quenched with 10% perchloric acid (10 ml) and then extracted with CH_2Cl_2. The solvent was evaporated under reduced pressure, and the residue was washed with MeOH and then recrystallized from EtOH/Et_2O to give colorless crystals of **3** (1.36 g, 66% yield), m.p. 175–176 °C. ^{1}H NMR (400 MHz, CD_3CN): $\delta = 5.08$ (s, 1H), 7.59–7.64 (m, 8H), 7.69–7.74 (m, 4H), 8.02–8.06 ppm (m, 8H); ^{13}C NMR (100 MHz, CD_3CN): $\delta = 49.3$, 127.9, 131.0, 135.2, 140.8 ppm; IR (KBr): $\tilde{\nu} = 3315$, 3269, 3094, 3062, 1095 cm^{-1}; elemental analysis calcd for $C_{25}H_{23}ClN_2O_4S_2$: C 58.30, H 4.50, N 5.44; found: C 58.29, H 4.46, N, 5.46.

5: A mixture of **4** (414 mg, 1.0 mmol) and methyl iodide (187 μL, 3 mmol) in acetonitrile (10 mL) was stirred at room temperature for 1 h. A solution of sodium perchlorate (184 mg, 1.5 mmol) in acetonitrile (10 mL) was added, and then the solvent was evaporated under reduced pressure. The residue was dissolved in water (10 mL) and extracted with CH_2Cl_2. After removal of the solvent, the residue was purified by recrystallization from MeOH/Et_2O to afford **5** as colorless crystals (152 mg),[7] m.p. 184–185 °C. ^{1}H NMR (400 MHz, CD_3CN): $\delta = 2.75$ (s, 6H), 5.18 (s, 1H), 7.52–7.57 (m, 8H), 7.65–7.70 (m, 4H), 7.87–7.90 ppm (m, 8H); ^{13}C NMR (100 MHz, CD_3CN): $\delta = 30.4$, 39.3, 128.9, 131.0, 135.3, 136.8 ppm; IR (KBr): $\tilde{\nu} = 2917$, 2872, 2803, 1194, 1091 cm^{-1}; elemental analysis calcd for $C_{27}H_{27}ClN_2O_4S_2$: C 59.71, H 5.01, N 5.16; found: C 59.72, H 4.97, N, 5.17.

6: A solution of **5** (100 mg) in methanol was passed through a column of Amberlite IRA-410 ion-exchange resin (strong base, OH^- form) followed by evaporation of the solvent to give **6** as a pale yellow powder (74 mg, 98%), m.p. 163–164 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.62$ (s, 6H), 7.28–7.35 (m, 12H), 8.00 ppm (dd, $J_1 = 8.0$ Hz, $J_2 = 1.4$ Hz, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 30.1$, 39.7, 127.7, 128.3, 130.5, 144.4 ppm; IR (KBr): $\tilde{\nu} = 2947$, 2840, 2776, 1147 cm^{-1}; elemental analysis calcd for $C_{27}H_{26}N_2S_2$: C 73.26, H 5.92, N 6.33; found: C 73.11, H 5.99, N, 6.29.

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[2] Attempts to prepare $R_2S{=}C{=}SR_2$ from $[R_2S{-}CH_2{-}SR_2]^{2+}$ or $[R_2S{=}CH{-}SR_2]^+$ ions (R = Me, Et) were unsuccessful; see: C. P. Lillya, E. F. Miller, P. Miller, *Int. J. Sulfur Chem*. **1971**, *1*, 89–96.

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[4] Compound **4** could not be isolated from the reaction mixture of lithiated **1** and **2**, and was therefore isolated by converting it into the corresponding perchloric salt **3** upon treatment with perchloric acid (See Experimental Section).

[5] Unexpectedly, ^{13}C NMR spectra of **4** showed only one set of phenyl groups, and methyne proton and carbon resonances were not observed in the temperature range −80 to 100 °C in CD_3OD and [D_6]DMSO. IR and elemental analyses were consistent with the structure of **4**, although the structure of **4** in the solution is still not certain. **4**: m.p. 155–156 °C; IR (KBr): $\tilde{\nu} = 1259$ cm^{-1} (S≡N); elemental analysis calcd for $C_{25}H_{22}N_2S_2$: C 72.43, H 5.35, N 6.76; found: C 72.36, H 5.38, N, 6.77.

[6] Compounds **4** and **6** are considerably basic. Treatment of **4** and **6** with perchloric acid afforded, almost quantitatively, **3** and **5**, respectively.

[7] The side products in the reaction with methyl iodide were **3** and the *N*-monomethylated compound, $[(MeN)Ph_2S{=}CH{-}SPh_2(NH)]^+\ [ClO_4]^-$ (**8**). The structure of **8** is still preliminary as it has been difficult to effect the separation of **3** and **8** successfully.

[8] Crystal data for **5**: $C_{27}H_{27}ClN_2O_4S_2$, $M_r = 547.09$, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 12.769(6)$, $b = 16.503(4)$, $c = 14.031(6)$ Å, $\beta = 115.99(3)°$, $V = 2657(1)$ Å^3, $\rho_{calcd} = 1.367$ cm^{-1}. X-ray diffraction data were collected on a Rigaku AFC7R diffractometer with graphite monochromated $Mo_{k\alpha}$ radiation ($\lambda = 0.71069$ Å) at 296 K, and the structure was solved by direct methods (SIR 92) and expanded using Fourier techniques (DRIFT). The final cycle of full-matrix least-squares refinement was based on 5006 observed reflections ($I > 3\sigma(I)$) and 338 variable parameters and converged to $R = 0.050$ and $R_w = 0.071$. **6**: $C_{27}H_{26}N_2S_2$, $M_r = 442.64$, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 7.40(5)$, $b = 15.63(8)$, $c = 20.36(6)$ Å, $\beta = 91.6(5)°$, $V = 2352(20)$ Å^3, $\rho_{calcd} = 1.250$ cm^{-1}. X-ray diffraction data were collected on a Rigaku AFC7R diffractometer with graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å) at 296 K, and the structure was solved by direct methods (SIR 92) and expanded using Fourier techniques (DRIFT). The final cycle of full-matrix least-squares refinement was based on 4039 observed reflections ($I > 3\sigma(I)$) and 280 variable parameters and converged to $R = 0.042$ and $R_w = 0.058$. CCDC-180279 (**5**) and CCDC-180280 (**6**) contain 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).

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Reaction of 2-Butyne with *nido*-[1,2-(Cp*RuH)$_2$B$_3$H$_7$]: Improved Kinetic Control Leads to Metallacarboranes of Novel Composition and Structure**

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The conventional route to metallacarboranes proceeds in a sequence of steps leading from polyborane to carborane to metallacarborane.[1–4] Although a fruitful strategy, it is also one in which strong bonds are formed before weak ones. Access to more diverse chemistry might arise by adoption of the reverse strategy, that is, formation of B–B/B–M before B–C/M–C bonds, thereby generating the most stable products

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last. Having in hand an efficient, general route to metallaboranes by the reaction of monocyclopentadienyl metal chlorides with monoboranes, we were in a position to test this hypothesis.[5] Insertion of an alkyne into a metallaborane has precedence but, in the absence of efficient routes to metallaboranes, has not been extensively explored.[6–8] The results described below illustrate the increased scope of metallacarborane chemistry accessible when kinetic barriers are significantly lowered.

Reaction of *nido*-[1,2-$(Cp^*RuH)_2B_3H_7$] (**1**; $Cp^* = \eta^5$-C_5Me_5)[9] with excess 2-butyne at room temperature yields a major product, **2**, and two minor ones, **3** and **4** (Scheme 1). The major product results from addition of the alkyne followed by loss of H_2. The spectroscopic data were not consistent with formation of a single 9 skeletal-electron-pair (sep) *nido* 7-framework-atom cluster as suggested by the molecular formula of **2**[10, 11] and it took a solid-state structure determination[12] (Figure 1) to show that the cluster framework adopted by **2** is a *nido* 6-framework-atom cluster. The seventh atom, boron, is found as an exopolyhedral BH_2 fragment bridging an apical Ru-basal boron edge giving *nido*-[1,2-$(Cp^*Ru)_2(\mu$-H$)(\mu$-$BH_2)$-4,5-Me_2-4,5-$C_2B_2H_4$] (**2**).

Formally, the BH_2 fragment on **2** is a one-electron ligand and **2** has an 8 sep count appropriate for its shape. The NMR spectra and the structure data show that the BH_2 fragment forms a BHB interaction with the terminal hydrogen atom of the basal boron atom it bridges, thus, **2** can also be considered to possess an exopolyhedral BH_3 unit. Although **2** is unique, related compounds are: a metallaborane with a terminal BH_2PR_3 fragment;[13] a ferraborane with a BH_3 unit replacing the hydrogen atom of a B-H-B bridge;[14] and a compound with a BX fragment bridging two metal atoms.[15]

Addition of the alkyne to **1** and loss of BH_3 gives [1,2-$(Cp^*RuH)_2$-4,5-Me_2-4,5-$C_2B_2H_4$] (**3**) as a minor product. The structure of an analogue of **3** which has different substituents on the carbon atoms was reported earlier to provide a contrast to the reaction of isoelectronic [1,2-$(Cp^*Rh)_2B_3H_7$] with alkynes leading to catalytic cyclotrimerization.[16] Considerably more surprising is the isolation of [1,2-$(Cp^*RuH)_2$-4-Et-4,5-$C_2B_2H_5$] (**4**), a product that would be expected to arise from 1-butyne. No detectable 1-butyne was present in the reagent used and, although the isomerization of internal alkenes to terminal alkenes by boranes is well known,[17] similar isomerization of alkynes is not. However, **4** is clearly a product of the reaction of **1** with 2-butyne. Related complex chemistry occurs when the alkenyl pentaborane formed from B_5H_9 and 2-butyne is converted thermally into 2-Me-3-Et-2-CB_5H_7.[18] Although mechanistically suggestive, the high reaction barrier makes it unlikely that an alkenyl borane is a precursor to either **3** or **4**.

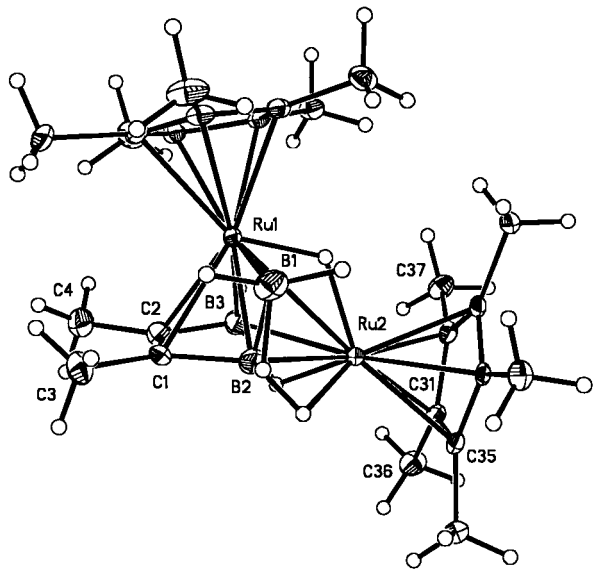
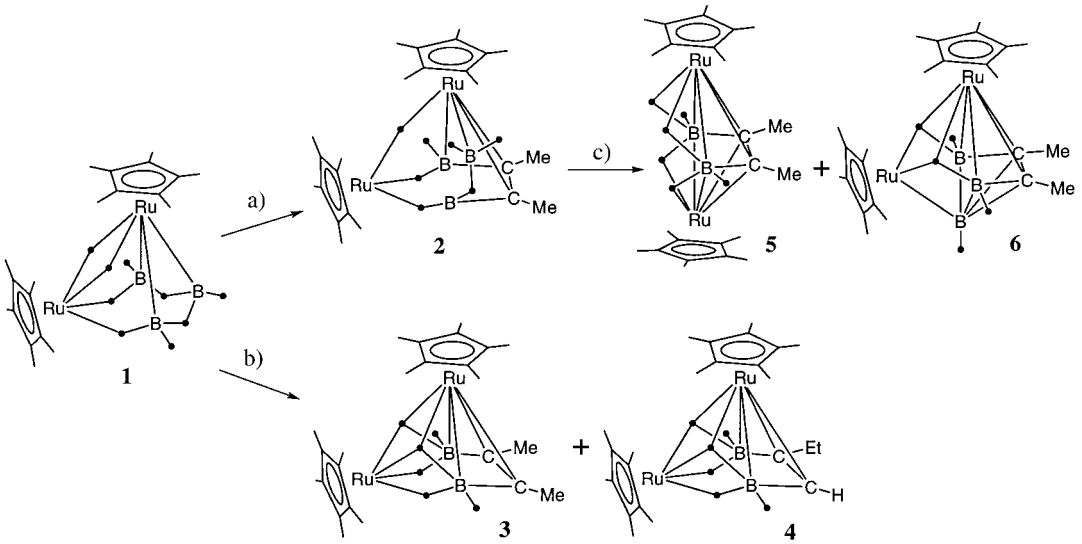


Figure 1. Molecular structure of **2**. Selected bond lengths [Å]: Ru1-B2 2.155(5), Ru1-B1 2.278(6), Ru1-C2 2.292(5), Ru1-B3 2.332(5), Ru1-Ru2 2.9134(5), C1-C2 1.391(8), C1-C3 1.508(7), C1-B2 1.558(7), B1-B2 1.760(9), Ru2-B2 2.293(6), Ru2-B3 2.327(6), C2-C4 1.519(7), C2-B3 1.520(8).

Heating **2** generates *nido*-[1,7-$(Cp^*Ru)_2$-4,5-Me_2-4,5-$C_2B_2H_6$] (**5**) and *closo*-[1,2-$(Cp^*RuH)_2$-4,5-Me_2-4,5-$C_2B_3H_3$] (**6**). Complex **5** has a molecular formula identical to **3** but very different spectroscopic properties. A solid-state structure[12]



Scheme 1. Conditions; a), b) 2-butyne, room temperature, 24 h, THF; c) 85 °C, 25 h, toluene. ● = H.

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(Figure 2) shows it to be a cluster geometric isomer of **3**. Both are 8 sep clusters based on a pentagonal-bipyramidal geometry. Compound **3** has a vacant 5-connect vertex, common for a polyborane, whereas **5** has a vacant 4-connect vertex,

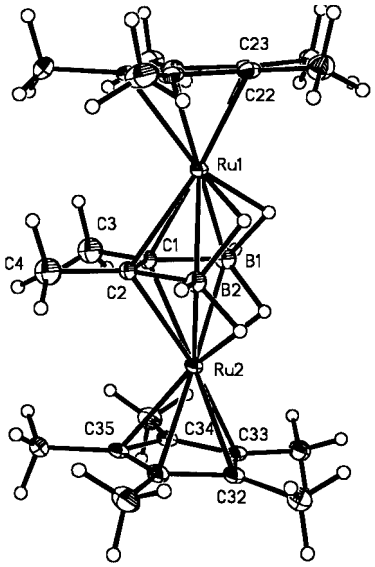

Figure 2. Molecular structure of **5**. Selected bond lengths [Å]: Ru1-C1 2.197(7), Ru1-C2 2.271(8), Ru1-B1 2.290(8), Ru1-B2 2.425(8), Ru2-C1 2.200(7), Ru2-C2 2.284(8), Ru2-B1 2.286(8), Ru2-B2 2.424(8), B1-C1 1.543(12), B2-C2 1.593(12), C1-C2 1.455(11), C1-C3 1.512(11), C2-C4 1.503(12), Ru1-Ru2 3.6383(5).

unusual for a polyborane. Both are stable up to 90 °C. Observation of **3** and **5** in the same reaction system under different conditions is a clear demonstration of kinetic control. The solid-state structure of **6**[12] (Figure 3) reveals a *closo* geometry consistent with its sep = 8. Along with loss of H_2, the exopolyhedral borane of **2** has reentered the skeletal network.

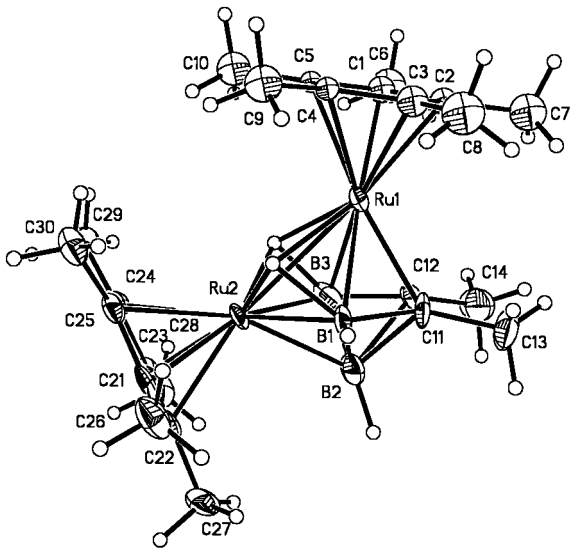

Figure 3. Molecular structure of **6**. Selected bond lengths [Å]: Ru1-C12 2.170(9), Ru1-C11 2.206(10), Ru2-B2 2.172(11), Ru2-B3 2.180(11), Ru2-B1 2.196(9), Ru1-Ru2 2.8832(9), B1-C11 1.573(13), B1-B2 1.802(17), B2-C11 1.738(15), B2-C12 1.751(14), B2-B3 1.813(18), B3-C12 1.582(14), C11-C12 1.411(15), C11-C13 1.512(13), C12-C14 1.541(13).

This work clearly demonstrates that combining metal and boron before carbon permits access to metallacarboranes of types not previously seen. The work constitutes part of a continuing realization of the potential of the inorganometallic chemistry of boron.[19]

Experimental Section

2–**4**: MeC≡CMe (0.8 g, 14.8 mmol) was added to an orange solution of **1** (150 mg, 0.29 mmol)[9] in THF (40 mL). Reaction for 24 h at ambient temperature, removal of solvent and excess alkyne, and chromatography (silica gel, ICN 32-63 D, hexane:toluene = 20:1) gave **2** (83.8 mg, 51 %): ^{1}H (400 MHz, 22 °C, [D$_6$]benzene; t = terminal): δ = 4.44 (br, 1H, B-Ht), 3.70 (br, 1H, B-Ht), 3.63 (br, 1H, B-Ht), 1.93 (s, 3H, Me), 1.82 (s, 15H, Cp*), 1.80 (s, 3H, Me), 1.61 (s, 15H, Cp*), −3.25 (br d, J = 65 Hz, 1H, B-H-B), −11.02 (pcq = partially collapsed quartet, 1H, B-H-Ru), −14.92 (s, 1H, Ru-H-Ru), −14.94 ppm (br, 1H, B-H-Ru); ^{11}B (128 MHz, 22 °C, [D$_6$]benzene): δ = 26.1, 20.1, 11.4 ppm (all br 1:1:1); ^{13}C (125 MHz, 22 °C, [D$_6$]benzene): δ = 10.76 (Cp*), 12.17 (Cp*), 15.01 (Me), 19.98 (Me), 88.71 (Cp*), 93.73 (Cp*), 111.50 (br, C-B), 128.30 ppm (br, C-B); FAB-MS: 563 (100 %, [M^+ − 4H]); IR (KBr): $\tilde{\nu}$ = 2411, 2461 cm^{-1} ($\nu_{B\text{-}H}$); then **3** (27.4 mg, 17 %) ^{1}H (400 MHz, 22 °C, [D$_6$]benzene): δ = 2.12 (s, 6H, Me), 2.05 (br, 1H, B-Ht), 1.87 (s, 15H, Cp*), 1.78 (s, 15H, Cp*), −11.52 (br, s, 2H, Ru-H-Ru), −12.57 ppm (br, 2H, B-H-Ru); ^{11}B (128 MHz, 22 °C, [D$_6$]benzene): δ = −16.2 ppm (br); ^{13}C (125 MHz, 22 °C, [D$_6$]benzene): δ = 11.49 (Cp*), 12.42 (Cp*), 21.20 (Me), 86.71 (Cp*), 90.37 (Cp*), 108.52 ppm (br, C-B); MALDI-MS: 555 ([M^+]); IR(KBr): $\tilde{\nu}$ = 2427 ($\nu_{B\text{-}H}$); then **4** (13 mg, 8 %) ^{1}H (400 MHz, 22 °C, [D$_6$]benzene): δ = 4.40 (br s, 1H, CH), 2.31 (m, 2H, CH$_2$), 2.09 (br, 1H, B-Ht), 1.99 (br, 1H, B-Ht), 1.85 (s, 15H, Cp*), 1.79 (s, 15H, Cp*), 1.45 (t, ^3J(H,H) = 7.4 Hz, 3H, CH$_3$), −11.67 (s, 1H, Ru-H-Ru), −11.83 (s, 1H, Ru-H-Ru), −12.18 (br s, 1H, B-H-Ru), −12.60 ppm (br s, 1H, B-H-Ru); ^{11}B (128 MHz, 22 °C, [D$_6$]benzene): δ = −18.2, −14.7 ppm (all br 1:1); ^{13}C (125 MHz, 22 °C, [D$_6$]benzene): δ = 11.73 (Cp*), 12.38 (Cp*), 20.79 (Me), 33.18 (CH$_2$), 86.63 (Cp*), 91.14 (Cp*), 97.54 (br, B-C-H) and 118.77 ppm (br, C-B); MALDI-MS: 555 ([M^+]); IR (KBr): $\tilde{\nu}$ = 2436 ($\nu_{B\text{-}H}$).

5 and **6**: **2** (96 mg, 0.17 mmol) in toluene (20 mL) was heated for 25 h at 85 °C under N_2. After removal of the solvent and chromatography (silica gel, ICN 23-60 D, hexane) gave **6** (44.2 mg, 46 %); ^{1}H (400 MHz, 22 °C, [D$_6$]benzene): δ = 3.82 (pcq, 3H, B-Ht), 2.13 (s, 6H, Me), 2.07 (s, 15H, Cp*), 1.68 (s, 15H, Cp*), −11.12 ppm (s br 2H, B-H-Ru); ^{11}B (128 MHz, 22 °C, [D$_6$]benzene): δ = 11.07 (d, ^2J(B,H) = 145 Hz, 2B), 8.72 ppm (d, ^2J(B,H) = 145 Hz, 1B); ^{13}C (125 MHz, 22 °C, [D$_6$]benzene): δ = 11.52 (Cp*), 12.29 (Cp*), 21.25 (Me), 86.24 (Cp*), 87.80 (br, C-B), 93.95 ppm (Cp*); FAB: 563.3 (100 %, [M^+ − 2H]); IR (KBr): $\tilde{\nu}$ = 2477 ($\nu_{B\text{-}H}$); and (hexane:toluene = 20:1) gave **5** (19.8 mg, 21 %); ^{1}H (400 MHz, 22 °C, [D$_6$]benzene): δ = 2.41 (s, 6H, Me), 1.66 (s, 30H, Cp*), 1.18 (br, 2H, B-H-B), −10.07 ppm (br s, 4H, B-H-Ru); ^{11}B (128 MHz, 22 °C, [D$_6$]benzene): δ = −32.9 ppm br; ^{13}C (125 MHz, 22 °C, [D$_6$]benzene): δ = 10.92 (Cp*), 21.00 (Me), 84.63 ppm (Cp*); FAB: 553 (100 %, [M^+ − 2H]); IR (KBr): $\tilde{\nu}$ = 2420 ($\nu_{B\text{-}H}$).

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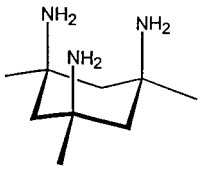
A 1,3,5-Triaxial Triaminocyclohexane: The Triamine Corresponding to Kemp's Triacid**

Fredric M. Menger,* Jianwei Bian, and Vladimir A. Azov

Kemp's triacid is a cyclohexane derivative in which 1,3,5-*cis* methyl groups force three 1,3,5-*cis* carboxy groups into an all-axial conformation.[1] In the two decades since its inception, Kemp's triacid has served as a useful framework for the design of enzyme models. For example, an aliphatic monoamide of Kemp's triacid hydrolyzes in only minutes at neutral pH and 22 °C because of enzyme-like catalysis by a neighboring carboxy group.[2] Herein, we examine the properties of triamine **1**, an analogue of Kemp's triacid which has, until now, escaped synthesis.

cis,cis-1,3,5-Triaminocyclohexane[3] was first prepared in 1957 and, a decade later, its metal complexes were investigated.[4] More pertinently, triamine **2**, an isomer of our compound, was previously synthesized and examined,[5] which provided us with a valuable comparison.[6] As will be seen, the two systems (**1** and **2**) differ substantially in their basicity and nucleophilicity.



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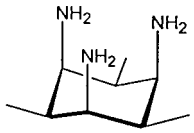

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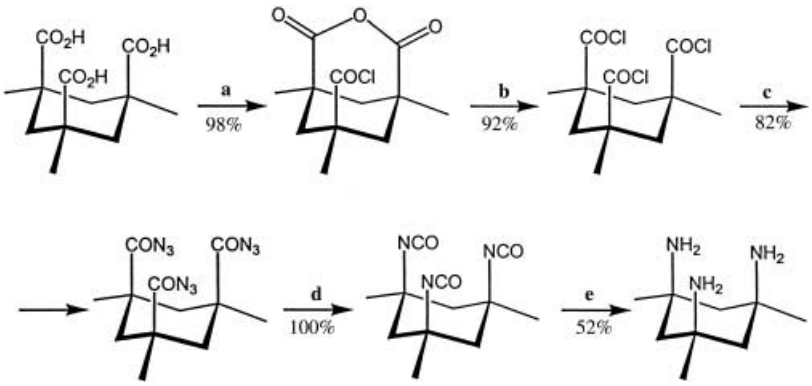
The synthesis of triamine **1**, which started with the addition of 2 – 4 g Kemp's triacid to $SOCl_2$, is given in Scheme 1. The product was, however, not the desired triacid chloride but the anhydride/acid chloride. Fortunately, this difficulty could be circumvented with the aid of a literature procedure in which an anhydride is converted into two acid chlorides.[7] The key step, a stereospecific tris-Curtius rearrangement of triazide (purified chromatographically with $CHCl_3$), proceeded with high yield in refluxing dioxane or toluene (caution!).[8] The resulting triisocyanate was hydrolyzed under harsh conditions (37% HCl/THF), from which the trihydrochloride salt precipitated. Treatment with an ion-exchange resin released the free triamine **l** (m.p. of hydrate 86 – 90 °C), which was characterized by ^1H and ^{13}C NMR spectroscopy, MS, elemental analysis, and X-ray crystallography.[9]



Scheme 1. Synthesis of triamine **1**; a) $SOCl_2$, ether, RT, b) $ZnCl_2$, $CHCl_2OCH_3$, reflux, c) NaN_3, Bu_4NBr, CH_2Cl_2/H_2O, 0 °C, d) dioxane, reflux, e) 37% HCl, THF, reflux, then Dowex 550A OH^-, CH_3OH.

X-ray analyses of the crystalline triamine **1**, **1**·1HCl, and the diacetyl derivative established in each case a preference for three axial nitrogen atoms. Only the **1**·3HCl adopted a conformation with three equatorial nitrogens caused, no doubt, by electrostatic repulsion among the three cationic ammonium groups. A similar dependence of conformation upon the protonation level of triamine **2**, as deduced by NMR spectroscopy, was reported previously.[5] Three factors favor axial nitrogen atoms: a) the slightly smaller size of an amino group relative to a methyl group,[10] b) hydrogen bonding among the amine groups, and c) a beneficial antiperiplanar $\sigma_{C\text{-}H} - \sigma^*_{C\text{-}N}$ interaction.[11]

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author. CCDC-183190 to CCDC-183202 contain 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).

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