.552992 |
| MPW1PW91 | cc-pVDZ | 139 | 147.01 | 117.77 | −548.556824 |
| MPW1PW91 | 6-31G(3d) | 144 | 143.37 | 119.34 | −548.580389 |
| MPW1PW91 | 6-311G(3d) | 146 | 143.18 | 119.37 | −548.646360 |
| B3LYP | 6-311G(3d) | 146 | 143.99 | 119.43 | −548.690367 |

[a] Zero-point energies were added without scaling. [b] Microwave structure, *CRC Handbook of Chemistry and Physics*, 81st edition, 9−22.

Table 2. Computational (**5Me**) and experimental (**5′**[9b]) structures of imidazol-2-ylidene·$SO_2$ adducts

| | HF 6-31G(d) | MPW1PW91 6-31G(d) | MPW1PW91 6-31G(2d) | B3LYP 6-31G(2d) | X-ray [9b] |
|---|---|---|---|---|---|
| S−C | 192.54 | 199.56 | 198.96 | 237.89 | 169 |
| S−O | 146.30 | 148.86 | 147.56 | 146.78 | 161 |
| | 146.43 | 149.21 | 147.83 | 146.78 | ? |
| C−N | 132.34 | 133.88 | 133.75 | 135.35 | ? |
| | 132.56 | 134.09 | 133.92 | 135.35 | ? |
| $C-C_{ring}$ | 133.61 | 135.63 | 135.48 | 135.56 | ? |
| O−S−O | 114.46 | 114.83 | 114.14 | 115.54 | 127 |
| O−S−C | 97.86 | 96.73 | 96.74 | 98.25 | ? |
| | 98.10 | 98.28 | 97.88 | 98.36 | ? |
| S−C−N | 127.86 | 128.80 | 130.10 | 127.84 | ? |
| | 124.48 | 124.24 | 123.21 | 127.52 | ? |
| N−C−N | 107.92 | 106.57 | 106.57 | 104.62 | 112 |
| O−S−C−N[a] | 59.18 | 56.56 | 57.33 | 31.99 | ? |
| | −57.18 | −60.81 | −58.27 | 149.47 | ? |
| $\varphi$ [b] | 1.69 | 2.36 | 3.45 | 0.85 | ? |
| $\theta$[b] | 2.56 | 6.99 | 3.92 | 0.16 | ? |
| $\nu_1$ [c] | 56 | 54 | 50 | 22 | |
| Symmetry | $C_1$ | $C_1$ | $C_1$ | $C_1$ | ? |

[a] Torsional angles with *syn*-nitrogen. [b] See Figure 2. [c] Lowest vibrational mode in $cm^{-1}$.

Structures obtained with density functional methods are usually more accurate than Hartree−Fock structures but the effect can be obscured by internal error compensation and can become apparent only for larger than usual basis sets. The MPW1PW91/6-31G(d)[20] structure of $SO_2$ (Table 1) is very similar to the HF/6-31G(d) structure, but the higher accuracy of the MPW1PW91 approach becomes obvious for more extended basis sets.

The superior accuracy of MPW1PW91 structures[20] has been established through calculations on large test sets of organic and inorganic compounds[20a] and is also obvious for the structures calculated in this study. While the C-S bond length of **7Me** calculated at the MPW1PW91/6-31G(2d) level (202.02 pm) is in excellent agreement with the experimental value[24] [**7**: 203.0(2) pm], the B3LYP/6-31G(2d) value of 234.27 pm deviates significantly.

Table 4. Natural charges of selected carbenes (**3Me**, **6Me**) and their $SO_2$ adducts (**5Me**, **7Me**); MPw1PW91/ 6-31G(2d)//MPw1PW91/ 6-31G(2d) level

| Atom | 7Me | | 5Me | $SO_2$ | 6Me | 3Me |
|---|---|---|---|---|---|---|
| S | 1.60 | 1.60 | +1.64 | – | – | |
| O | −0.99 | −0.99 | −0.82 | – | – | |
| $N_2$*C* | +0.31 | +0.22 | – | +0.22 | +0.13 | |
| N | −0.45 | −0.40 | – | −0.51 | −0.46 | |
| C*C* | −0.29 | −0.07 | – | −0.30 | −0.10 | |
| $H_3$*C* | −0.45 | −0.50 | – | −0.48 | −0.48 | |

At the MPW1PW91/6-31G(2d) level, the structures of **5Me** (Table 2) and **7Me** (Table 3) are very similar. In particular, they display a *pyramidal* geometry at the sulfur atom and *long* C-S bonds (**5Me**: 199 pm, **7Me**: 202 pm). The computational structure of **5Me** is thus in qualitative disagreement with the structure published for **5′**. The possibility of a second minimum with a planar $CSO_2$ geometry and a short C-S bond was considered as a possible source for the discrepancy and studied by starting the optimization pro-

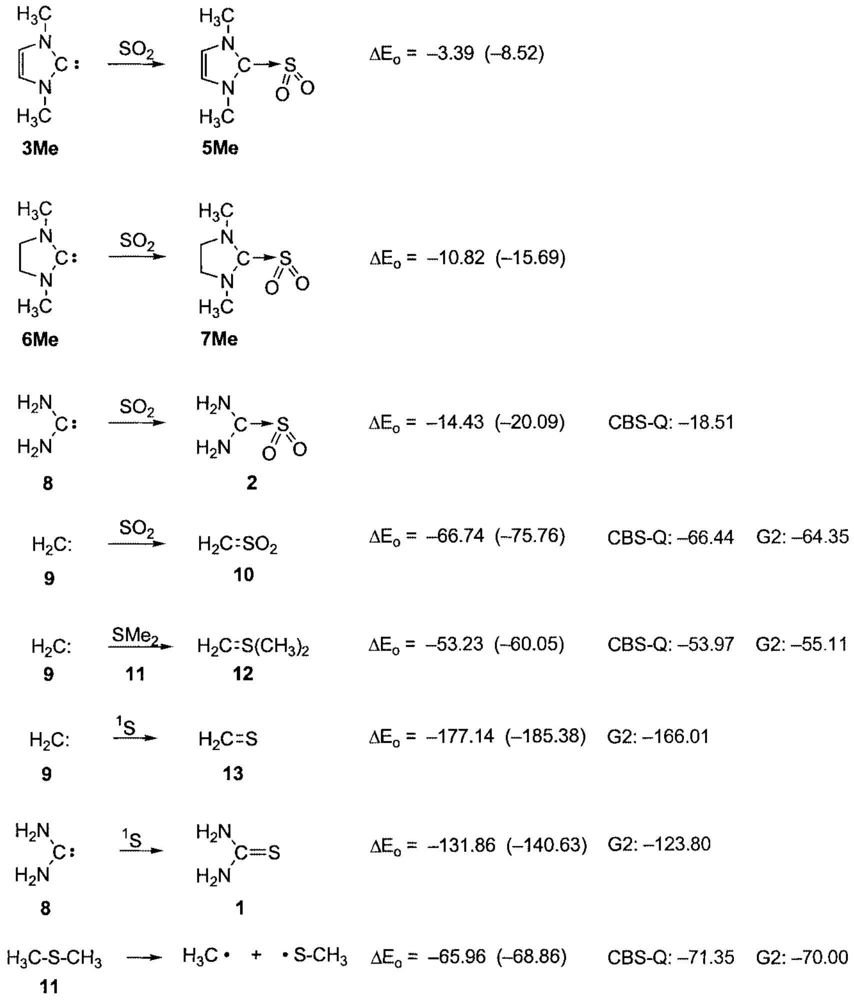
Table 3. Computational (**7Me**) and experimental (**7**) structures of imidazolidine-2-ylidene•$SO_2$ adducts

| | HF<br>6-31G(d) | MPW1PW91<br>6-31G(d) | MPW1PW91<br>6-31G(2d) | B3LYP<br>6-31G(2d) | X-ray<br>this work |
|---|---|---|---|---|---|
| S−C | 194.50 | 201.55 | 202.02 | 234.27 | 203.0(2) |
| S−O | 146.17 | 148.91 | 147.55 | 146.69 | 146.85(13) |
| | 146.13 | 148.91 | 147.54 | 146.85 | 146.93(13) |
| C−N | 131.78 | 132.07 | 132.69 | 133.40 | 132.9(2) |
| | 131.05 | 132.01 | 132.18 | 132.97 | 133.9(2) |
| ring C−C | 153.60 | 153.54 | 153.59 | 154.13 | 151.8(2) |
| O−S−O | 114.75 | 115.08 | 114.81 | 115.32 | 113.09(8) |
| O−S−C | 99.27 | 94.79 | 95.24 | 94.89 | 100.25(7) |
| | 96.91 | 99.74 | 99.38 | 99.38 | 104.04(7) |
| S−C−N | 123.84 | 123.30 | 125.23 | 127.03 | 129.94(11) |
| | 124.88 | 124.86 | 123.41 | 121.48 | 117.33(11) |
| N−C−N | 111.23 | 110.72 | 110.60 | 109.13 | 111.61(3) |
| O−S−C−N[a] | 59.19 | 54.09 | 54.26 | 52.93 | 77.93(15) |
| | −57.17 | −62.38 | −61.98 | −63.75 | −39.20(15) |
| $\varphi$ [b] | 0.52 | 0.78 | 0.91 | 2.78 | 6.3 |
| $\theta$[b] | 2.50 | 10.64 | 9.69 | 17.4 | 10.8 |
| $\nu_1$ [c] | 56 | 54 | 52 | 26 | – |
| Symmetry | $C_1$ | $C_1$ | $C_1$ | $C_1$ | $C_1$ |

[a] Torsional angles with *syn*-nitrogen. [b] See Figure 2. [c] Lowest vibrational mode in $cm^{-1}$.

Table 5. Experimental (**3**,[11] **6**[12]) and computational (**3Me**, **6Me**) structures of selected carbenes

| | | X-ray | HF<br>6-31G(d) | MPW1PW91<br>6-31G(d) | MPW1PW91<br>6-31G(2d) | B3LYP<br>6-31G(2d) |
|---|---|---|---|---|---|---|
| **6** | C−$N_{ring}$ | 134.83(13) | 134.15 | 134.66 | 134.40 | 134.94 |
| | | 134.73(13) | 134.15 | 134.66 | 134.40 | 134.94 |
| | C−$C_{ring}$ | 151.2(2) | 153.22 | 153.16 | 153.09 | 153.80 |
| | N−C−N | 106.44(9) | 105.55 | 105.05 | 105.23 | 105.36 |
| | Point group | $C_1$ | $C_1$ | $C_1$ | $C_1$ | $C_1$ |
| **3** | C−$N_{ring}$ | 136.6(2) | 135.20 | 134.60 | 136.42 | 137.07 |
| | | 138.0(2) | 135.20 | 134.61 | 136.42 | 137.07 |
| | C−$C_{ring}$ | 134.1(2) | 133.27 | 153.29 | 135.12 | 135.44 |
| | N−C−N | 102.19(2) | 102.52 | 105.065 | 101.50 | 101.51 |
| | Point group | $C_1$ | $C_1$ | $C_1$ | $C_1$ | $C_1$ |



Scheme 2. CS bond energies of selected sulfur compounds; B3LYP/6-311G(3df,p)//MPW1PW91/6-31G(2d) and, in parentheses), MPW1PW91/6-311G(3df,p)//MPW1PW91/6-31G(2d); zero-point energies of the DFT calculations are at the MPW1PW91/6-31G(2d) level and were added without scaling

cess of **5Me** with a sulfene structure analogous to **5′**. The sulfene geometry reported for **5′** (Table 2) is unstable at all levels investigated (HF, MPW1PW91, or B3LYP methods with 6-31G(d) or 6-31G(2d) basis sets) and reverts to structures with long C-S bonds and pyramidally coordinated sulfur atoms.

The computational instability of the sulfene structure and the fact that we were unable to obtain **5′** or to observe the spectroscopic data ($^1$H NMR, $^{13}$C NMR) published for it suggest that the compound may indeed be nonexistent.[10b]

Computational charge densities (Table 4) of **5Me** and **7Me** show a net transfer of charge density from the carbenes **3Me** and **6Me** to $SO_2$ and are consistent with the description of $SO_2$ acting as a Lewis acid. The net transfer of charge density occurring in the formation of **5Me** and **7Me** is very similar. The electron-deficient sulfur atom in $SO_2$ (+1.64) accepts only a small additional charge (0.04) from the carbene in both cases: most of the transferred electron density ultimately resides on the more electronegative oxygen atoms. The carbene carbon atoms show a loss of 0.09 charge units, with some of the electron depletion relayed to the nitrogen atoms (0.06 in **7Me** and 0.09 in **5Me**)

To further study the possible existence of **5′**, C-S bond-dissociation energies were obtained from DFT, CBS-Q, and G2 calculations.

### Thermochemistry of the C-S bond

The C-S bond energies of **2**, **5Me**, **7Me**, sulfene ($H_2C{=}SO_2$, **10**), *S,S*-dimethylsulfoniumylide [$H_2C{=}S(CH_3)_2$, **12**], thioformaldehyde ($H_2C{=}S$, **13**), and dimethyl sulfide [$(CH_3)_2S$, **11**] were calculated from the reaction energies $\Delta E_o$ of the respective bond formation reactions (Scheme 2 and Table 6). The established accuracy of the G2 and CBS-Q method assures an absolute error of less than 2 kcal·mol$^{-1}$ which is significantly better than the maximum absolute error of about 10 kcal·mol$^{-1}$ obtained with current DFT methods.[22,26]

The computationally derived C-S bond energies fall into four distinct groups which are readily identified with dative bonds (**2**, **5**, **7**), single bonds (**11**), double bonds (**1**, **13**) and

Table 6. Selected electronic ($E_o$) and zero-point vibrational energies used for the determination of carbon sulfur bond energies (Scheme 2)

| | ZPE MPW1PW9/6-31G(2d) | $E_o$ MPW1PW91/6-311G(3df,p)[a] | $E_o$ B3LYP/6-311G(3df,p)[a] | $E_o$ CBS-Q (G2) | $E_o$ G2 |
|---|---|---|---|---|---|
| $SO_2$ | 0.007004 | −548.659528 | −548.703037 | −548.035075 | −548.015737 |
| 1 | 0.062112 | −548.209841 | −548.249307 | 547.533352 | −547.525021 |
| 2 | 0.068589 | −698.615621 | −698.694602 | −697.784525 | – |
| 3Me | 0.127553 | −304.686454 | −304.767787 | – | – |
| 5Me | 0.148869 | −853.359555 | −853.476229 | – | – |
| 6Me | 0.150455 | −305.867894 | −305.948725 | – | – |
| 7Me | 0.161255 | −854.552419 | −854.668997 | – | – |
| 8 | 0.057466 | −149.921832 | −149.966888 | −149.719961 | −149.716975 |
| 9 | 0.016713 | −39.109961 | −39.130423 | −39.056539 | −39.058392 |
| 10 | 0.034253 | −587.890200 | −587.939822 | −587.197478 | −587.176680 |
| 11 | 0.076207 | −477.976372 | −477.999719 | −477.375022 | −477.369000 |
| 12 | 0.101272 | −517.182016 | −517.214969 | −516.517553 | −516.515213 |
| $CH_3^{\cdot}$ | 0.029693 | −39.810590 | −39.825444 | −39.745168 | −39.745086 |
| $CH_3S^{\cdot}$ | 0.036749 | −438.056051 | 438.069180 | −437.516154 | −437.512381 |
| 13 | 0.024867 | −437.469279 | −437.484993 | −436.937353 | −436.933692 |
| S | 0 | −398.063932 | −398.072317 | – | −397.610779 |

[a] Single point energies of MPW1PW91/6-31G(2d) structures with zero-point energies (first column) added without scaling.

bond orders which are intermediate between single and double bonds (sulfur ylides **10**, **12**).

The C-S bond dissociation energy of sulfene (**10**; CBS-Q: 66.44 kcal·mol$^{-1}$) is significantly lower than that of thioformaldehyde (**13**; G2: 166.01 kcal·mol$^{-1}$) and only slightly higher than that of the sulfur ylide **12** (G2: 55.11 kcal·mol$^{-1}$). This allows the conclusion that the C-S bond in **10**, despite its short distance and the planar coordination of the sulfur atom, is also ylidic in nature. The C-S bond dissociation energies of **2**, **5** and **7** (3.39−20.09 kcal·mol$^{-1}$) are of a magnitude commonly observed for Lewis acid-base adducts and rule out a description of these compounds as sulfur ylides.

While the accuracy of the CBS-Q and G2 approach leaves little room for interpretation, the modifying influence of steric hindrance remains to be discussed.

The free rotation of the $SO_2$ group in **7**[27] is evidence against the presence of a strong steric interaction between the *tert*-butyl groups and the $SO_2$ fragment. The presence of steric effects would also manifest itself in a specific elongation of the C-S bond lengths. However, the computational C-S bond length obtained for the methyl-substituted **7Me** is virtually identical to that observed for the *tert*-butyl-substituted compound **7**.

A sterically induced transformation of a dative C-S bond (**5Me**) into a double bond (as the one claimed for **5′**) can be ruled out because steric hindrance can only lead to a decrease of the C-S bond energy. The marginal C-S bond energy of **5Me** correlates well with the fact that the formation of **5** and **5′** could not be observed in this study.

## Conclusion

Based on thermochemical data, thiourea *S*,*S*-dioxides must be descrided as Lewis acid-base complexes of diaminocarbenes with $SO_2$. This description of the bonding situation is consistent with their reactivity as reducing agent[4] and formamidine synthons.[4] The synthesis of the carbene complex, thiourea *S*,*S*-dioxide (**2**), by de Berry Barnett in 1910,[5] thus precedes the synthesis of the first transition metal carbene complex reported by Fischer and Maasböl[25] by more than 50 years.

## Experimental Section

All operations were performed under argon (99.995%) with usual Schlenk techniques. The stable carbenes **3**[11b−11d] and **6**[11a] were obtained by published procedures.

**Synthesis and Characterization of 1,3-Di-*tert*-butylimidazolidin-2-ylidene·$SO_2$ (7):** A slow stream of $SO_2$ was passed over a magnetically stirred solution of **6**[11a] (5.20 g, 28.2 mmol) in 150 mL of dry THF at 25 °C. The colorless solution became slightly turbid and a crystalline, colorless precipitate formed after a few minutes. Filtration through a medium porosity Schlenk frit gave 6.94 g of **7** (quantitative yield). m.p. 123 °C (dec.). $^1H$ NMR ($C_6D_6$): $\delta = 1.25$ (s, 18 H, *t*Bu), 2.78 (s, 4 H, $CH_2$). $^{13}C$($C_6D_6$): 29.7 [$C(\mathit{C}H_3)_3$], 44.6 ($\mathit{C}H_2$), 55.2 [$\mathit{C}(CH_3)_3$], 231.0 ppm ($N_2\mathit{C}$) ppm. MS ($CI^+$, Methane): *m*/*z* (%) = 245 (14) $[M]^+$, 229 (10), 183 (62) $[LC-H]^+$, 167 (10), 126 (61), 111 (56), 99 (31), 84 (10), 71 (100) $[C_3H_7N_2]^+$, 57 (51). IR (Nujol): $\tilde{\nu} = 1629$ cm$^{-1}$ m, 1490 s, 1404 m, 1284 s, 1230 s, 1198 s, 1158 s, 1091 w, 1052 s, 1018 m, 905 m, 646 w, 613 s.

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[13] $^1$H NMR and tentative assignment of the hydrolysis product **[6 H]$^+$[HSO$_3^-$]**: $^1$H NMR (CDCl$_3$): δ = 1.50 [$C(CH_3)_3$], 4.03 ($CH_2$), 8.31 ($N_2CH^+$).

[14] **Crystal data for 7:** $C_{11}H_{22}N_2O_2S_2$, $M_r$ = 246.37, monoclinic, space group $P2_1/n$, $a$ = 7.649(1), $b$ = 19.239(1), $c$ = 8.736(1) Å, β = 95.51(1)°, $V$ = 1279.6(4) Å$^3$, $Z$ = 4, $\rho_{calcd.}$ = 1.284 g cm$^{-3}$, λ(Mo-$K_\alpha$) = 0.71073 Å, μ(Mo-$K_\alpha$) = 0.243 mm$^{-1}$, $T$ = 150.0(1) K, total number of collected reflections 10008, independent reflections 3162. (4.15 < θ < 28.29°) and scalepack absorption correction. Structure refined on $F^2$ (full-matrix-least-squares) and hydrogen atoms were refined with isotropic thermal parameters. Final $R1$ [$I > 2\sigma(I)$] = 0.0365 for 3162 observed reflections and $wR2$ (all data) = 0.0523. Maximum and minimum peaks in final $\Delta F$ map were 0.329 and −0.428 e·Å$^{-3}$.

[15] Structures solved and refined using SHELXTL/PC.[16] Crystallographic data (excluding structure factors) for **7** have been deposited. CCDC-165466 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[27] PM3 calculations show low rotational barriers for **7Me** (3.65 kcal·mol$^{-1}$) and **7** (5.75 kcal·mol$^{-1}$).

[28] Estimated errors for the computational structures of **7Me/5Me** can be inferred from a comparison of the MPW1PW91/6-31G(d) structure of $SO_2$ with the experimental structure. This leads to estimated errors of 0.84 pm (0.59%) for the SO bond lengths and 0.23 deg (0.19%) for the O−S−O angles. For the remainder of the geometrical parameters, the errors obtained for the G2 test set of molecules (ref.[20]) may be assumed.

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