was set at 500 μm giving a spectral resolution of 5 cm^{-1}. A He/Ne laser at 632.8 nm was used as the excitation source. IR spectra in diffuse reflectance were recorded on a Bruker IFS-66 FT-IR spectrometer. XRD was performed on a Stoe Theta-Theta diffractometer in reflection ($Cu_{K\alpha}$ radiation).

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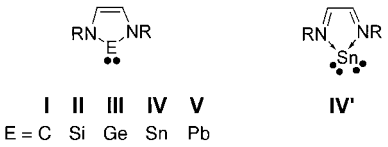
Tin Analogues of “Arduengo Carbenes”: Synthesis of 1,3,2λ^2-Diazastannoles and Transfer of Sn Atoms between a 1,3,2λ^2-Diazastannole and a Diazadiene[**]

Timo Gans-Eichler, Dietrich Gudat,* and
Martin Nieger

The discovery of persistent and in preparative-scale isolable carbenes launched not only a rapid development of carbene chemistry,[1] but stimulated as well investigations on carbene homologues with heavier Group 14 elements. Utilization of the concept that mesomeric interaction with the π electrons of two nitrogen atoms and a C–C double bond allows efficient electronic stabilization of the divalent carbon atom in imidazoyl (“Arduengo-type”) carbenes **I**[2] lead to the isolation of analogous silylenes **II**;[3] and germylenes **III** (Scheme 1).[4] Homologues of **I** with Sn (**IV**) and Pb (**V**) are—apart from a few annellated 1,3,2λ^2-diazastannoles[5]—still unknown, although divalent compounds of these elements should become increasingly more stable descending the group from C to Pb.[6] We report here the preparation and first reaction studies of monocyclic 1,3,2λ^2-diazastannoles **IV** which reveal that the reactivity of these compounds displays some striking dissimilarities when compared to the lighter homologues **I**–**III**.



Scheme 1.

λ^2-Diazagermoles **III** and annellated λ^2-diazastannoles can be prepared by metathesis of dilithiated diazadienides or *o*-phenylene diamides with $GeCl_2 \cdot$dioxane or $SnCl_2$, respectively.[4, 5] Analogous reactions of $SnCl_2$ with the dilithiumdiamides **2a**, **b** (Scheme 2) failed,[7] but the desired monocyclic diazastannoles **7a**,**b** were found to be accessible by transamination of the *α*-amino aldimines **3a**,**b**[8] with $[Sn(N(SiMe_3)_2)_2]$ (**4**) at 40–45 °C in nonpolar solvents. Mechanistically, the formation of **7a**,**b** can be explained by a multistep sequence (Scheme 2) which involves the initial condensation of **3a**,**b** and **4** to give stannylenes **5**, a subsequent 1,3-H-shift to afford **6**, and finally intramolecular elimination of $HN(SiMe_3)_2$ to produce the final products **7a**,**b** which were isolated after workup as red, air sensitive, and rather thermolabile solids. Experimental support for this

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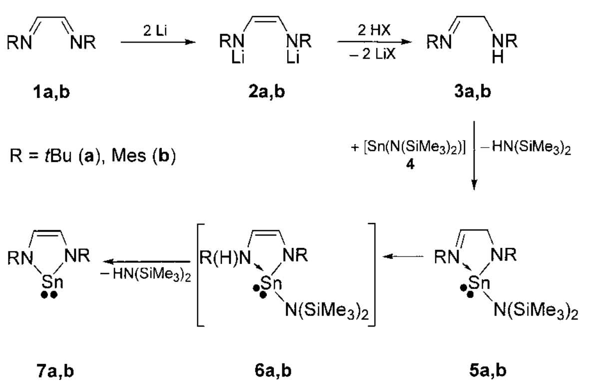


Scheme 2.

mechanism comes from detection of the intermediate **5a**[9, 10] by NMR spectroscopy.

The constitution of the λ^2-diazastannoles **7a,b** follows unequivocally from their analytic and spectroscopic data. The shielding of the ^{119}Sn NMR signals ($\delta(^{119}\mathrm{Sn}) = 237$ (**7a**), 259 ppm (**7b**)), compared to benzannellated ($\delta(^{119}\mathrm{Sn}) = 269$–455 ppm[5]) and acyclic $\mathrm{Sn^{II}}$ amides ($\delta(^{119}\mathrm{Sn}) = \approx 750$ ppm[5]), is remarkable; analogous effects are also known for compounds of type **I** and **II**[1, 3, 11] and diazaphospholenium cations,[12] and originate from the raising of the π* orbital and the associated blue shift of the n-π* transition as a consequence of π conjugation.[11, 12] A single-crystal X-ray diffraction study[13] of **7b** (Figure 1) revealed, in contrast to λ^2-benzo-diazastannole, [1,2-$\mathrm{C_6H_4(NCH_2}t\mathrm{Bu)_2Sn}$] (**8**), the presence of isolated molecules without intermolecular contacts.[5a] The C3/C4 and N2/N5 atoms in the five-membered ring lie in one plane while the Sn atom is found in a split position and occupies two positions slightly above and below this plane.[14] We interpret this finding by assuming the presence of two superimposed disordered molecules with flat envelope conformations. The C3–N2/C4–N5 (1.378(5) Å) and C3–C4 bonds in the ring (1.356(6) Å) match those in the **II** and **III**[3, 4] and are intermediate between pure single and double bonds. The Sn1–N bonds (2.084(3), 2.102(3) Å) are longer than, and the N-Sn1-N angle (77.63(13)°) is similar to, those in **8** (Sn–N 2.051(5), 2.067(5) Å, N-Sn-N 78.5(2)°[5a]).

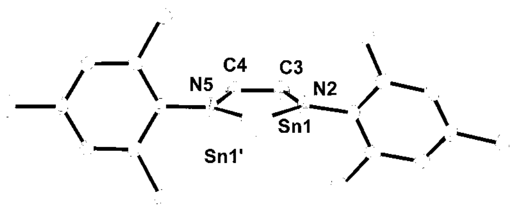
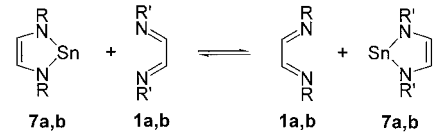


Figure 1. Molecular structure of **7b** (thermal ellipsoids set at 50% probability, H atoms omitted for clarity). The Sn atom is disordered over two positions (relative populations Sn1:Sn1′ 60:40); important distances [Å] and angles [°]: Sn1-N2 2.084(3), Sn1-N5 2.102(3), N2-C3 1.378(5), C3-C4 1.356(6), C4-N5 1.378(5); N2-Sn1-N5 77.63(13).

Compounds **7a,b** are distinguished by a remarkable thermal instability and decompose at 60 °C in a cheletropic reaction to the diazadienes **1a,b**, and Sn.[15] In contrast to **I**–**III**, no formation of stannylene complexes occurred with [$\mathrm{Ni(CO)_4}$], [$\mathrm{W(CO)_5(C_8H_{16})}$], or [$\mathrm{Pt(C_2H_4)(PPh_3)_2}$]. The observed decrease of the $\delta(^{119}\mathrm{Sn})$ resonance signal ($\Delta\delta(^{119}\mathrm{Sn}) = -26$ ppm (**7b**)) upon addition of excess 4-dimethylamino pyridine (DMAP) suggests the formation of donor–acceptor adducts and implies that **7a,b** react like **8**,[5a] as Lewis acids.[16]

A surprising behavior, which is unprecedented for **I**–**III** and **8**, was observed with diazadienes: reactions of **7a** (**7b**) with **1b** (**1a**) did not proceed as in the case of silylenes **II**[17] by oxidative addition, but rather by metathesis to afford the complementary $2\lambda^2$-diazastannoles and diazadienes (Scheme 3) which were identified by NMR spectroscopy.



Scheme 3. Sn-transfer reaction between 1,3,2-λ^2-diazastannoles and diazadienes having different (R = tBu, R′ = Mes) and the same (R = R′ = Mes) substituents; Mes = 2,4,6-trimethylphenyl.

Experimental proof for a direct transfer of an Sn atom from a diazastannole to a diazadiene group in these reactions was obtained by the "degenerate" metathesis between **7b** and **1b**: the appearance of intense exchange cross-peaks in ^{1}H EXSY NMR spectra (Figure 2) certifies that the exchange between both reactants is reversible and proceeds at a considerable rate and without participation of further detectable intermediates even at 30 °C.

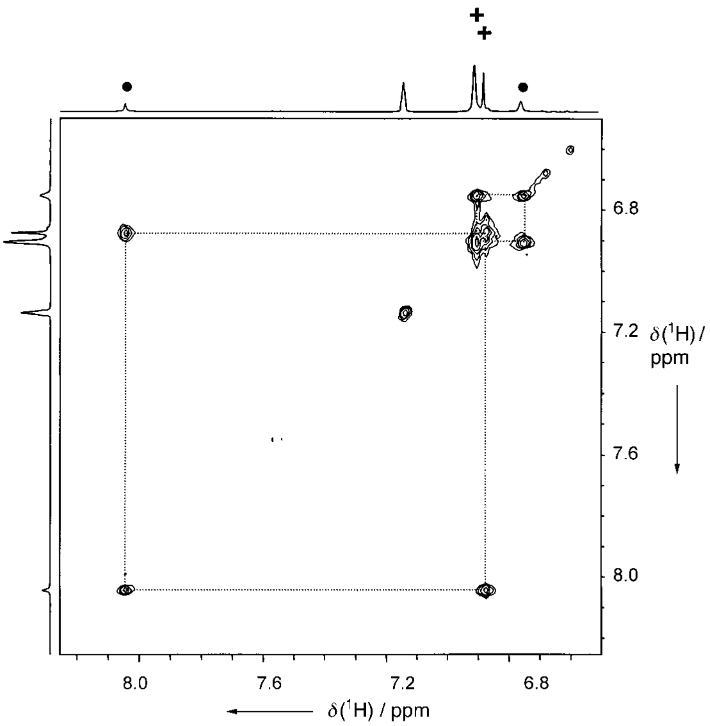


Figure 2. Expansion of a gradient-selected ^{1}H EXSY NMR spectrum (300 MHz, $\mathrm{C_6D_6}$, 30 °C, mixing time 0.5 sec, ^{1}H spectra as projections, only positive contours) of a mixture of **1b** and **7b**. The marked signals are assigned to the NCH and $\mathrm{C_6}\mathit{H}_2\mathrm{Me_3}$ hydrogen atoms of **1b** (●) and **7b** (+). The visible cross-peaks prove the presence of intermolecular exchange between both reactants.

To understand the unusual reactivity of **7a, b**, we carried out quantum-chemical studies on the model compounds **IV**-H (R = H) and **IV**-Ar (R = 2,6-$Me_2C_6H_3$).[18] Energy optimization of the molecular structures afforded planar five-membered rings with similar bond lengths (**IV**-Ar: Sn–N 2.116, N–C 1.382, C–C 1.374 Å) as had been found experimentally for **7b**. Natural bond order (NBO) population analyses[19] of the Kohn–Sham orbitals show a high degree of s character (**IV**-H: 88 %) for the lone pair at the Sn atom, which accounts for the low nucleophilicity observed for **7a, b**. The population of the $p^\pi(E)$ orbital perpendicular to the C_2N_2E Ring (**IV**-H: n[p^π(Sn)] 0.57) comes close to that in **I** and is larger than in **II** and **III** (n[p^π(E)] = 0.62 (**I**), 0.48 (**II**), 0.53 (**III**); R = H), which suggests more efficient π stabilization of the divalent Sn atom in **IV** than of the Si and Ge atoms of **II** and **III**, respectively.[11] Comparison of Wiberg bond indices (WBIs) and the atomic contributions to the localized σ(E–N) orbitals for the series **I** → **IV** reveals a continuous decrease of covalent E–N bond orders and a concomitant increasing polarization of the σ bonds towards nitrogen.[20] Both effects together imply an eventual weakening of E–N σ bonds in the sequence **I** → **IV** and suggest for **IV** an electronic polarization in the form of the "chelated atom" resonance structure **IV'**[21] (Scheme 1) which allows the easy cheletropic fragmentation of **7a, b** to be rationalized.

Assuming that transfer of an Sn atom from a diazastannole to a diazadiene group follows an associative mechanism, we modeled the interaction of **IV**-H with HN=CHCH=NH (**VI**-H). Two stationary states on the energy hypersurface were located of which **VIII**-H (ΔE + zpe = +1.6 kcal mol^{-1} relative to **IV**-H + **VI**-H) was assigned by vibrational analysis as a local minimum, and **VII**-H (ΔE + zpe = +5.5 kcal mol^{-1}) as a transition state between **VIII**-H and the separate molecules **IV**-H and **VI**-H (Figure 3). The adduct **VIII**-H is formally the product of oxidative addition of **VI** to **IV** and features an unusual Ψ-trigonal-bipyramidal geometry with different axial (2.269 Å) and equatorial (2.157 Å) Sn–N bonds. The resemblance of this structure to those of Sn^{II} amidinates[22] as well as an NBO analysis suggest a formal description of **VIII**-H as donor-stabilized Sn^{II} amide with a lone-pair on the Sn atom. Computational analysis of the oxidative addition of **VI**-H to the silylene **II** (R = H) revealed that the reaction is in this case strongly exothermic (ΔE + zpe = −56.5 kcal mol^{-1}) and gives, in accord with the experimental findings,[17] a D_{2d}-symmetric Si^{IV} spiro compound with distorted tetrahedral coordination at the silicon center and four equal Si–N bonds(1.724 Å). The strong distortion from tetrahedral coordination at the tin atom in **VIII**-H is for geometric reasons—the small diazadienide "bite angle" forces contraction of endocyclic and concomitant widening of exocyclic N-Sn-N angles—and is considered to be the main reason that the oxidative addition of **VI**-H to **IV**-H is endothermic (and not as for **II** exothermic). Upon introducing 2,6-$Me_2C_6H_3$ substituents to the N atom, the corresponding adduct **VIII**-Ar is further destabilized (ΔE + zpe = 31.9 kcal mol^{-1}), because of the increased steric congestion, and is thus no longer a local minimum, but the transition state of the Sn-transfer reaction.

Experimental Section

3a: Solid Et_3NHCl (0.22 mol) was added to a solution of freshly prepared **2a** (0.11 mol)[3, 17] in THF (250 mL) until complete decolorization occurred. The solvent was evaporated in vacuum, the residue washed with hexane, and dissolved in a small volume of toluene. Filtration and evaporation of the filtrate produced a colorless solid of composition **1a** · LiCl (m.p. 80 °C, yield 30 %) which was used for further reactions. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.11 (s, 9H; *t*Bu), 1.17 (s, 9H; *t*Bu), 1.32 (br, 1H; NH), 3.36 (dd, ^3J(H,H) = 3.4 Hz, 7.3 Hz; NCH_2), 7.67 ppm (t, ^3J(H,H) = 3.4 Hz, 1H; N=CH); IR (KBr): $\tilde{\nu}$ = 3230 (NH), 1674 cm^{-1} (C=N).

3b: Absolute EtOH (140 mmol) and a solution of freshly prepared **2a** (70 mmol)[3, 17] in THF (150 mL) and were added simultaneously, dropwise, to a flask containing THF (50 mL). After the reaction was complete, the mixture was evaporated to dryness and the residue dissolved in hexane (50 mL). Precipitated LiOEt was removed by filtration and the product left to crystallize at −2 °C, yield 45 %; ^1H NMR (300 MHz, C_6D_6): δ = 2.01 (m, 6H; CH_3), 2.16 (m, 3H; CH_3), 2.19 (m, 3H; CH_3), 2.27 (m, 6H; CH_3), 3.62 (dd, ^3J(H,H) = 2.2 Hz, 5.2 Hz; NCH_2), 4.73 (t, ^3J(H,H) = 5.2 Hz, 1H; NH), 6.78 (m, 1H; Mes-CH), 6.79 (m, 1H; Mes-CH), 7.22 ppm (t, ^3J(H,H) = 2.2 Hz; N=CH); MS (EI, 12 eV): *m/z* (%): 294 (90) [M^+]; IR (KBr): $\tilde{\nu}$ = 3350 (NH), 1666 cm^{-1} (C=N).

7a, b: A solution of **3a, b** (1.7 mmol) in toluene (**3a**; 10 mL) or hexane (**3b;** 10 mL) was combined with a solution of **4** (1.7 mmol) in a small volume of hexane and the mixture stirred for 2 h at 40–45 °C. The resulting red solution was cooled to ambient temperature and evaporated to dryness (**3a**), or concentrated until a dark red solid precipitated (**3b**). The crude products were recrystallized from a small volume of hexane, yield 35 % (**7a**), 50 % (**7b**); satisfactory elemental analyses; **7a**: ^1H NMR (C_6D_6): δ = 1.41 (s, 18H; *t*Bu), 7.44 ppm (s, 2H, ^3J(^{119}Sn,H) = 8 Hz; NCH); $^{13}C\{^1H\}$ NMR: δ = 33.9 (CH_3), 56.7 (NC), 125.5 ppm (NCH); ^{15}N NMR: δ = −111.9 ppm; ^{119}Sn NMR: δ = 237 ppm; **7b**: ^1H NMR: δ = 2.22 (m, 6H; CH_3), 2.27 (m, 12H; CH_3), 6.88 (s, 2H, ^3J(^{119}Sn,H) = 10 Hz; NCH), 6.89 ppm (m, 4H; Mes-CH); $^{13}C\{^1H\}$ NMR: δ = 18.5 (CH_3), 20.9 (CH_3), 128.7 (NCH), 129.2 (*m*-C), 133.3 (*p*-C), 134.3 (*o*-C), 146.1 ppm (*i*-C); ^{15}N NMR: δ = −135.0 ppm; ^{119}Sn NMR: δ = 259 ppm; MS (EI, 16 eV): *m/z* (%): 408(20) [M^+].

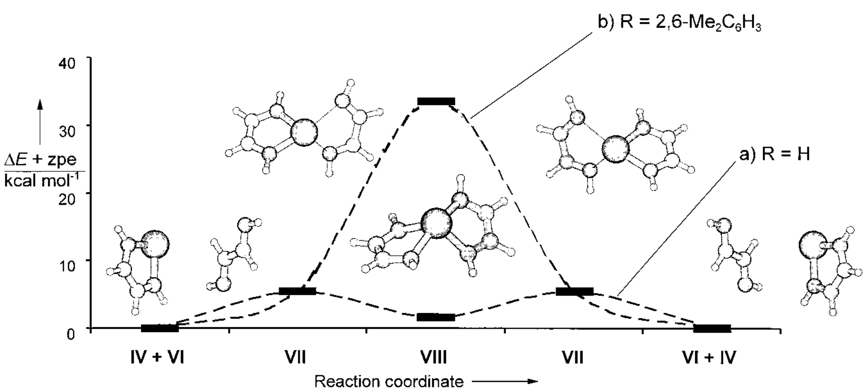


Figure 3. Computed energy profile[15] for the Sn-transfer reaction between a diazadiene (**VI**-H) and a 1,3,2-λ^2-diazastannole (**IV**-H), and MOLDEN plots[23] of the molecular structures of **VII**-H and **VIII**-H. Relative energies of the stationary states: **VII**: 1.1 (R = H), 28.6 kcal mol^{-1} (R = 2,6-$Me_2C_6H_3$); **VIII**: 5.6 (R = H) kcal mol^{-1}.

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[7] The reactions produced mainly insoluble solids which were assigned on the basis of solid-state magic-angle spinning (MAS) NMR spectroscopic studies ($\delta(^{119}\mathrm{Sn})$ -590 ppm (broad); $\delta(^{13}\mathrm{C})$ 164 ppm, CH signal of coordinated CH=N moiety) as polymeric $\mathrm{SnCl_2}$ – diazadiene adducts.

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[9] NMR data ($\mathrm{C_6D_6}$, 30 °C): ^{1}H NMR: $\delta = 0.37$ (s, 18 H; $\mathrm{SiMe_3}$), 1.06 (s, 9 H; *t*Bu), 1.32 (s, 9 H; *t*Bu), 3.86 (dd, $^2J(\mathrm{H,H}) = 25$ Hz, $^3J(\mathrm{H,H}) = 1.2$ Hz, $^3J(^{119}\mathrm{Sn,H}) = 22$ Hz, 1 H; $\mathrm{CH_2}$), 4.50 (dd, $^2J(\mathrm{H,H}) = 25$ Hz, $^3J(\mathrm{H,H}) = 1.2$ Hz, $^3J(^{119}\mathrm{Sn,H}) = 22$ Hz, 1 H; $\mathrm{CH_2}$); 7.43 ppm (t, $^3J(\mathrm{H,H}) = 1.2$ Hz, $^3J(^{119}\mathrm{Sn,H}) = 25$ Hz, 1 H; N=CH); ^{119}Sn NMR: $\delta = 118$ ppm.

[10] Reaction of **3a** with $[\mathrm{Pb(N(SiMe_3)_2)_2}]$ gave, beside $\mathrm{HN(SiMe_3)_2}$, a product with a constitution similar to **5a**, which was characterized by NMR spectroscopy (^{1}H NMR: $\delta = 0.38$ (s, 18 H; $\mathrm{SiMe_3}$), 1.05 (s, 9 H; *t*Bu), 1.35 (s, 9 H; *t*Bu), 4.51 (d, $^2J(\mathrm{H,H}) = 25$ Hz, $^3J(^{207}\mathrm{Pb,H}) = 32$ Hz, 1 H; $\mathrm{CH_2}$), 5.91 (d, $^2J(\mathrm{H,H}) = 25$ Hz, 1 H; $\mathrm{CH_2}$), 8.08 ppm (s, $^3J(^{207}\mathrm{Pb,H}) = 56$ Hz, 1 H; N=CH); ^{207}Pb NMR: $\delta = 2590$ ppm) but decayed to **1a**, $\mathrm{HN(SiMe_3)_2}$, and Pb without further detectable intermediates.

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[13] Crystal data for **7b**: $\mathrm{C_{20}H_{24}N_2Sn}$, dimensions $0.60 \times 0.40 \times 0.20$ mm, $M_r = 411.1$, triclinic, space group $P\bar{1}$ (No. 2), $a = 8.1282(2)$, $b = 10.3477(2)$, $c = 12.4490(3)$ Å, $\alpha = 92.12(1)$, $\beta = 104.45(1)$, $\gamma = 111.76(1)^\circ$, $V = 931.80(4)$ Å^3, $Z = 2$, $\mathrm{Mo_{K\alpha}}$ radiation, $\mu(\mathrm{Mo_{K\alpha}}) = 1.37$ mm^{-1}, $T = 123(2)$ K, $F(000) = 416$; data collection: Nonius Kappa CCD, 12 237 reflections up to $2\theta_{\max} = 50^\circ$, 3284 independent reflections, $R_{\mathrm{int}} = 0.048$; structure solution (direct methods: G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467) and refinement (on F^2, C,N atoms anisotropically, Sn atom isotropically, H atoms with a riding model; SHELXL-97, G. M. Sheldrick, Universität Göttingen, **1997**): empirical absorption correction, 213 parameters, 14 restraints, $R(I > 2\sigma(I)) = 0.042$, $wR2$ (all data) $= 0.105$, max./min. residual electron density (near the disordered Sn atoms) $2.96/-1.10$ e Å^{-3}. CCDC-172771 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[14] Crystal structure studies on several crystals obtained from different reactions and solvents revealed in all cases identical disorder phenomena.

[15] The observed acceleration of the fragmentation upon addition of $\mathrm{Cl^-}$ ions suggested that formation of diazadiene – $\mathrm{SnCl_2}$ adducts from **2** and $\mathrm{SnCl_2}$ may occur by decomposition of intermediate λ^2-diazastannole species and subsequent reaction of the resulting diazadiene with excess $\mathrm{SnCl_2}$.

[16] Spectroscopic data indicate that as for DMAP adducts of diazaphospholenes (cf. ref. [12]) in solution, dynamic equilibria between adducts and separated molecules are present.

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[18] DFT calculations were performed using the Gaussian suite of programs: Gaussian 98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**. Basis sets and methods: B3LYP/SDD with relativistic pseudo potentials at the Sn atom and polarization functions on all heavy atoms for **I** – **III**, **IV**-H – **VII**-H; two-level ONIOM using B3LYP/SDD + d for the bicyclic ring system and MNDO for the aryl groups for **IV**-Ar – **VI**-Ar.

[19] NBO 5.0: E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, F. Weinhold, Theoretical Chemistry Institute, Univ. of Wisconsin, Madison, WI, **2001**; http://www.chem.wisc.edu/~nbo5.

[20] WBI(E-N) = 1.27 (**I**), 0.79 (**II**), 0.77 (**III**), 0.70 (**IV**-H); contribution (in %) of E to the σ(E-N) LMO: 32.6 (**I**), 14.8 (**II**), 14.5 (**III**), 11.8 (**IV**-H).

[21] A. J. Arduengo, H. Bock, H. Chen, M. Denk, D. A. Dixon, J. C. Green, W. A. Herrmann, N. L. Jones, M. Wagner, R. West, *J. Am. Chem. Soc.* **1994**, *116*, 6641; the increased importance of canonical structure **IV′** is substantiated by concomitant shifts in bond orders (WBI(N−C/C=C) = 1.12/1.67 (**I**), 1.21/1.57 (**IV**-H)).

[22] b) Y. Zhou, D. S. Richeson, *J. Am. Chem. Soc.* **1996**, *118*, 10 850; b) S. R. Foley, Y. Zhou, G. P. A. Yap, D. S. Richeson, *Inorg. Chem.* **2000**, *39*, 924.

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