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Supporting Information

69451 Weinheim, Germany

The Exciting Chemistry of Tetraazidomethane**

Klaus Banert, Young-Hyuk Joo, Tobias Rüffer, Bernhard Walfort, and Heinrich Lang*

Experimental procedure

Safety instructions: Tetraazidomethane (**1**) is extremely dangerous as a pure substance. It can explode at any time – without a recognizable reason. Less than a drop of this compound isolated by gas chromatography is able to destroy not only the glass trap but also the Dewar vacuum flask of the cooling bath completely. Therefore, the isolated substance should only be diluted by vapor deposition of a solvent behind a safety shield but not by taking manual measures (pipette, syringe). However, solutions of **1** can also lead to an explosion after mechanical stress (swivel closure) or after evaporating of a volatile solvent, for example, in a pipette. Finally, it should be considered that **3**, **5**, and **7** are also explosive azides.

Tetraazidomethane (1) from 2h: Sodium azide (7.50 g, 115 mmol) was given to a solution of freshly distilled trichloroacetonitrile (**2h**, 2.50 g, 17.3 mmol) in acetonitrile (150 mL). The suspension was stirred at 50°C for 18 h and then diluted with water (100 mL) after cooling and removal of insoluble matter. The aqueous phase was extracted with *n*-pentane (3 x 70 mL), and the combined organic layers were washed with water (3 x 100 mL) and dried over $MgSO_4$. The solvent was removed in vacuo to give a residue (ca. 20–30 mL, **caution, safety screen**), which was filtered. The filtrate could be used for reactions of **1** or for purification of **1** by preparative gas chromatography. Alternatively, it could be utilised for NMR spectroscopy after addition of CD_3CN (3 mL) and evaporation of the solvent in vacuo to yield a volume of 1–2 mL. Compound **1** could be analysed by gas chromatography using capillary columns, 30 m, 80°C (methyl phenyl silicone, retention time 7.5 min; polyethylene glycol, retention time 6.5 min).

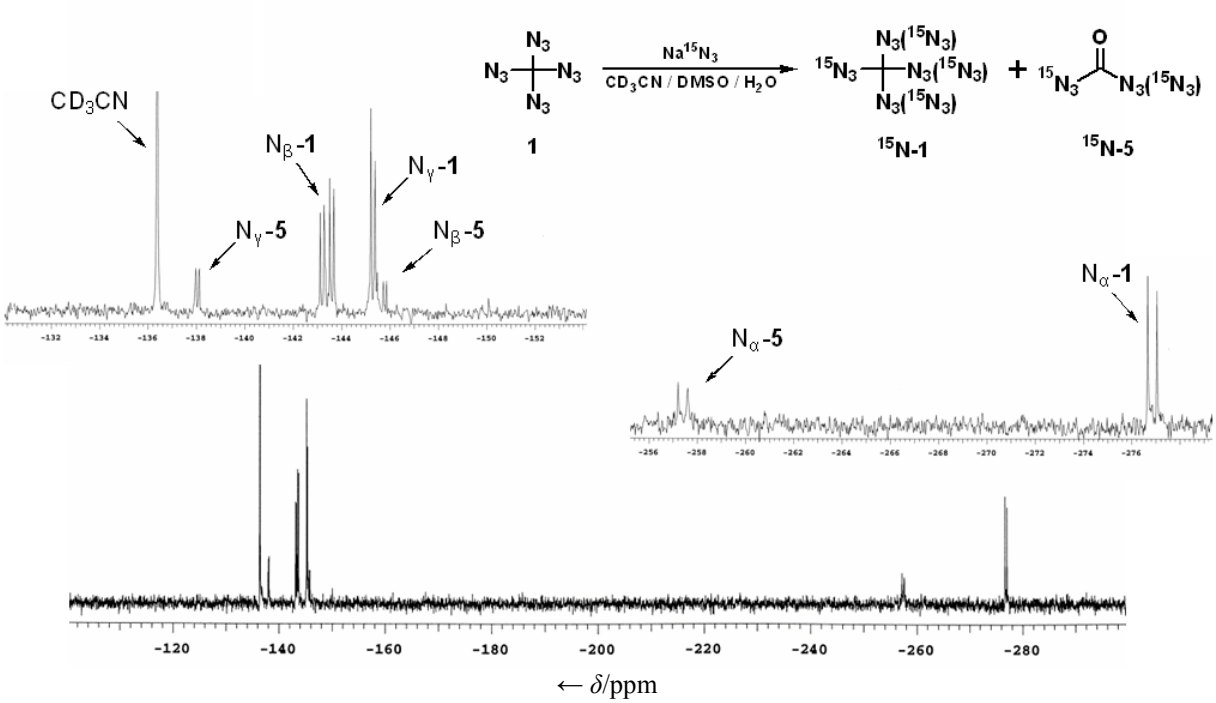


Figure S1: ^{15}N NMR spectrum after the reaction of **1** with $Na^{+}\ ^{15}N_3^{-}$ in CD_3CN + H_2O (2 vol%) + DMSO (5 vol%), formation of ^{15}N-**1** and ^{15}N-**5**.

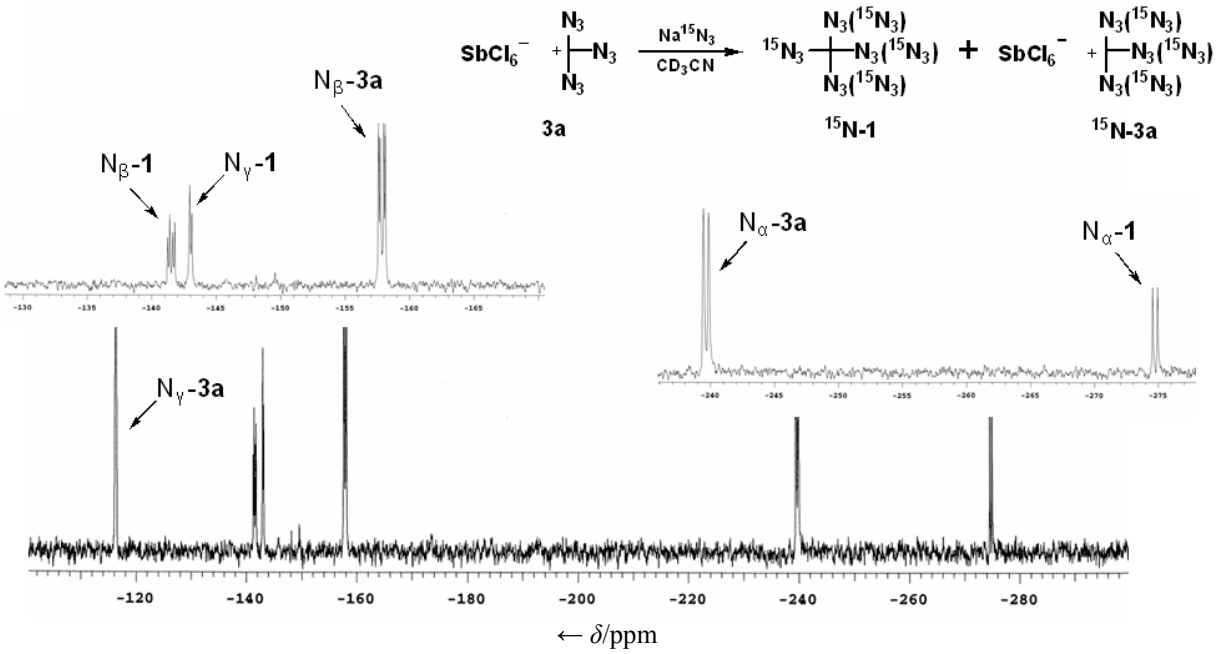


Figure S2: ^{15}N NMR spectrum after the reaction of **3a** in CD_3CN with a substoichiometric amount of $Na^{+}\ ^{15}N_3^{-}$, formation of ^{15}N-**1** and ^{15}N-**3a**.

Table S1: Selected physical data of the compounds **4a**,**b**, **6**, **8**, **9a**,**b**, **10a**,**b** as well as the mono-oxide of 1,2-bis(diphenylphosphino)ethene (for comparison with the data of **8**) and diazido(diphenoxy)methane.[a]

4a: Colorless crystals, m.p. 85–87°C; IR ($CDCl_3$): $\tilde{\nu}$ = 2941 cm^{-1}, 2857, 2138 (N_3); ^1H NMR ($CDCl_3$): δ = 1.47 (br. s, 12H), 1.61 (br. s, 6H), 1.76–1.79 (m, 6H), 2.45 (br. s, 6H), 2.93–2.96 (m, 6H); ^{13}C NMR ($CDCl_3$): δ = 21.4 (t), 24.5 (t), 24.7 (t), 25.9 (t), 26.1 (t), 27.9 (t), 96.4 (s), 135.9 (s), 147.5 (s); C,H,N analysis (%): calcd for $C_{25}H_{36}N_{12}$ (504.63): C 59.50, H 7.19, N 33.31; found C 59.71, H 7.12, N 31.95.

4b: Colorless crystals, m.p. 218°C; IR ($CDCl_3$): $\tilde{\nu}$ = 2935 cm^{-1}, 2859; ^1H NMR ($CDCl_3$): δ = 1.29–1.82 (m, 36H), 2.37–2.47 (m, 4H), 2.93–2.99 (m, 8H); ^{13}C NMR ($CDCl_3$): δ = 22.8 (t), 24.2 (t), 24.4 (t), 25.2 (t), 25.9 (t), 27.0 (t), 95.5 (s), 137.8 (s), 147.2 (s); MS (ESI) *m*/*z* (%) = 651.5 (100) $[M + K]^+$; C,H,N analysis (%): calcd for $C_{33}H_{48}N_{12}$ (612.81): C 64.68, H 7.89, N 27.43; found C 64.63, H 7.87, N 27.30.

6: Colorless crystals, m.p. 192–194°C; IR ($CDCl_3$): $\tilde{\nu}$ = 2179 cm^{-1} (CN); ^1H NMR ($CDCl_3$): δ = 7.47–7.52 (m, 6H), 7.59–7.66 (m, 9H); ^{13}C NMR ($CDCl_3$): δ = 118.6 (s), 126.4 (d, $^1J_{PC}$ = 97.7 Hz, *i*-Ph), 129.0 (d, $^3J_{PC}$ = 12.9 Hz, *m*-Ph), 132.3 (d, $^2J_{PC}$ = 10.4 Hz, *o*-Ph), 133.2 (d, $^4J_{PC}$ = 2.8 Hz, *p*-Ph).

8: Colorless oil; IR ($CDCl_3$): $\tilde{\nu}$ = 2176 cm^{-1} (CN); ^1H NMR ($CDCl_3$): δ = 2.25–2.31 (m, 2H), 2.40–2.49 (m, 2H), 7.33–7.34 (m, 10H), 7.47–7.52 (m, 4H), 7.59–7.64 (m, 6H); ^{13}C NMR ($CDCl_3$): δ = 19.0 (dd, $^1J_{PC}$ = 16.9 Hz , $^2J_{PC}$ = 5.2 Hz, CH_2P), 24.2 (dd, $^1J_{PC}$ = 67.5 Hz, $^2J_{PC}$ = 18.9 Hz, $CH_2P{=}N$), 118.5 (s), 126.2 (d, $^1J_{PC}$ = 97.7 Hz, *i*-Ph), 128.7 (d, $^3J_{PC}$ = 6.7 Hz, *m*-Ph), 129.2–129.4 (several signals, *m*-Ph and *p*-Ph), 131.2 (d, $^2J_{PC}$ = 10.1 Hz, *o*-Ph), 132.7 (d, $^2J_{PC}$ = 18.9 Hz, *o*-Ph), 133.3 (d, $^4J_{PC}$ = 2.7 Hz, *p*-Ph), 136.4 (d, $^1J_{PC}$ = 13.2 Hz, *i*-Ph); ^{31}P NMR ($CDCl_3$): δ = –12.1 (d, ^3J = 48.1 Hz), 29.6 (d, ^3J = 48.1 Hz); MS (ESI) *m*/*z* (%) = 439.1 (100) $[M + H]^+$; HR-MS (ESI) *m*/*z* = 439.1501 [calcd 439.1488].

9a: White solid, m.p. 183–185°C; IR ($CDCl_3$): $\tilde{\nu}$ = 3414 cm^{-1} (NH), 1585 (N–C=N); ^1H NMR ($CDCl_3$): δ = 0.99–1.03 (m, 2H, *endo*-H-5 (norbornene) and *endo*-H-6 (norbornene)), 1.35–1.37 (m, 2H, nortricyclane), 1.44 (m, 1H, nortricyclane), 1.49–1.52 (m, 2H,

nortricyclane), 1.57–1.61 (m, 2H, nortricyclane), 1.85–1.89 (m, 2H, *exo*-H-5 (norbornene) and *exo*-H-6 (norbornene)), 2.29 (m, 1H, H-4 (nortricyclane)), 2.94 (m, 1H, H-1 (norbornene) or H-4 (norbornene)), 2.97 (m, 1H, H-1 (norbornene) or H-4 (norbornene)), 3.90 (d, ^3J = 9.6 Hz, 1H, H-7 (norbornene)), 4.08 (m, 1H, H-3 (nortricyclane)), 4.78 (d, ^3J = 9.3 Hz, NH), 6.07–6.08 (m, 2H, H-2 (norbornene) and H-3 (norbornene)); ^{13}C NMR ($CDCl_3$): δ = 11.4 (d, nortricyclane), 12.3 (d, nortricyclane), 13.0 (d, nortricyclane), 22.8 (t, C-5 (norbornene) or C-6 (norbornene)), 22.8, (t, C-5 (norbornene) or C-6 (norbornene)), 29.3 (t, nortricyclane), 31.1 (t, nortricyclane), 34.7 (d, C-4 (nortricyclane)), 45.7 (d, 2C, C-1 (norbornene) and C-4 (norbornene)), 62.1 (d, C-3 (nortricyclane)), 70.6 (d, C-7 (norbornene)), 132.5 (d, C-2 (norbornene) or C-3 (norbornene)), 132.8 (d, C-2 (norbornene) or C-3 (norbornene)), 155.4 (s, C-5 (tetrazole)); MS (ESI) *m*/*z* (%) = 308.1 (100) $[M + K]^+$, 577.3 (48) $[2M + K]^+$; C,H,N analysis (%): calcd for $C_{15}H_{19}N_5$ (269.34): C 66.89, H 7.11, N 26.00; found C 66.52, H 7.42, N 25.72.

9b: White solid, m.p. 220–222°C; IR ($CDCl_3$): $\tilde{\nu}$ = 3440 cm^{-1} (NH), 1587 (N–C=N); ^{1}H NMR ($CDCl_3$): δ = 1.19–1.69 (m, 14H) 2.23 (m, 1H, H-4'), 2.36 (m, 1H, H-4), 3.79 (d, ^3J = 6.6 Hz, 1H, H-3'), 4.10 (m, 1H, H-3), 4.38 (d, ^3J = 6.6 Hz, 1H, NH); ^{13}C NMR ($CDCl_3$): δ = 10.6 (d), 11.7 (d), 12.4 (d), 12.5 (d), 13.2 (d), 15.0 (d), 29.5 (t), 29.7 (t), 31.3 (t), 31.5 (t), 33.4 (d, C-4'), 34.9 (d, C-4), 59.8 (d, C-3'), 62.3 (d, C-3), 154.9 (s, C-5 (tetrazole)); MS (ESI) *m*/*z* (%) = 308.1 (42) $[M + K]^+$, 578.2 (100) $[2M + K]^+$; HR-MS (ESI) *m*/*z* = 308.1293 [calcd 308.1272].

10a: Yellow crystals, unstable compound, m.p. >320°C (decomp.); IR ($CDCl_3$): $\tilde{\nu}$ = 2104 cm^{-1} (N_3); ^{1}H NMR ($CDCl_3$): δ = 1.31 (d, ^3J = 8.7 Hz, 1H, H-8 (norbornene)), 1.54 (d, ^2J = 11.8 Hz, 1H, H-7 *syn* next to C-5 (nortricyclane)), 1.58 (d, ^2J = 11.8 Hz, 1H, H-7 *syn* next to C-3 (nortricyclane)), 1.68 (m, 1H), 1.79 (m, 1H), 1.87 (d, ^2J = 8.7 Hz, 1H, H-8 (norbornene)), 2.05 (m, 1H), 2.53 (br. s, 1H, H-4 (nortricyclane)), 3.09 (d, ^3J = 5.8 Hz, 1H, H-2 (norbornene) or H-4 (norbornene)), 3.13 (d, ^3J = 5.8 Hz, 1H, H-2 (norbornene) or H-4 (norbornene)), 3.14–3.16 (m, 2H, H-1 (norbornene) and H-5 (norbornene)), 3.92 (m, 1H, H-5 (nortricyclane)), 4.74 (m, 1H, H-3 (nortricyclane)), 6.42–6.43 (m, 2H, H-6 (norbornene) and H-7 (norbornene)); ^{13}C NMR ($CDCl_3$): δ = 14.3 (d, nortricyclane), 14.4 (d, nortricyclane), 16.2 (d, nortricyclane), 28.2 (t, C-7 (nortricyclane)), 38.4 (d, C-4 (nortricyclane)), 41.2 (t, C-8 (norbornene)), 42.4 (d, C-1 (norbornene) or C-5 (norbornene)), 42.5 (d, C-1 (norbornene) or C-5 (norbornene)), 50.0 (d, C-2 (norbornene) or C-4 (norbornene)), 50.2 (d, C-2 (norbornene)

or C-4 (norbornene)), 60.1 (d, C-3 (nortricyclane)), 66.4 (d, C-5 (nortricyclane)), 139.7 (d, C-6 (norbornene) or C-7 (norbornene)), 139.7 (d, C-6 (norbornene) or C-7 (norbornene)), 159.0 (s, C-5 (tetrazole)); MS (ESI) *m*/*z* (%) = 347.1 (100) $[M + K]^+$, 655.2 (43) $[2M + K]^+$; HR-MS (ESI); *m*/*z* = 347.1192 [calcd 347.1130].

10b: Colorless oil; IR (CCl_4): $\tilde{\nu}$ = 2103 cm^{-1} (N_3), 1522 (N–C=N); ^1H NMR ($CDCl_3$): δ = 1.51 (d, ^2J = 11.7 Hz, 1H, H-7 *syn* next to C-5 (nortricyclane)), 1.62 (d, ^2J = 11.7 Hz, 1H, H-7 *syn* next to C-3 (nortricyclane)), 1.65–1.66 (m, 2H, H-7 (homoquadricyclane)), 1.69 (m, 1H, H-6 (nortricyclane)), 1.81 (m, 1H, H-1 (nortricyclane)), 2.00 (m, 1H, H-2 (nortricyclane)), 2.08–2.09 (m, 2H, H-1 and H-2 (homoquadricyclane)), 2.32 (m, 1H, H-8 (homoquadricyclane)), 2.35 (m, 1H, H-4 (nortricyclane)), 2.80 (m, 1H, H-6 (homoquadricyclane)), 3.91 (m, 1H, H-5 (nortricyclane)), 4.48–4.50 (m, 2H, H-3 and H-5 (homoquadricyclane)), 4.51 (m, 1H, H-3 (nortricyclane)); ^{13}C NMR ($CDCl_3$): δ = 14.5 (d, C-1 (nortricyclane)), 14.9 (d, C-2 (nortricyclane)), 16.1 (d, C-6 (nortricyclane)), 24.0 (d, C-1 or C-2 (homoquadricyclane)), 24.1 (d, C-1 or C-2 (homoquadricyclane)), 28.2 (t, C-7 (nortricyclane)), 31.3 (t, C-7 (homoquadricyclane)), 33.8 (d, C-8 (homoquadricyclane)), 38.5 (d, C-4 (nortricyclane)), 45.0 (d, C-6 (homoquadricyclane)), 59.8 (d, C-3 (nortricyclane)), 66.5 (d, C-5 (nortricyclane)), 70.5 (d, C-3 or C-5 (homoquadricyclane)), 71.2 (d, C-3 or C-5 (homoquadricyclane)), 158.3 (s, C-5 (tetrazole)); MS (ESI) *m*/*z* (%) = 346.9 (100) $[M + K]^+$, 654.9 (20) $[2M + K]^+$; HR-MS (ESI) *m*/*z* = 347.1163 [calcd 347.1130].

$Ph_2P(O)CH_2CH_2PPh_2$:[b] 1H NMR ($CDCl_3$): δ = 2.26–2.30 (m, 4H), 7.29–7.37 (m, 10H), 7.40–7.47 (m, 4H), 7.47–7.51 (m, 2H), 7.59–7.65 (m, 4H); ^{13}C NMR ($CDCl_3$): δ = 19.1 (dd, $^1J_{PC}$ = 15.3 Hz, $^2J_{PC}$ = 4.3 Hz, CH_2P), 25.8 (dd, $^1J_{PC}$ = 69.6 Hz, $^2J_{PC}$ = 16.6 Hz, $CH_2P{=}O$), 128.5–128.9 (several signals, *m*-Ph und *p*-Ph), 130.7 (d, $^2J_{PC}$ = 10.1 Hz, *o*-Ph), 131.8 (d, $^4J_{PC}$ = 2.7 Hz, *p*-Ph), 132.2 (d, $^1J_{PC}$ = 98.6 Hz, *i*-Ph), 132.7 (d, $^2J_{PC}$ = 18.5 Hz, *o*-Ph), 137.2 (d, $^1J_{PC}$ = 13.4 Hz, *i*-Ph); ^{31}P NMR ($CDCl_3$): δ = –11.6 (d, ^3J = 48.9 Hz), 33.3 (d, ^3J = 48.9 Hz); MS (ESI) *m*/*z* (%) = 415.1 (100) $[M + H]^+$.

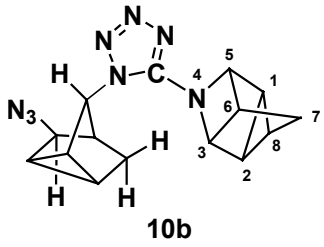
$(PhO)_2C(N_3)_2$:[c] Colorless liquid; IR ($CDCl_3$): $\tilde{\nu}$ = 2139 cm^{-1} (N_3), 1593 (Ph), 1491 (Ph), 1408 (Ph); ^1H NMR ($CDCl_3$): δ = 7.20–7.46 (m). ^{13}C NMR ($CDCl_3$): δ = 114.16 (s, C-N_3), 120.92 (d), 125.27 (d), 129.47 (d), 151.82 (s).

[a] ^{1}H NMR: 400 MHz, ^{13}C NMR: 100.6 MHz, ^{31}P NMR: 162 MHz. The assignments of NMR signals were performed with the help of ^{1}H,^{1}H double resonance and ^{1}H NMR NOE experiments, ^{1}H,^{1}H (COSY) and ^{13}C,^{1}H shift correlations, DEPT135 and GATED experiments with utilization of $^{1}J(^{13}C,^{1}H)$.

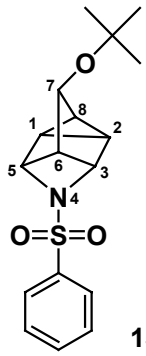
[b] This compound was prepared according to a known procedure, see: D. S. Amenta, B. R. Ayres, J. Jurica, J. W. Gilje, *Inorg. Chim. Acta* **2002**, *336*, 115–119.

[c] This compound was treated with cyclooctyne, and the resulting triazole derivative was analysed to determine the number of azido groups.

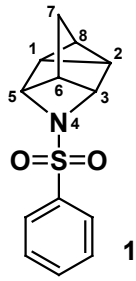
Table S2: Selected ^{1}H NMR and ^{13}C NMR data of **10b** and the known[a] compounds **15** and **16** in order to get evidence for the tetracyclic part of **10b**.



10b



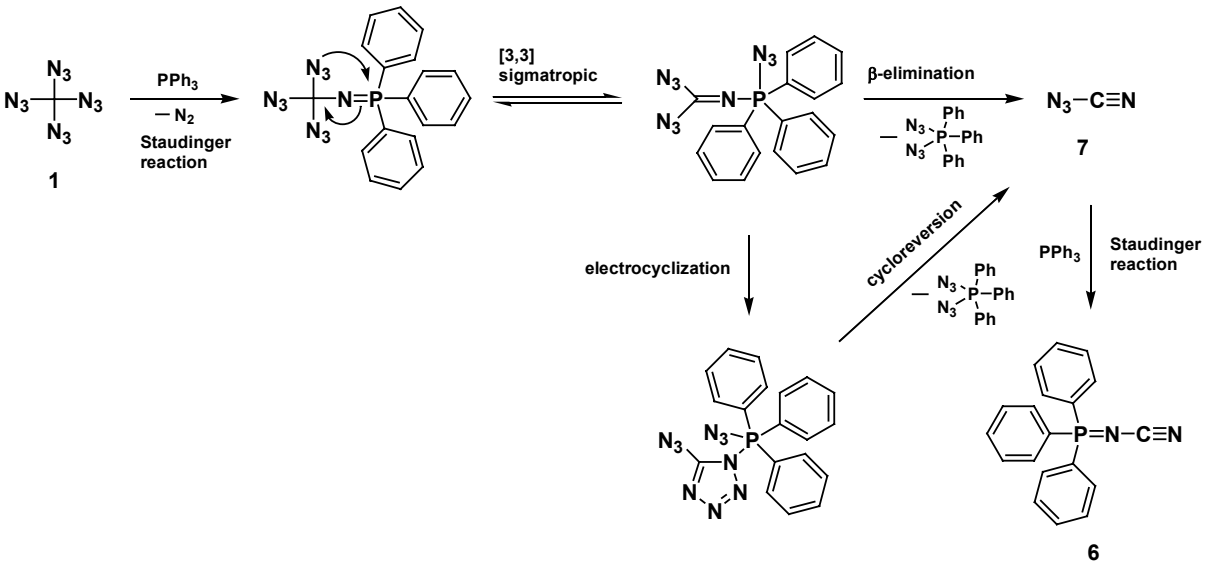
15



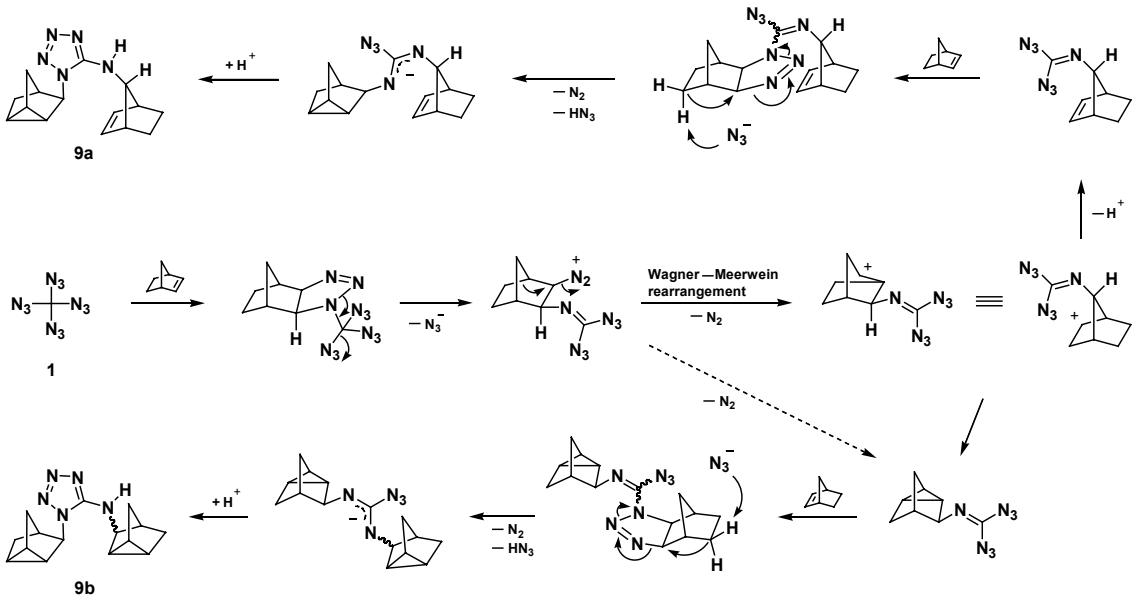
16

Position	^{1}H NMR δ values (ppm)			^{13}C NMR δ values (ppm)			^{1}J (^{13}C,^{1}H) (Hz)		
	10b	**15**	**16**	**10b**	**15**	**16**	**10b**	**15**	**16**
1	2.08–2.09	2.05–2.45	2.06	23.97 and 24.09	25.3	25.1	^{1}J=182	^{1}J=186	^{1}J=180
2					24.5		^{1}J=182	^{1}J=186	
3	4.48–4.50	4.23	4.30	70.53 and 71.20	69.3	72.1	^{1}J=168	^{1}J=170	^{1}J=175
5		4.62			72.9		^{1}J=168	^{1}J=174	
6	2.80	2.05–2.45	2.50	44.95	47.3	43.9	^{1}J=156	^{1}J=160	^{1}J=163
7	1.65–1.66	3.90	1.46	31.28	72.5	29.2	^{1}J=132	^{1}J=145	^{1}J=133
8	2.32	2.05–2.45	2.29	33.81	40.4	35.8	^{1}J=170	^{1}J=170	^{1}J=169

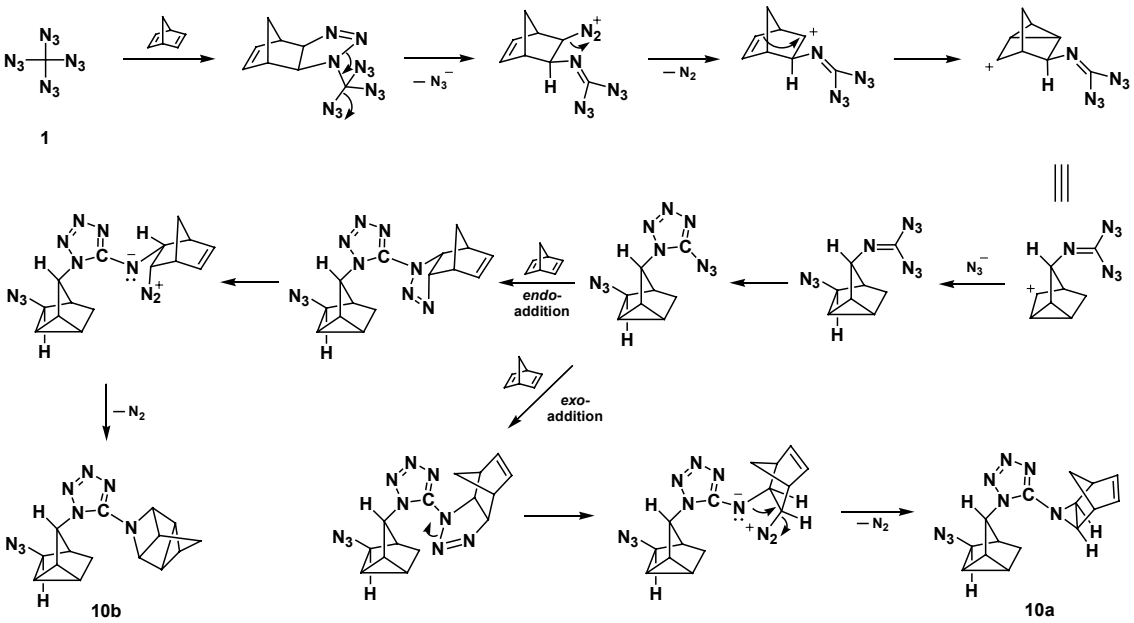
[a] For the synthesis of **15** and **16**, see: E. Huda, H.-D. Martin, B. Mayer, K.-H. Somnitz, A. Steigel, H. Haddad, G. Distefano, A. Modelli, *Chem. Ber.* **1991**, *124*, 2879–2895.



Scheme S1: Reaction mechanism to explain the formation of **6** from **1** and PPh_3.



Scheme S2: Alternative reaction mechanism to explain the products **9a** and **9b**; the simultaneousness and the order of the single steps are arbitrary.



Scheme S3: Reaction mechanism to explain the formation of **10a** and **10b**; the simultaneousness and the order of the single steps are arbitrary.