# Captodative Stabilization in Geminally Substituted Allylic Radicals Assessed by Means of the EPR-Spectral D Parameter of 1,3-Cyclopentanediyl Triplet Diradicals

**Waldemar Adam*[a] and Claudio M. Ortega Schulte[a]**

**Keywords:** Captodativity / *D* Parameter / EPR spectroscopy / Substituent effects / Triplet diradicals

The EPR-spectral zero-field parameter *D* of low-temperature persistent triplet diradicals **T** was used to assess the electronic substituent effects in EA/ED and ED/ED geminally substituted allylic radicals. From these EPR data, the interaction parameter ($\Delta S$) was calculated for a set of doubly functionalized radicals, which expresses the ability of the unpaired electron to interact either individually with the functional groups or simultaneously in either a synergistic or antagonistic way. We show that the ED/ED combinations interact antagonistically with the odd electron, whereas the $R_2N$/EA and the MeO/EA pairs display a pronounced captodative delocalization. Compared to MeO/EA, the MeS/EA functionalities manifest just an additive effect of the individual substituents. These results are rationalized in terms of appropriate electron-transfer-type mesomeric structures.

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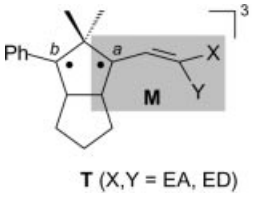
## Introduction

The most extensive systematic assessment of the electronic stabilization derived from two functional groups attached to the same radical center has been conducted on benzylic radicals. When one of the substituents is an electron acceptor (EA) and the other an electron donor (ED), the unpaired electron experiences an additional stabilization through the cooperative delocalization by the EA/ED pair, a phenomenon known as captodativity.[1] To evaluate quantitatively the cumulative electronic effects of two functional groups, Viehe and Stella,[1a] and subsequently Korth and Sustmann,[2] utilized Arnold's EPR-spectral $\sigma^{\cdot}$ radical scale, processed in terms of the Fischer increment relation.[3] An interaction parameter ($\Delta S$) was defined [see Equation (2), Discussion],[1c] which serves as a measure of the mutual electronic interaction between the two functional groups at the benzylic radical center. When $\Delta S = 0$, there is no electronic interaction between the two substituents and additivity applies; for $\Delta S > 0$ synergy (higher spin delocalization) and for $\Delta S < 0$ (lower spin delocalization) antagonism operates between these geminal functional groups.

The incentive of the present work was to determine the $\Delta S$ parameter for a set of geminally substituted allylic radicals, in an effort to evaluate additive, synergetic and antagonistic effects on the spin-density distribution. Such allylic radical fragments **M** are contained in the low-temperature persistent 1,3-cyclopentanediyl triplet diradicals **T**, which may be readily generated through the photochemical deazetation of diazabyciclo[2.2.1]heptene (DBH) derivatives.[4] These triplet diradicals are characterized by the EPR-spectral zero-field-splitting (zfs) parameter *D*, which depends on the interspin distance $d_{ab}$ and the spin densities $\rho_a$ and $\rho_b$ at the respective radical sites *a* and *b*, as displayed in Equation (1). The spin-density as well as the distance dependences have been confirmed experimentally and computationally,[5] and provide valuable structural and electronic information on spin delocalization and radical stabilization in triplet diradicals.




**T** (X,Y = EA, ED)

$$D = \frac{3 \cdot \mu_0 \cdot g_e^2 \cdot \mu_B^2}{16\pi} \left( \frac{\rho_a \cdot \rho_b}{d_{ab}^3} \right) \quad (1)$$

When one radical site is kept electronically constant (e.g., phenyl substitution at the radical site b), and a set of triplet diradicals is considered for which $d_{ab}$ is constant (1,3-cyclopentanediyl triplet diradicals), the *D* parameter is a sensitive probe of the electronic effects exerted by the substituents at the radical center *a* through its spin density $\rho_a$. This provides an accurate measure of radical stabilization in terms of the efficacy of spin delocalization in the allylic radical fragment M by the geminal X,Y substituent pair. The results reported herein demonstrate unequivocally that the *D* parameter provides valuable data to assess the electronic interaction of geminally bonded functional groups and con-

[a] Institute of Organic Chemistry, University of Würzburg, Am Hubland, 97074 Würzburg, Germany
Fax: (internat.) +1-787-8070389
E-mail: wadam@chemie.uni-wuerzburg.de

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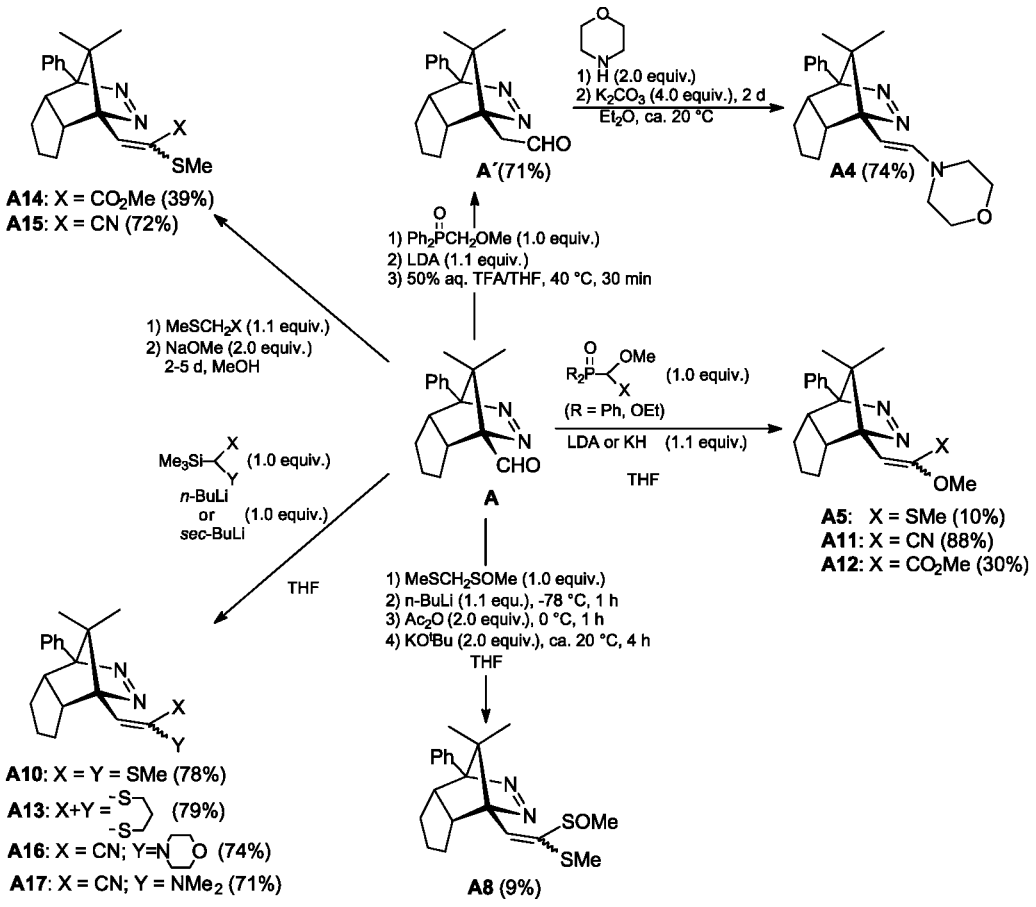


Scheme 1. Synthesis of the azoalkanes **A′**, **A4**, **A8** and **A10**−**17**

firm that appropriate EA/ED substituent pairs display captodativity.

## Results

The known azoaldehyde **A** was prepared in an overall yield of 24% from the commercially available benzoylacetone according to the Hünig route.[6] The synthetic details for the preparation of the azoalkanes **A′**, **A4**−**5** and **A10**−**17**, in which the azoaldehyde **A** was utilized as starting material, are summarized in Scheme 1.

The homologation of the azoaldehyde **A** to **A′** was carried out by acid-catalyzed hydrolysis of the corresponding intermediary enol ether,[7] derived from **A** by Horner−Emmons olefination, in an overall yield of 71%. The subsequent conversion of the homologous azoalkane **A′** to its enamine **A4** was achieved in 74% yield with potassium carbonate as base at room temperature.

The functionalized azoalkanes **A5**, **A11**, and **A12** with terminally disubstituted vinyl groups were prepared by the Horner−Emmons reaction from the corresponding phosphonates (R = OEt) or phosphane oxides (R = Ph).[8] Whereas a high yield (88%) was obtained for the cyano-substituted enol ether **A11**, the methylthio (**A5**) and methoxycarbonyl (**A12**) derivatives were isolated in poor yields, particularly **A5** (10%). The problem is that most of the labile azoaldehyde **A** decomposes under the Horner−Emmons conditions to its housane by nitrogen loss.

The azoalkane with the olefinic sulfoxide/sulfide functionalities (**A8**) was prepared in a one-pot synthesis according to the Ogura method,[9] by condensation of the appropriate active methylene component with the azoaldehyde **A**. The poor yield (9%) is again due to extensive decomposition of the labile azoaldehyde **A** under these reaction conditions.

The symmetrically substituted sulfur derivatives **A10** and **A13** were obtained by a Peterson olefination according to the reported method.[10] The high yields manifest the efficiency of this transformation.

Analogous to **A8**, the Knoevenagel reaction was also employed for the synthesis of the methoxycarbonyl (**A14**) and the cyano (**A15**) derivatives by condensation of the respective active methylene partners with the azoaldehyde **A**; sodium methoxide sufficed as base (72%).[11] While the yield of the cyano derivative **A15** was good (72%), the low (39%) amount of the ester **A14** is due to the longer reaction time needed for the condensation, which again was responsible for the extensive decomposition of the labile azoaldehyde **A**.

In the case of the α-cyanoenamines **A16** and **A17**, a mild Peterson olefination had to be developed because all other

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condensation methods failed. For this purpose, *sec*-BuLi proved particularly advantageous as a deprotonating agent for the appropriately functionalized silane, such that the α-cyanoenamines **A16** (78%) and **A17** (71%) were obtained in good yields. This improved Peterson olefination method constitutes to date the best synthetic methodology for the preparation of such enamines.[12]

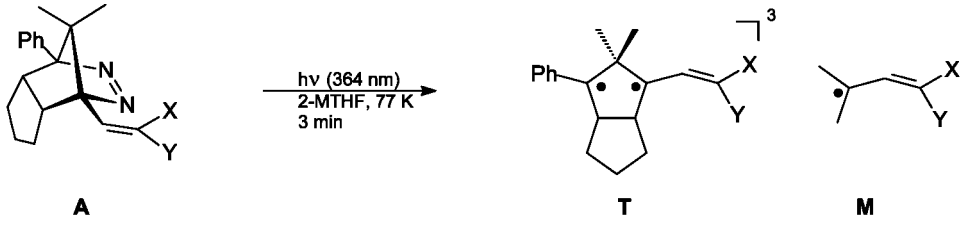
The triplet diradicals **T** were generated in a 2-methyltetrahydrofuran (MTHF) matrix at 77 K by irradiation with the 364-nm line of an argon-ion laser. In all cases, the characteristic half-field signals ($\Delta m_s = \pm 2$) of the triplet diradicals **T1**−**17** are located at 1650−1680 G; the relevant diradical *z* signals ($\Delta m_s = \pm 1$) are $B_{min.} = 1650 \pm 60$ and $B_{max.} = 3924 \pm 60$ G at a microwave frequency of 9.43 GHz. The symmetry parameter (*E*) of the triplet diradical is very small and estimated to be $\pm 0.0001$ cm$^{-1}$. All triplet diradicals were persistent for hours at this temperature, as evidenced by the constant EPR signal intensities.

The experimental EPR-spectral *D* values of the triplet diradicals **T1**−**17** are listed in Table 1, together with the theoretical spin densities (ρ) of the monoradicals **M**, both parameters arranged in descending order. The geometry optimization of the model monoradical fragments **M** was carried out by the semiempirical PM3 method with annihilated UHF wave functions. The spin densities (ρ) in Table 1 were obtained by means of a CI calculation (Table 1).[13]

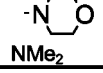
The theoretical spin density (ρ) at the radical site of the **M** monoradical is related to the experimental *D* value of the **T** diradical by Equation (1), which allows us to assess the efficiency of the spin delocalization at the radical-carrying center in this species. The good linear correlation ($r^2 = 0.945$) of the *D* versus ρ values confirms this (Figure 1).

The fact that for the monosubstituted derivative the methoxy group in **T1** (**M1**) localizes spin density (less conjugation), whereas the cyano group in **T9** (**M9**) delocalizes it (more conjugation) compared to the parent case **T2** (**M2**) has already been scrutinized.[7] The incentive, however, of the present study was to assess cooperative effects (captodativity) in disubstituted species. Indeed, a definite trend is noticeable in Table 1, in that the SMe/OMe disubstitution in **T5** (**M5**) enhances spin delocalization compared to the parent H/H system **T2** (**M2**), but not nearly as pronounced as the CN/$NR_2$ combination in **T16** and **T17** (**M16** and **M17**). The pertinent question is whether these effects are

Table 1. *D* values of the triplet diradicals **T** and the PM3(AUHF/CI)-calculated spin densities of the corresponding monoradical fragments **M**




**A** **T** **M**

| | azoalkanes X | Y | *ID*/hcl [a] T [c] | spin density (ρ) [b] M | delocalization parameter ($S^{exp}$) [d] |
|---|---|---|---|---|---|
| **A 1** | H | OMe | 0.0480[e] | 0.578 | -0.010 |
| **A 2** | H | H | 0.0473[e] | 0.573 | 0.000 |
| **A 3** | H | SOMe | 0.0447[e] | 0.530 | 0.055 |
| **A 4** | H |  | 0.0443 | 0.491 | 0.064 |
| **A 5** | SMe | OMe | 0.0432 | 0.462 | 0.086 |
| **A 6** | H | $CO_2Et$ | 0.0414[e] | 0.487 | 0.125 |
| **A 7** | H | SMe | 0.0407[e] | 0.480 | 0.140 |
| **A 8** | SMe | SOMe | 0.0404 | 0.461 | 0.146 |
| **A 9** | H | CN | 0.0400[e] | 0.474 | 0.155 |
| **A10** | SMe | SMe | 0.0377 | 0.356 | 0.203 |
| **A11** | OMe | CN | 0.0375 | 0.366 | 0.208 |
| **A12** | OMe | $CO_2Me$ | 0.0373 | 0.354 | 0.212 |
| **A13** |  | | 0.0373 | 0.396 | 0.212 |
| **A14** | SMe | $CO_2Me$ | 0.0354 | 0.352 | 0.252 |
| **A15** | SMe | CN | 0.0340 | 0.308 | 0.282 |
| **A16** | CN |  | 0.0312 | 0.239 | 0.341 |
| **A17** | CN | $NMe_2$ | 0.0308 | 0.269 | 0.349 |

[a] The *D* values were measured by EPR spectroscopy (see Exp. Sect.) and are given in cm$^{-1}$, accuracy 0.0001 cm$^{-1}$. [b] The spin densities were computed for the monoradical fragments **M** with the semiempirical PM3(AUHF/CI) method. [c] The triplet diradicals **T** were generated from the respective azoalkanes by irradiation with the 364-nm laser line of the argon-ion laser for 3 min in a 2-methyltetrahydrofuran (2-MTHF) matrix at 77 K. [d] Calculated from the corresponding *D* values of the monosubstituted triplet diradicals. [e] *D* values taken from ref.[7]

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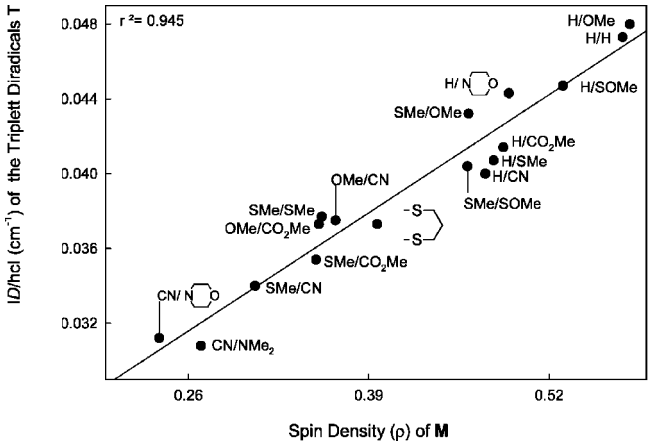



Figure 1. Correlation between the *D* values of the triplet diradicals **T** and the semiempirical PM3(AUHF/CI) spin densities of the monoradicals **M**

simply additive, and thereby predictable from the corresponding monosubstituted cases, or does a synergistic (also antagonistic) interplay operate in the disubstituted derivatives. To allow a quantitative comparison rather than address qualitative trends of the data displayed in Figure 1, we shall employ in the subsequent discussion the interaction parameter ($\Delta S$) [1a,1c] as a measure of the efficacy of spin delocalization by the geminal substitution.

## Discussion

The central parameter in our discussion is the spin density (ρ), which is a quantitative measure of the electronic substituent effect in terms of the extent of delocalization of the unpaired electron at the radical site: a higher ρ value implies a lower spin-delocalization. Experimentally, the spin density of the allylic radical fragment **M** has been assessed in this study (Figure 1) through the *D* parameters of the triplet diradical **T**, which are interrelated by means of Equation (1). To determine the composite electronic effect of the geminal substituents X and Y on the radical center, we utilize the interaction parameter ($\Delta S$), as given in Equation (2). $D_{XY}$ refers to the *D* value of the geminally substituted species, DXH and DYH to those of the respective monosubstituted derivatives, and DHH is that of the unsubstituted case as reference system.

$$\Delta S = \frac{S_{XY}^{exp} - S_{XY}^{ref}}{S_{XY}^{ref}} x100 \quad \begin{cases} > 0 \text{ synergism} \\ = 0 \text{ additivity} \\ < 0 \text{ antagonism} \end{cases}$$

$$\text{where} \quad S_{XY}^{ref} = 1-[(1-S_{XH}^{exp})(1-S_{YH}^{exp})] \qquad (2)$$
$$S_{XY}^{exp} = 1-(D_{XY}/D_{HH})$$
$$S_{YH}^{exp} = 1-(D_{YH}/D_{HH})$$
$$S_{XH}^{exp} = 1-(D_{XH}/D_{HH})$$

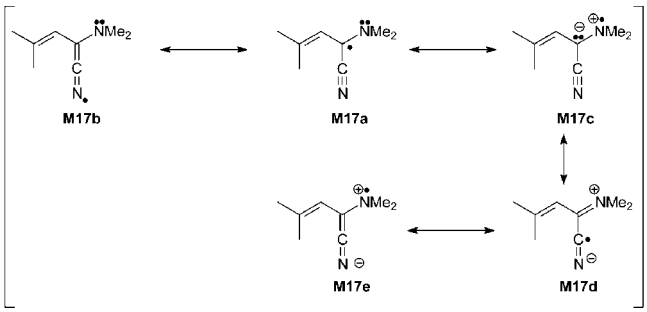
As already stated in the introduction, when $\Delta S = 0$, both substituents X and Y delocalize spin as if each were acting alone (additivity), for $\Delta S$ values greater than 0 there is an increased delocalization (synergism), whereas for $\Delta S$ values less than 0 a localizing effect (antagonism) is observed. The $\Delta S$ values in Table 2 have been computed according to Equation (2) from the data in Figure 1 (Table 1) and shall now be analyzed and discussed for the various X,Y substituent combinations in the allylic radical fragments **M**. Before entering into the details, it is gratifying to point out that the general trends in the $S^{exp}$ and $\Delta S$ data agree reasonably well with the few available published values.[1b,2]2

Table 2. The delocalization ($S^{exp}$ and $S^{ref}$) and the interaction ($\Delta S$) parameters of the disubstituted (X,Y) allylic monoradical fragments **M**, computed from the *D* parameter of the corresponding triplet diradicals **T**

| M[a] | X | Y | $S^{exp}$ | $S^{ref}$ | $\Delta S$ |
|---|---|---|---|---|---|
| **M17** | $NMe_2$ | CN | 0.349 | 0.209 | +67[b] |
| **M16** | $N(-C_2H_4OC_2H_4-)$ | CN | 0.341 | 0.209 | +63 |
| **M12** | OMe | $CO_2Me$ | 0.212 | 0.260 | +59 |
| **M11** | OMe | CN | 0.208 | 0.163 | +42 |
| **M15** | SMe | CN | 0.282 | 0.273 | +3 |
| **M14** | SMe | $CO_2Me$ | 0.252 | 0.247 | +2 |
| **M10** | SMe | SMe | 0.203 | 0.041 | −22 |
| **M 8** | SMe | SOMe | 0.146 | 0.187 | −22 |
| **M 5** | SMe | OMe | 0.086 | 0.131 | −34 |

[a] The $\Delta S$, $S^{exp}$ and the $S^{ref}$ values for radical fragment **M** were calculated from the corresponding *D* values of the respective mono- and disubstituted diradicals **T**. [b] $\Delta S$ of the **M17** allylic radical fragment was determined from **M4**, because the derivative with the $NMe_2$/H substitution was not available.

The $\Delta S$ values of the monoradical fragments **M** have been arranged in descending order. The most pronounced synergetic interaction ($\Delta S > 0$) in Table 2 corresponds to the ED/EA-substituted **M17** (Entry 1) and **M16** (Entry 2) allylic radical fragments, in which the amino functionality acts as an electron-donating and the cyano group as an electron-accepting substituent. The highly positive values [$\Delta S = +67$ for **M17** (Entry 1) and $\Delta S = +63$ for **M16** (Entry 2)] testify that the odd electron is especially well delocalized, and presumably thereby extraordinarily stabilized, which confirms the captodative effect.[1] Thus, as a conse-




Scheme 2. The mesomeric structures for the captodative effect in the allylic radical fragment **M17**

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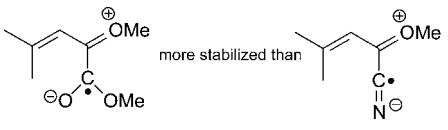
quence of this geminal EA/ED substitution, the unpaired electron is not only delocalized by one or the other functional group, but especially well delocalized by the combination. This pronounced captodativity may be accounted for in terms of additional mesomeric structures of the electron-transfer type, as shown for **M17** in Scheme 2. Whereas the **M17b** and **M17c** contributing structures describe the individual electronic effects for the CN and for the $Me_2N$ functionalities, the additional valence-bond structures **M17d** and **M17e** manifest a synergism between the two interacting groups. As expected, such a captodative radical is electronically better stabilized than merely adding the individual effects of the monosubstituted derivatives.

The next two ED/EA combinations, namely the OMe/$CO_2Me$ pair in the allylic radical fragment **M12** (Entry 3) and OMe/CN in **M11** (Entry 4), also exhibit a high synergistic effect, as evidenced by the large positive $\Delta S$ values (Table 2). It is not surprising that the $Me_2N$/CN combination in Entry 1 displays a higher captodativity than the MeO/CN pair (Entry 4), because the amino group ($S^{exp}$ = +0.064) in the monosubstituted radical fragment **M4** (Entry 4 in Table 1) is a better radical delocalizing functionality than the methoxy group ($S^{exp}$ = −0.010) in **M1** (Entry 1, Table 1). However, the MeO/$CO_2Me$ combination ($\Delta S$ = +59) is captodatively more effective than the MeO/CN pair ($\Delta S$ = +42); in fact, this is contrary to the delocalization ability of the individual EA-type groups, which is lower for $CO_2Me$ than for CN, as shown by the $S^{exp}$ values of the monosubstituted radical fragment **M6** ($S^{exp}$ = +0.125) for the methoxycarbonyl and **M9** ($S^{exp}$ = +0.155) for the cyano case (Entries 6 and 9, Table 1). These data reveal that the methoxy group interacts better synergistically with the methoxycarbonyl group than with a cyano one. The higher affinity of the methoxycarbonyl versus the cyano group to interact synergistically with a methoxy substituent means that the captodative effect does not necessarily obey the radical-stabilizing trend displayed by the corresponding monosubstituted allylic radicals. Evidently, the ketyl-type[14] mesomeric structure **M12d** contributes more to the spin delocalization than the iminyl-type **M11d** structure.




**M12d** **M11d**

The small $\Delta S$ values, namely +3 for **M17** (MeS/CN) and +2 for **M14** (MeS/$CO_2Me$), disclose that for these geminal substituent combinations the synergistic interplay is essentially negligible. The lack of captodative interaction between these geminal functional groups is even more amazing if the $\Delta S$ values of the MeS/EA combination are compared with those of the MeO/EA pairs: Whereas the $\Delta S$ values for MeO/EA (+42 and +59) exhibit a high captodativity, the corresponding values for the MeS/EA (+2 and +3) analogs indicate solely additive electronic substituent effects. This difference in the electronic behavior between the MeS/EA and MeO/EA pairs becomes still more remarkable when it is realized that in the spin delocalization by the individual MeO and MeS functionalities alone, the latter is considerably more effective (Table 3). Also, the $S^{exp}$ values of the monosubstituted allylic radicals in Table 2 confirm unequivocally this trend for **M1** ($S^{exp}$ = −0.010) versus **M7** ($S^{exp}$ = 0.140).

Table 3. Comparison of the $\sigma^{\cdot}$ and the $\Delta D$ values for the MeO and MeS groups

| X | $\sigma^{\cdot}_F$ [a] | $\sigma^{\cdot}_J$ [b] | $\sigma^{\cdot}_C$ [c] | $\sigma^{\cdot}_{JJ}$ [d] | $\Delta D$[e] |
|---|---|---|---|---|---|
| OMe | −0.12 | 0.43 | 0.24 | 0.23 | −0.02 |
| SMe | | 0.63 | 0.43 | 0.62 | 0.14 |

[a] Ref. 15. [b] Ref. 16. [c] Ref. 17. [d] Ref. 18. [e] Ref. 19.

Although such differences in the spin delocalization between MeO/EA and MeS/EA pairs have been reported before,[2,17] these electronic effects have not as yet been rationalized. We propose that the electron-transfer-type mesomeric structures in Figure 2 are responsible for this unusual behavior.

For the singly acting MeO and MeS groups in the allylic radical fragments **M1** and **M7**, the dipolar electron-transfer-type mesomeric structure **M1c** is less favorable than **M7c** due to the higher electronegativity of oxygen versus sulfur; consequently, MeS delocalizes the spin better than OMe (see Table 3). In contrast, in combination with an electron acceptor, exemplified for the MeO/$CO_2Me$ and MeS/$CO_2Me$ pairs in the respective allylic radical fragments **M12** and **M14** (Figure 2), the doubly bonded structures **M12d** and **M14d** must be considered in order to express the cooperative spin delocalization by both geminal substituents.

Sulfur, an element of the third row, possesses a lower propensity to form double bonds than oxygen, so that the contribution of the mesomeric structure **M14d** is negligible compared to **M12d**. Thus, the electronegativity effect (oxygen worse than sulfur) in the electron-transfer-type structures **M12e** versus **M14e** competes with the double-bonding ability (oxygen better than sulfur) in the structures **M12d** versus **M14d**. Evidently, the latter effect dominates such that the MeO/$CO_2Me$ pair delocalizes more efficiently (higher captodativity) than MeS/$CO_2Me$ ($\Delta S$ = +2); thus, the joint action of the two geminal substituents is essentially additive, whereas for MeO/$CO_2Me$ ($\Delta S$ = +59) it is highly synergistic (captodative).

An alternative rationalization is provided by the frontier-molecular-orbital (FMO) analysis in Figure 3. As a model, we have chosen the methoxy- and thiomethoxy-substituted cyanomethyl radicals MeO−CH·−CN and Me−HC·−CN and MeS−C·H−CN. For the SOMO energy of the $\cdot CH_2CN$ radical, the experimentally assessed ionization potential of the $\cdot CH_2CN$ radical was taken (10.30 eV).[20] The HOMO energies of the methoxy and thiomethoxy groups were approximated by the experimental ionization potentials of methanol (10.03 eV)[21] and thiomethanol (8.67 eV).[22]

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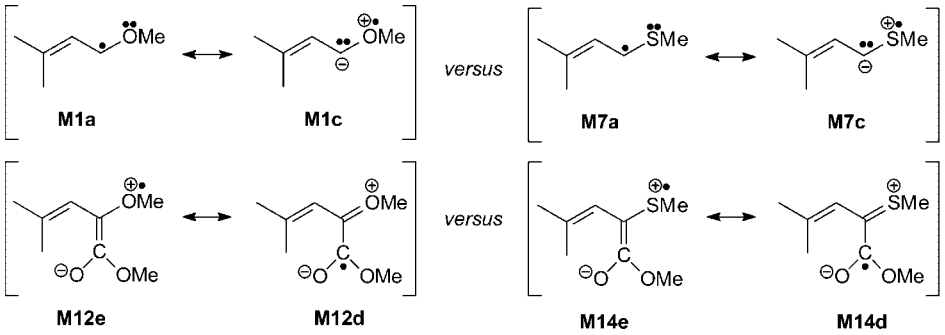



Figure 2. Electron-transfer-type resonance structures for the allylic radical fragments **M1** versus **M7** and **M12** versus **M14**

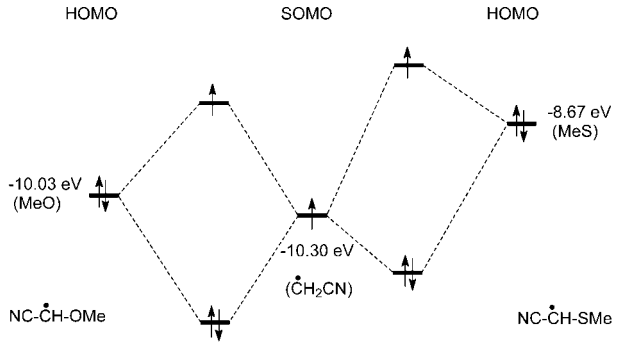
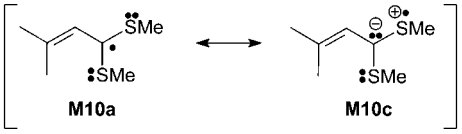



Figure 3. FMO scheme for the SOMO/HOMO interaction in the Me−HC·−CN versus MeS−C·H−CN radicals

As becomes conspicuous from the energy-level ordering of the HOMO'S relative to the SOMO, the electronic stabilization in the MeO/CN pair is considerably more effective than in the MeS/CN combination and the latter is presumably therefore a more effective captodative system.

The last three Entries in Table 2 possess negative $\Delta S$ values, which indicates an antagonistic interaction of the various combinations with sulfur functionalities. For the donor-donor combination SMe/SMe in the **M10** allylic radical fragment ($\Delta S = -22$), the dipolar electron-transfer-type mesomeric structure **M10c** applies, in which a positive charge is favorably accommodated on the sulfur atom.[1,5]




Nevertheless, the incipient negative charge at the carbanionic site induces lone-pair repulsion with the proximate thiomethyl group, which effectively counteracts the intended spin delocalization. Overall, such electron-transfer-type delocalization in the ED/ED-disubstituted radical species **M10** is disadvantageous, as confirmed by the antagonistic effect. This antagonism of the MeS/MeO pair ($\Delta S = -34$) in **M5** is more pronounced than that of the MeS/MeS ($\Delta S = -22$) combination in **M10**. This may again be reconciled in terms of the larger individual effects in the monosubstituted allylic radical fragments: The MeO substituent ($S^{exp} = -0.010$) in **M1** (Entry 1, Table 1) resists delocalization more than the MeS substituent ($S^{exp} = 0.140$) in **M7** (Entry 7, Table 1).

The SMe/SOMe combination in the **M8** allylic radical fragment (Entry 8) is unusual, as the interaction parameter ($\Delta S = -22$) shows that this radical species belongs to the antagonistic type despite the fact that this disubstitution is that of an ED/EA pair. The sulfoxide functionality, although classified electronically as an electron-accepting group,[3] has a low propensity to delocalize spin in radicals. This is also expressed by the similar $S^{exp}$ values for the individual MeS (0.140) and MeSO (0.055) substituents in the respective monosubstituted allylic fragment **M7** (Entry 7, Table 1) versus the MeSO group in **M3** (Entry 3, Table 1). Presumably, in regard to its interaction with a radical center, the MeSO group acts more like an ED substituent through its lone pair, for which the electron-transfer-type mesomeric structure **M8c** (analogous to **M10c**) is undesirable on account of lone-pair/lone-pair repulsion.

## Conclusion

The present study on the spin delocalization by geminal substituents in allylic radicals has shown that the captodative behavior of the EA/ED combinations is principally assigned to dipolar mesomeric structures, in which the spin is delocalized simultaneously on both functionalities. The electronic interaction of the geminal substituents in the MeO/EA combination is strongly synergistic (captodative), but only additive in the MeS/EA pair. Evidently, the efficacy of captodative stabilization is a sensitive function of the particular combination of the EA and ED substituents on the radical center. The antagonistic interaction in the ED/ED combinations derives from the electrostatic repulsion of the unpaired electron with the non-conjugating donor substituent.

## Experimental Section

**General Remarks:** The melting points are not corrected. The combustion analyses were performed by the Microanalytical Division of the Institute of Inorganic Chemistry (University of Würzburg). Solvents and commercially available chemicals were purified by

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standard procedures or used as bought. Column chromatography was carried out on silica gel (0.032−0.063 mm, Wolem) with an adsorbent/substrate ratio of ca. 100:1. Thin-layer chromatography (TLC) was performed on Polygram Sil G/UV254 (40 × 80 nm) from Macherey & Nagel. Irradiations were carried out with the 364-nm UV line (widened beam) of a CW argon-ion laser (INNOVA 100, Coherent Co.). The known azoaldehyde A was prepared according the method described in the ref.[7]. The required phosphonates and phosphane oxides were either synthesized as reported in the literature or acquired from commercial sources.

**(1′b*R**,4′*R**,4′a*S**,7′a*R**)-(4′,4′a,5′,6′,7′,7′a-Hexahydro-8′,8′-dimethyl-4′-phenyl-1*H*-1′,4′-methanocyclopenta[*d*]pyridazinyl)-acetaldehyde (A′):** Under argon, a solution of 207 mg (2.04 mmol, 287μL) of diisopropylamine, 1.27 mL (2.00 mmol, 1.6 M) of *n*BuLi in hexane and 60 mL of abs. THF was prepared at −78 °C and stirred magnetically for 45 min. At this temperature, a solution of (methoxymethyl)diphenylphosphane oxide (469 mg, 1.90 mmol) in 10 mL of abs. THF was added within 15 min to the LDA solution and the reaction stirred for 1 h at −78 °C. A solution of azoaldehyde **A** (500 mg, 1.85 mmol) in 10 mL of abs. THF was added to the intense red-colored solution within 10 min by means of a syringe. The reaction mixture was then allowed to warm to about 20 °C and stirred magnetically for a further 3 h at the same temperature. After addition of 20 mL of diethyl ether, the solution was washed with water (1 × 20 mL), brine (2 × 50 mL), and dried with $MgSO_4$. After removal of the solvent (40 °C, 20 mbar), the residue was purified by column chromatography to afford 416 mg (1.40 mmol, 76%) of azoalkane **A1**.[7] The enol ether **A1** [416 mg (1.40 mmol)] was dissolved in 40 mL of THF and, after addition of 20 mL of 50% aqueous TFA, the solution was magnetically stirred for 1 h at 40 °C. The solvent was removed by distillation (40 °C, 20 mbar) and the residue redissolved in 40 mL of diethyl ether and dried with $K_2CO_3$. After removal of the solvent, the residue was recrystallized from 40 mL of dry *n*-pentane at −20 °C to afford 382 mg (1.36 mmol, 97%) of acetaldehyde **A′** as colorless needles, m.p. 106−107 °C. IR (KBr): $\tilde{\nu}$ = 2931, 2910, 1703, 1628, 1498, 1124, 1099 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): δ = 0.31 (s, 3 H), 0.90 (s, 3 H), 1.12−1.82 (m, 6 H), 2.85−3.00 (m, 1 H), 3.06 (dd, $^2J$ = 13.0, $^3J$ = 3.0 Hz, 1 H) 3.21 (dd, $^2J$ = 13.0, $^3J$ = 3.3 Hz, 1 H) 3.30−3.50 (m, 1 H), 7.28−7.34 (m, 3 H), 7.45−7.68 (m, 2 H), 10.25 (dd, $^3J$ = 3.3, $^3J$ = 3.0 Hz, 1 H) ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 17.3, 18.6, 26.5, 27.2, 29.0, 50.2, 51.2, 62.1, 68.6, 97.5, 98.3, 128.4, 129.5, 129.6, 130.2, 197.2 ppm. $C_{18}H_{22}N_2O$ (282.3): calcd. C 76.56, H 7.85, N 9.92; found C 76.51, H 7.91, N 9.80.

**(1*R**,4*R**,4a*S**,7a*R**)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1-[*E*-2′-(4′′-morpholinyl)ethenyl]-4-phenyl-1*H*-1,4-methanocyclopenta[*d*]-pyridazine (A4):** Under argon, a sample of 250 mg (885 μmol) of azoacetaldehyde **A′** was dissolved in 30 mL of dry diethyl ether at about 20 °C, freshly distilled morpholine (154 mg, 1.77 mmol) and 2.00 g of powdered $K_2CO_3$ were added and the suspension stirred magenetically for 2 days. After filtration of the $K_2CO_3$, the solvent was evaporated by distillation (40 °C, 20 mbar) and the residue recrystallized from diethyl ether/*n*-pentane (1:1) at −20 °C. The colorless needles were dried for 2 days over $P_2O_5$, to afford 229 mg (655 μmol, 74%) of the azoalkane **A4**; m.p. 113−114 °C. IR (KBr): $\tilde{\nu}$ = 2945, 2921, 2219, 1620, 1598, 1322, 1114, 1072 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): δ = 0.26 (s, 3 H), 0.66 (s, 3 H), 1.12-.1.91 (m, 6 H), 2.11−2.25 (m, 4 H), 2.87−3.04 (m, 1 H), 3.30−3.53 (m, 1 H), 3.59−3.65 (m, 4 H), 4.98 (d, $^2J$ = 12.1 Hz, 1 H), 5.71 (d, $^2J$ = 12.1 Hz, 1 H), 7.29−7.32 (m, 3 H), 7.62−7.75 (m, 2 H) ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 16.3, 17.2, 26.1, 27.1, 29.0, 43.1, 48.2, 50.2, 57.5, 68.6, 97.5, 98.3, 120.5, 126.3, 128.4, 128.9, 129.5, 130.2 ppm. $C_{22}H_{29}N_3O$ (351.5): calcd. C 75.18, H 8.32, N 11.95; found C 74.84, H 8.26, N 11.93.

**(1*R**,4*R**,4a*S**,7a*R**)-4,4a,5,6,7,7a-Hexahydro-1-(2′-methoxy-2′-methylthiovinyl)-8,8-dimethyl-4-phenyl-1*H*-1,4-methanocyclopenta-[*d*]pyridazine (A5):** Under argon, a solution of 145 mg (1.42 mmol, 201μL) of diisopropylamine and 888 μL (1.40 mmol, 1.6 M) of *n*BuLi in hexane in 50 mL of abs. THF was prepared at −78 °C and stirred magnetically for 45 min. At this temperature, a solution of (methoxymethylthio)methyldiphenylphosphane oxide (389 mg, 1.33 mmol) dissolved in 10 mL of abs. THF was added within 15 min to the LDA solution and the reaction mixture stirred for 1 h at 78 °C. A solution of the azoaldehyde **A** (350 mg, 1.30 mmol) in 10 mL of abs. THF was added within 10 min by means of a syringe. Immediately after the addition of **A**, the reaction mixture was warmed to about 20 °C and stirred magnetically for a further 4 h at this temperature. After addition of 20 mL of diethyl ether, the reaction mixture was washed with water (1 × 20 mL), brine (2 × 50 mL), and dried with $MgSO_4$. After removal of the solvent (40 °C, 20 mbar), the residue was purified by column chromatography to afford 45.0 mg (130 μmol, 10%) of azoalkane **A5** as an *E*/*Z* mixture, m.p. 91−93 °C. IR (KBr): $\tilde{\nu}$ = 2945, 2921, 1600, 1468, 1202, 1194, 1012 $cm^{-1}$; (*Z*)-diastereomer: $^1H$ NMR (200 MHz, $CDCl_3$): δ = 0.31 (s, 3 H), 0.94 (s, 3 H), 1.28−1.77 (m, 6 H), 2.31 (s, 3 H), 3.28−42 (m, 1 H), 3.51−3.61 (m, 1 H), 3.73 (s, 3 H), 5.33 (s, 1 H), 7.36−7.48 (m, 3 H), 7.67−7.72 (m, 2 H) ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 17.7, 18.1, 24.2, 25.4, 25.7, 28.6, 48.9, 49.2, 58.0, 64.9, 96.1, 97.7, 113.2, 127.9, 128.2, 128.8, 136.9, 152.2 ppm; (*E*)-diastereomer: $^1H$ NMR (200 MHz, $CDCl_3$): δ = 0.35 (s, 3 H), 0.89 (s, 3 H), 1.28−1.77 (m, 6 H), 2.29 (s, 3 H), 3.28−42 (m, 1 H), 3.51−3.61 (m, 1 H), 3.79 (s, 3 H), 5.52 (s, 1 H), 7.36−7.48 (m, 3 H), 7.67−7.72 (m, 2 H) ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 17.1, 18.4, 22.0, 25.9, 25.2, 28.3, 48.2, 49.7, 58.8, 65.2, 97.4, 98.1, 114.1, 127.2, 126.3, 128.8, 136.7, 151.0 ppm. $C_{20}H_{26}N_2OS$ (342.5): calcd. C 70.14, H 7.65, N 8.18, S 9.36; found C 69.87, H 7.84, N 8.25, S 8.94.

**(1*R**,4*R**,4a*S**,7a*R**)-4,4a,5,6,7,7a-Hexahydro-1-(2′-methylthio-2′-methylsulfinylethenyl)-8,8-dimethyl-4-phenyl-1*H*-1,4-methanocyclopenta[*d*]pyridazine (A8):** Under argon, 1.05 mL (1.69 mmol, 1.6 M) of *n*BuLi in hexane was added to a solution of 160 mg (1.30 mmol, 131 μL) of (methylthio)methylsulfinylmethane in 40 mL of abs. THF, and stirred magnetically for 45 min at −78 °C. A solution of the azoaldehyde **A** (350 mg, 1.30 mmol) in 5 mL of abs. THF was then added at −78 °C. The reaction mixture was slowly warmed to room temperature and then stirred for a further hour. The reaction mixture was cooled to 0 °C, acetic anhydride (265 mg, 2.60 mmol) was added and stirred for 1 h at ca. 20 °C. After addition of potassium *tert*-butoxide (292 mg, 2.60 mmol), the reaction mixture was stirred for 4 h at about 20 °C, 40 mL of diethyl ether was added, and the solution washed with water (1 × 20 mL), brine (2 × 50 mL), and dried with $MgSO_4$. After removal of the solvent (40 °C, 20 mbar), the residue was purified by radial chromatography (Chromatotron) to afford 44.0 mg (117 μmol, 9%) of the azoalkane **A8** as a colorless oil; $R_F$ = 0.34 (silica gel, dichloromethane/ethyl acetate, 3:2). IR (KBr): $\tilde{\nu}$ = 2925, 2921, 1676, 1578, 1402, 1014, 1052 $cm^{-1}$; (*Z*)-diastereomer: $^1H$ NMR (200 MHz, $CDCl_3$): δ = 0.32 (s, 3 H), 1.01 (s, 3 H), 1.47−1.66 (m, 6 H), 2.44 (s, 3 H), 2.87 (s, 3 H) 3.21−3.45 (m, 2 H), 7.14 (s, 1 H), 7.41−7.46 (m, 3 H), 7.63−7.70 (m, 2 H) ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 17.7, 18.1, 20.4, 25.4, 25.5, 28.4, 42.4, 48.6, 49.6, 64.4, 96.1, 97.7, 127.5, 128.1, 128.6, 131.5, 136.4, 143.5 ppm; *E*-diastereomer: $^1H$ NMR (200 MHz, $CDCl_3$): δ = 0.37 (s, 3 H), 1.04 (s, 3 H), 1.47−1.66 (m, 6 H), 2.56 (s, 3 H), 2.77 (s, 3 H) 3.21−3.45 (m, 2 H), 7.14 (s, 1 H),

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7.41−7.46 (m, 3 H), 7.63−7.70 (m, 2 H) ppm. $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 17.0, 18.9, 20.3, 25.1, 25.4, 28.5, 41.2, 48.5, 49.8, 64.5, 96.0, 97.9, 127.4, 128.2, 128.8, 131.4, 136.1, 143.0 ppm. $C_{20}H_{26}N_2OS$ (374.6): calcd. C 64.13, H 7.00, N 7.48, S 17.12; found C 64.00, H 7.04, N 7.57, S 16.62.

**(1*R**,4*R**,4a*S**,7a*R**)-1-[2′,2′-Bis(methylthiovinyl)]-4,4a,5,6,7,7a-hexahydro-8,8-dimethyl-4-phenyl-1*H*-1,4-methanocyclopenta[*d*]pyridazine (A10):** Under argon, 500 μL (800 μmol, 1.6 M) of *n*BuLi in hexane was added to a solution of 145 mg (800 μmol) of bis-methylthiotrimethylsilylmethane in 50 mL of abs. THF and stirred magnetically for 4 h at −20 °C. Then, a solution of 200 mg (743 μmol) of the azoaldehyde **A** in 10 mL of abs. THF was added to the reaction mixture within 5 min and, after warming to about 20 °C, the mixture was stirred for a further 18 h. Afterwards 50 mL of diethyl ether was added and the solution washed with water (1 × 20 mL), brine (2 × 20 mL), and dried with $MgSO_4$. After removal of the solvent (40 °C, 20 mbar), the residue was submitted to radial chromatography (Chromatotron) to afford 252 mg (117 μmol, 88%) of the azoalkane **A10** as a colorless powder, m.p. 108−109 °C; $R_f$ = 0.21 [silica gel, dichloromethane] IR (KBr): $\tilde{\nu}$ = 2900, 1531, 1245, 1118, 1077, 1025 cm$^{-1}$. $^1$H NMR (200 MHz, $CDCl_3$): δ = 0.37 (s, 3 H), 0.74 (s, 3 H), 1.22−1.98 (m, 6 H), 2.02 (s, 3 H), 2.17 (s, 3 H), 2.99−3.04 (m, 1 H), 3.19−3.28 (m, 1 H), 6.42 (s, 1 H), 7.18−7.29 (m, 3 H), 7.71−7.76 (m, 2 H) ppm. $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 17.1, 17.8, 18.9, 19.1, 24.9, 25.4, 28.2, 48.3, 49.1, 66.9, 96.1, 98.2, 116.6, 126.0, 127.8, 127.9, 136.2, 142.0 ppm. $C_{20}H_{26}N_2S_2$ (358.6): calcd. C 67.00, H 7.31, N 7.81, S 17.88; found C 66.98, H 7.31, N 8.01, S 17.39.

**(1′*R**,4′*R**,4′a*S**,7′a*R**)-(*Z*)-3-(4′,4′a,5′,6′,7′,7′a-Hexahydro-8′,8′-dimethyl-4′-phenyl-1*H*-1′,4′-methanocyclopenta[*d*]pyridazinyl)-2-methoxyacrylonitrile (A11):** Under argon, a solution of 91.0 mg (890 μmol, 126 μL) of diisopropylamine and 888 μL (1.40 mmol, 1.6 M) of *n*BuLi in 50 mL of abs. THF was prepared at −78 °C and stirred magnetically for 45 min. At this temperature, a solution of 157 mg (758 μmol) of diethyl (cyanomethoxy)-methylphosphonate in 5 mL of abs. THF was added within 5 min and the reaction mixture stirred magnetically for 1 h. Then a solution of 200 mg (741 μmol) of azoaldehyde **A** and 5 mL abs. THF was added to the reaction mixture within 10 min by means of a syringe. Immediately after the addition of **A**, the reaction mixture was warmed to 0 °C and stirred magnetically for a further 2 h at this temperature. A solution of 20 mL of diethyl ether was then added to the reaction mixture, washed with water (1 × 20 mL), brine (2 × 50 mL), and dried with $MgSO_4$. After removal of the solvent (40 °C, 20 mbar), the residue was purified by column chromatography to afford 209 mg (652 μmol, 88%) of the azoalkane **A11** as a colorless powder, m.p. 137−139 °C. IR (KBr): $\tilde{\nu}$ = 2296, 2905, 2200, 1309, 1228, 1094, 1004 cm$^{-1}$. $^1$H NMR (200 MHz, $CDCl_3$): δ = 0.34 (s, 3 H), 1.00 (s, 3 H), 1.18-.1.86 (m, 6 H), 2.80−3.03 (m, 1 H), 3.30−3.46 (m, 1 H), 3.68 (s, 3 H) 6.08 (s, 1 H), 7.28−7.32 (m, 3 H), 7.62−7.75 (m, 2 H) ppm. $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 18.1, 19.1, 26.3, 27.4, 29.9, 46.2, 49.2, 56.2, 68.6, 97.5, 98.3, 114.5, 123.3, 128.6, 129.6, 130.0, 130.2, 149.3 ppm. $C_{20}H_{23}N_3O$ (321.4): calcd. C 74.74, H 7.21, N 13.07; found C 74.95, H 7.48, N 13.24.

**Methyl (1′*R**,4′*R**,4′a*S**,7′a*R**)-3-(4′,4′a,5′,6′,7′,7′a-Hexahydro-8′,8′-dimethyl-4′-phenyl-1*H*-1′,4′-methanocyclopenta[*d*]pyridazinyl)-2-methoxyacrylate (A12):** Potassium hydride (oil free; 148 mg, 3.70 mmol) was added to a solution of diethyl (methoxymethoxycarbonyl)methylphosphonate in 30 mL of abs. THF under argon and the resulting suspension stirred magnetically for 20 min at 0 °C. Then a solution of 200 mg (741 μmol) of the azoaldehyde **A** and 10.0 mg (37.0 μmol) of 18-crown-6 in 5 mL of abs. THF was added by means of a syringe within 5 min and the suspension stirred at about 20 °C for 3 days. Afterwards, 20 mL of diethyl ether was added and the reaction mixture washed with water (20 mL), brine (2 × 50 mL), and dried with $MgSO_4$. After removal of the solvent (40 °C, 20 mbar), the residue was purified by column chromatography to afford 209 mg (652 μmol, 30%) of the azoalkane **A12** as an *E*/*Z* mixture; colorless needles, m.p. 88−91 °C; $R_F$ = 0.32 (silica gel, dichloromethane/ethyl acetate, 10:3). IR (KBr): $\tilde{\nu}$ = 2926, 2905, 1721, 1729, 1406, 1399, 1087 cm$^{-1}$; (*E*)-diastereomer: $^1$H NMR (200 MHz, $CDCl_3$): δ = 0.29 (s, 3 H), 0.95 (s, 3 H), 1.25−1.77 (m, 6 H), 2.86−2.94 (m, 1 H), 3.29−3.33 (m, 1 H), 3.33 (s, 3 H), 3.74 (s, 3 H), 4.91 (s, 1 H), 7.39−7.44 (m, 3 H), 7.65−7.69 (m, 2 H) ppm. $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 17.7, 18.1, 25.4, 25.5, 28.4, 48.6, 48.9, 58.0, 59.0, 64.5, 96.0, 97.9, 123.0, 127.4, 128.2, 128.8, 136.4, 147, 168.2 ppm; (*Z*)-diastereomer: $^1$H NMR (200 MHz, $CDCl_3$): δ = 0.32 (s, 3 H), 0.98 (s, 3 H), 1.25−1.77 (m, 6 H), 2.86−2.94 (m, 1 H), 3.29−3.33 (m, 1 H), 3.35 (s, 3 H), 3.86 (s, 3 H), 6.75 (s, 1 H), 7.39−7.44 (m, 3 H), 7.65−7.69 (m, 2 H) ppm. $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 17.2, 18.0, 25.3, 25.2, 28.2, 48.3, 49.1, 58.4, 59.9, 64.9, 96.2, 97.4, 123.4, 127.1, 128.0, 129.2, 134.0, 147.9, 166.2 ppm. $C_{21}H_{26}N_2O_3$ (354.4): calcd. C 71.16, H 7.39, N 7.90; found C 70.99, H 7.32, N 8.16.

**(1*R**,4*R**,4a*S**,7a*R**)-1-(1,3-Dithian-2′-ylidenemethyl)-4,4a,5,6,7,7a-hexahydro-8,8-dimethyl-4-phenyl-1*H*-1,4-methanocyclopenta[*d*]pyridazine (A13):** Under argon, 510 μL (817 μmol, 1.6 M) of *n*BuLi in hexane was added to a solution of 157 mg (817 μmol) of 2-trimethylsilyl-1,3-dithiane in 50 mL of abs. THF and the mixture stirred magnetically for 4 h at −20 °C. Then a solution of 200 mg (743 μmol) of the azoaldehyde **A** in 5 mL of abs. THF was added within 5 min and, after warming to about 20 °C, the reaction was stirred for a further 18 h. Afterwards, 50 of mL diethyl ether was added and the solution washed with water (20 mL), brine (2 × 20 mL), and dried with $MgSO_4$. After removal of the solvent (40 °C, 20 mbar), the residue was submitted to radial chromatography (chromatotron) to afford 252 mg (117 μmol, 79%) of the azoalkane **A13** as a colorless powder, m.p. 118−119 °C; $R_F$ = 0.72 (silica gel, dichloromethane/ethyl acetate, 10:1). IR (KBr): $\tilde{\nu}$ = 2921, 2905, 2201, 1606, 1598, 1114. $^1$H NMR (200 MHz, $CDCl_3$): δ = 0.30 (s, 3 H), 0.81 (s, 3 H), 1.22−2.10 (m, 6 H), 2.13−2.19 (m, 2 H), 2.47−2.98 (m, 4 H), 3.00−3.11 (m, 1 H), 3.30−3.50 (m, 1 H), 6.50 (s, 1 H), 7.28−7.44 (m, 3 H), 7.78−7.91 (m, 2 H) ppm. $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 17.0, 17.3, 23.3, 24.9, 25.6, 28.1, 28.5, 48.2, 50.2, 66.6, 91.1, 95.6, 123.7, 127.7, 128.0, 128.3, 136.6, 137.1 ppm. $C_{21}H_{26}N_2S_2$ (370.6): calcd. C 68.07, H 7.07, N 7.56, S 17.30; found C 67.90, H 7.37, N 7.68, S 17.02.

**Methyl (1′*R**,4′*R**,4′a*S**,7′a*R**)-(*Z*)-3-(4′,4′a,5′,6′,7′,7′a-Hexahydro-8′8′-dimethyl-4′-phenyl-1*H*-1′,4′-methanocyclopenta[*d*]-pyridazinyl)-2-(methylthio)acrylate (A14):** Under argon, 90 mg (750 μmol) of methyl (methylthio)acetate was added to 2 mL of sodium methoxide solution in methanol (0.75 M) and stirred magnetically for 15 min at −5 °C. After addition of a solution of 200 mg (743 μmol) of THE azoaldehyde **A** in 1.00 mL of MeOH, the reaction mixture was warmed to about 20 °C and stirred for a further 5 days at room temperature. The solvent was removed by distillation (40 °C, 20 mbar) and the residue dissolved in 20 mL of diethyl ether, the solution washed with water (2 × 10 mL), brine (2 × 10 mL), and dried with $MgSO_4$. The residue was submitted to radial chromatography (Chromatotron) to afford, after further recrystallization (ethyl ether/*n*-pentane, 1:10), 68.0 mg (185 μmol, 39%) of azoalkane **A14** as colorless needles, m.p. 140−142 °C; $R_F$ = 0.31 (silica gel, dichloromethane/ethyl acetate, 10:1). IR (KBr): $\tilde{\nu}$ = 2921, 2905, 1782, 1538, 1312, 1114 cm$^{-1}$. $^1$H NMR (200 MHz,

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$CDCl_3$): δ = 0.36 (s, 3 H), 1.02 (s, 3 H), 1.28−1.62 (m, 6 H), 2.33 (s, 3 H), 3.38−3.55 (m, 1 H), 3.59−3.71 (m, 1 H), 3.89 (s, 3 H), 7.31−7.48 (m, 3 H), 7.42 (s, 1 H), 7.65−7.73 (m, 2 H) ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 17.1, 18.0, 21.2, 24.9, 25.4, 28.3, 48.5, 49.0, 52.6, 68.0, 96.7, 97.5, 127.8, 128.1, 128.6, 134.2, 135.9, 140.7, 166.5 ppm. $C_{21}H_{26}N_2O_2S$ (370.5): calcd. C 68.08, H 7.07, N 7.56, S 8.65; found C 67.72, H 7.14, N 7.72, S 8.49.

**(1′*R**,4′*R**,4′a*S**,7′a*R**)-3-(4′,4′a,5′,6′,7′,7′a-Hexahydro-8′,8′-dimethyl-4′-phenyl-1*H*-1′,4′-methanocyclopenta[*d*]pyridazinyl)-2-(methylthio)acrylonitrile (A15):** Under argon, 65.0 mg (750 μmol) of (methylthio)acetonitrile was added to 2 mL of a sodium methoxide solution in methanol (0.75 M) and stirred magnetically for 15 min at −5 °C. After addition of a solution of 200 mg (743 μmol) of the azoaldehyde **A** in 1.00 mL of MeOH, the reaction was warmed to about 20 °C and stirred for a further 2 days at room temperature. The solvent was removed by distillation (40 °C, 20 mbar) and the residue dissolved in 20 mL of diethyl ether, washed with water (2 × 10 mL), brine (2 × 10 mL), and dried with $MgSO_4$. The residue was submitted to radial chromatography (chromatotron) to afford 180 mg (535 μmol, 72%) of **A15** as colorless needles, m.p. 111−113 °C; $R_F$ = 0.61 (silica gel, dichloromethane/ethyl acetate, 10:1); (*Z*)-diastereomer: $^1H$ NMR (200 MHz, $CDCl_3$): δ = 0.27 (s, 3 H), 0.89 (s, 3 H), 1.25−1.75 (m, 6 H), 2.80−2.93 (m, 1 H), 3.25−3.48 (m, 1 H), 2.11 (s, 3 H), 6.28 (s, 1 H), 7.28−7.49 (m, 3 H), 7.68−7.75 (m, 2 H) ppm. $^{13}C$ NMR(50 MHz, $CDCl_3$): δ = 16.2, 18.9, 19.4, 26.3, 28.5, 30.1, 52.5, 55.0, 59.2, 91.2, 92.2, 113.9, 115.5, 126.8, 128.3, 128.6, 135.6, 135.7 ppm; (*E*)-diastereomer: $^1H$ NMR (200 MHz, $CDCl_3$): δ = 0.26 (s, 3 H), 0.93 (s, 3 H), 1.25−1.75 (m, 6 H), 2.80−2.93 (m, 1 H), 3.25−3.48 (m, 1 H), 2.10 (s, 3 H), 6.08 (s, 1 H), 7.28−7.49 (m, 3 H), 7.68−7.75 (m, 2 H) ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 16.1, 18.8, 19.5, 26.6, 28.4, 30.0, 52.7, 55.2, 59.2, 91.2, 92.4, 113.6, 119.5, 126.8, 128.4, 128.7, 135.7, 139.1 ppm. $C_{20}H_{23}N_3S$ (337.5): calcd. C 71.18, H 6.87, N 12.45, S 9.50; found C 71.49, H 7.10, N 12.34, S 9.05.

**(1′*R**,4′*R**,4′a*S**,7′a*R**)-(*E*)-3-(4′,4′a,5′,6′,7′,7′a-Hexahydro-8′,8′-dimethyl-4′-phenyl-1*H*-1′,4′-methanocyclopenta[*d*]pyridazinyl)-2-(4′′-morpholinyl)acrylonitrile (A16):** A solution of α-morpholinyl-α-trimethylsilylacetonitrile (198 mg, 1.00 mmol) in 20 mL of abs. THF was cooled under argon to −78 °C, 770 μL (1.3 M) of *sec*-BuLi was added dropwise by means of a syringe, and the reaction mixture stirred magnetically for 45 min at −78 °C. Azoaldehyde **A** (244 mg, 909 μmol) was added to this solution, the reaction mixture was warmed slowly to room temperature, and then stirred for an additional 2 h at about 20 °C. After addition of 20 mL of diethyl ether, the organic phase was washed with water (2 × 20 mL), brine (20 mL), and dried with $MgSO_4$. The solvent was removed by distillation (20 °C, 20 mbar) and the residue submitted to radial chromatography (Chromatotron). After crystallization from diethyl ether/*n*-pentane (1:1) at −20 °C, 253 mg (672 μmol, 74%) of the azoalkane **A16** was obtained as colorless needles, m.p. 126−127 °C. IR (KBr): $\tilde{\nu}$ = 2921, 2905, 2201, 1423, 1312, 1109 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): δ = 0.33 (s, 3 H), 0.99 (s, 3 H), 1.32−1.68 (m, 6 H), 3.09−3.14 (m, 4 H), 3.37−3.53 (m, 2 H), 3.72−3.85 (m, 4 H), 5.71 (s, 1 H), 7.38−7.46 (m, 3 H), 7.52−7.67 (m, 2 H) ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 16.8, 17.7, 24.9, 25.5, 28.2, 43.0, 48.4, 48.9, 66.1, 67.3, 95.6, 97.0, 114.5, 115.3, 127.0, 127.7, 128.1, 130.2, 136.0 ppm. $C_{23}H_{28}N_4O$ (376.5): calcd. C 73.37, H 7.50, N 14.88; found C 73.32, H 7.74, N 15.14.

**(*E*)-2-(Dimethylamino)-3-[(1*R**,4*R**,4a*S**,7a*R**)-4,4a,5,6,7,7a-hexahydro-8,8-dimethyl-4-phenyl-1*H*-1,4-methanocyclopenta[*d*]-pyridazinyl]acrylonitrile (A17):** A solution of α-dimethylamino-α-trimethylsilylacetonitrile (128 mg, 1.27 mmol) in 20 mL of abs. THF was cooled under argon to −78 °C, 1.00 mL (1.3 M) of *sec*-BuLi was added dropwise by means of a syringe, and the reaction mixture stirred magnetically for 45 min at −78 °C. Azoaldehyde **A** (340 mg, 1.20 mmol) was added to this solution, and the reaction mixture was allowed to warm slowly to room temperature, and then stirred for an additional 2 h at about 20 °C. After addition of 20 mL of diethyl ether, the organic phase was washed with water (2 × 20 mL), brine (20 mL), and dried with $MgSO_4$. The solvent was removed by distillation (20 °C, 20 mbar) and the residue submitted to radial chromatography (Chromatotron). After crystallization from diethyl ether/*n*-pentane (1:1) at −20 °C (555 mg, 1.65 mmol, 69%), the azoalkane **A17** was obtained as light yellow needles, m.p. 135−136 °C; $R_f$ = 0.36 (silica gel, dichloromethane/*n*-pentane (4:1). IR (KBr): $\tilde{\nu}$ = 2921, 2905, 2201, 1606, 1598, 1114 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$: δ = 0.31 (s, 3 H), 0.78 (s, 3 H), 1.12−1.82 (m, 6 H), 2.31 (s, 6 H), 2.85−3.00 (m, 1 H), 3.30−3.50 (m, 1 H), 6.14 (s, 1 H), 7.28−7.32 (m, 3 H), 7.62−7.75 (m, 2 H) ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 18.3, 19.0, 26.6, 27.1, 29.8, 42.2, 50.2, 51.2, 68.6, 97.5, 98.3, 111.5, 117.3, 128.4, 129.5, 129.6, 130.2, 138.3 ppm. $C_{21}H_{26}N_4$ (334.4): calcd. C 75.41, H 7.84, N 16.75; found C 75.45, H 7.69, N 17.22.

**(Methoxymethylthio)methyldiphenylphosphane Oxide:** Under argon, a solution of 456 mg (4.46 mmol, 651 μL) of diisopropylamine and 2.78 mL (4.46 mmol, 1.6 M) of *n*BuLi in hexane in 100 mL of abs. THF was prepared at −78 °C and stirred magnetically for 45 min. At this temperature, a solution of (methoxymethyl)diphenylphosphane oxide (1.00 g, 4.06 mmol) in 20 mL of abs. THF was added within 15 min to the LDA solution and the reaction mixture stirred for 1 h at −78 °C. Dimethyl disulfide (423 mg, 4.50 mmol) was added to the intense red-colored solution and the reaction mixture slowly warmed to room temperature. After addition of 20 mL of diethyl ether, the organic phase was washed with water (2 × 20 mL), brine (20 mL), and dried with $MgSO_4$. The solvent was removed by distillation (20 °C, 20 mbar) and the residue submitted to silica-gel column chromatography. After recrystallization from diethyl ether, the product was dried with $P_2O_5$ to afford 629 mg (2.15 mmol, 53%) of the desired phosphane oxide as a colorless powder, m.p. 196−198 °C. IR (KBr): $\tilde{\nu}$ = 1480, 1450, 1385, 1118, 1020, 1114 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): δ = 2.10 (s, 3 H), 3.48 (s, 3 H), 4.90 (d, $^2J$ = 5.4 Hz, 1 H), 7.46−7.49 (m, 6 H), 7.77−7.97 (m, 4 H) ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 13.2, 57.3, 86.2, 128.6, 131.5, 132.2, 132.4 ppm. $C_{15}H_{17}O_2PS$ (292.3): calcd. C 61.63, H 5.86, S 10.97; found C 61.68, H 6.01, S 10.68.

**α-Morpholinyl-α-(trimethylsilyl)acetonitrile:** A solution of (morpholin-4-yl)acetonitrile 4.00 g, 31.7 mmol) in 100 mL of abs. THF was cooled to −78 °C and a solution of chlorotrimethylsilane (3.44 g, 31.7 mmol) in 10 mL of abs. THF was added within 15 min by means of a syringe. The precipitated ammonium salt was stirred for 1 h at −78 °C, 17.5 mL (31.7 mmol, 2 M) of LDA solution was added within 30 min, the solution slowly warmed to 0 °C, and stirred for a further 2 h at this temperature. Afterwards, 20 mL of diethyl ether was added and the reaction mixture washed with a saturated solution of ammonium chloride (2 × 30 mL) and water (2 × 30 mL), and dried with $MgSO_4$. After removal of the solvent (40 °C, 20 mbar) the residue was submitted to a Kugelrohr distillation to afford the desired product, 5.64 g (28.5 mmol, 81%), b.p. 126−128 °C (10 mbar). IR (KBr): $\tilde{\nu}$ = 3000, 2890, 2220, 2871, 1470, 1340, 1261, 1126 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): δ = 0.23 (s, 9 H), 2.56−2.60 (m, 4 H), 3.02 (s, 1 H), 3.67−3.75 (m, 4 H) ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = −0.47, 44.2, 45.0, 64.7, 112.5 ppm. HRMS (CI,135 eV): $[M + H]^+$ $C_9H_{19}N_2OSi$ (199.3): calcd. 199.1266, found 199.1265.

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**EPR Spectroscopy:** A sample (5 μmol) of the appropriate azoalkane was dissolved in 0.3 mL of 2-MTHF, placed into an EPR sample tube (diameter approx. 2 mm), and degassed by purging for 10 min with argon gas. The sample was sealed and the matrices were prepared at 77 K by freezing in liquid nitrogen. The triplet diradicals were generated by irradiation with the 364-nm line of an INNOVA-100 CW argon-ion laser (widened beam, 2.5 W, 2 min) at 77 K. The EPR spectra were recorded with a Bruker EPR-300 spectrometer (9.43 GHz, spectra accumulation with the Bruker 1620 data systems). The *D* values were determined by analysis of the *Z* signals.

**Computations:** Full geometry optimization of the monoradicals **M** was carried out on the highest molecular symmetry, to achieve a planar arrangement of the substituents at the radical sites by using the semiempirical PM3 method with annihilated UHF. After geometry optimization, the spin densities were determined by a single-point CI calculation. The Gaussian 98 program package was used and run on a IRIS INDIGO R4000 Silicon Graphics workstation.

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