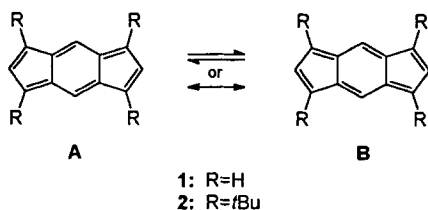


1,3,5,7-Tetra-*tert*-butyl-4-aza- and 1,3,5,7-Tetra-*tert*-butyl-4-phospha-*s*-indacene**

Teodor Silviu Balaban, Stefan Schardt, Volker Sturm, and Klaus Hafner*

Dedicated to Professor Wolfgang Lüttke on the occasion of his 75th birthday

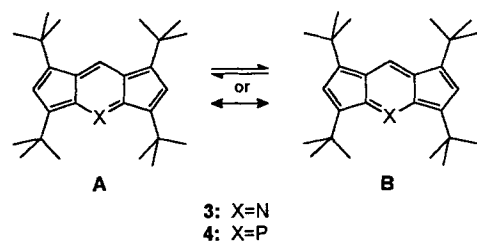
s-Indacene (**1**),^[1] a tricyclic, nonalternating [4n]π system, has been the subject of repeated theoretical and experimental investigations. Formally, **1** may be regarded as a [12]annulene perturbed by two σ bonds, and can therefore be considered as an antiaromatic compound. According to calculations carried out previously for **1**,^[2–4] a ground state structure with localized double bonds and the C_{2h}-symmetrical π-bonding was suggested for isomers **1A** and **1B**.



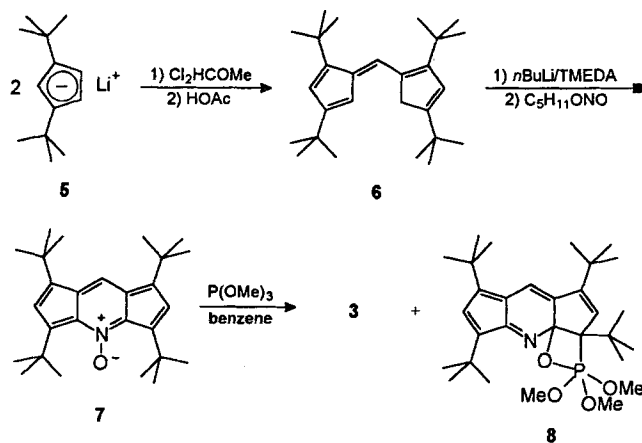
In contrast to **1**, which could not be isolated, the kinetically stabilized 1,3,5,7-tetra-*tert*-butyl-*s*-indacene **2** has been found to be a stable compound. The D_{2h} structure with equidistant bond lengths established for **2** by an X-ray structure analysis^[5,6] was attributed to an unusually strong electronic influence of the *tert*-butyl groups.^[7] On the other hand, according to recent quantum chemical calculations by Koch et al.,^[8] **1** is also expected to exist in the ground state as a delocalized π system with a D_{2h} structure. The limited stability of **1** is a consequence of the considerable singlet-diradical character of the *s*-indacene system.

Only a few investigations of hetero-*s*-indacenes have been carried out so far. Owing to the electronically stabilizing substituents, the donor-substituted 1,3,5,7-tetrakis(diethylamino)-2,6-diaza-*s*-indacene synthesized by Gompper et al.^[9] is not suitable for obtaining information about the influence of the nitrogen atoms on the π perimeter. The introduction of one nitrogen atom or a different heteroatom into the fully conjugated *s*-indacene system has not been described hitherto. Herein we report on the syntheses of 1,3,5,7-tetra-*tert*-butyl-4-aza-*s*-indacene (**3**) and its phospho-analogue (**4**) as well as on their bonding in comparison to that of the carbocycle **2**.

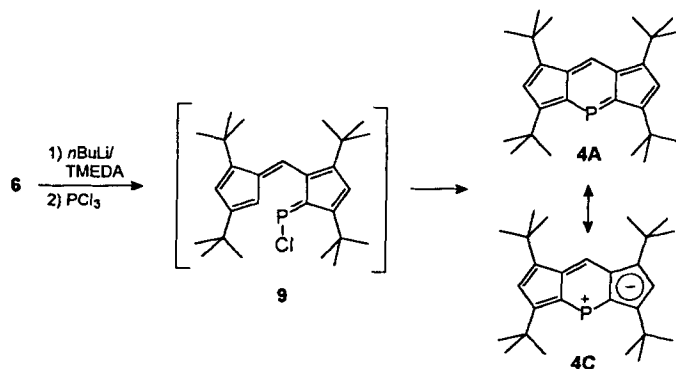
For the synthesis of **3**, (*E*)-1,3-di-*tert*-butyl-5-(2,4-di-*tert*-butylcyclopenta-1,3-dienylmethylidene)cyclopenta-1,3-diene (**6**) was prepared by reaction of lithium 1,3-di-*tert*-butylcyclopentadienide (**5**) with half an equivalent of 1,1-dichloromethyl methyl ether.^[10–12] This could be transformed by deprotonation with



n-butyllithium in the presence of TMEDA and subsequent treatment with isoamyl nitrite into 1,3,5,7-tetra-*tert*-butyl-4-aza-*s*-indacene-*N*-oxide (**7**), which was obtained in 42% yield as a dark blue, fine crystalline powder (m.p. 261–263 °C (decomp.)).^[13] Deoxygenation of **7** to give the 4-aza-*s*-indacene **3** was achieved with trimethyl phosphite in boiling benzene. This afforded the tricycle **3** in 75% yield as an extremely unstable, dark red solid (m.p. 136–138 °C (decomp.)). In addition to **3**, small amounts of the 1,2λ⁵-oxaphosphetane **8** (bordeaux red plates, m.p. 181 °C, 17% yield) were isolated, whose structure was established by an X-ray structure analysis.^[14]



In analogy to the synthesis of **7**, the pentafulvene **6** was deprotonated (*n*BuLi/TMEDA) and subsequently treated with phosphorus trichloride at –50 °C to give rise to the 1,3,5,7-tetra-*tert*-butyl-4-phospha-*s*-indacene **4**, which could be isolated as blue-black crystals with a metallic luster (m.p. 221–222 °C (decomp.), 75% yield). At room temperature **4** may be stored for several weeks under an inert atmosphere, and is only poorly soluble in organic solvents giving intense dark blue solutions. In the synthesis of **4**, the 6-phosphapentafulvene derivative **9**^[15] may be



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an intermediate, whose 12π -electrocyclization and subsequent hydrogen chloride elimination generate the heterocycle **4**.

The spectroscopic data of the azaindacene **3** (see below) suggest only a slight perturbation of the electronic structure by the introduction of the nitrogen atom into the 4-position of the 12π perimeter of **2**. A potential loss of symmetry through localized double bonds is not observed. The 300 MHz ^1H NMR spectrum shows, in addition to two singlets for the *tert*-butyl groups, a common singlet for 2-H and 6-H, as well as one for 8-H. In the ^1H broadband decoupled ^{13}C NMR spectrum, six singlets are observed for the eleven ring carbon atoms. These data may be interpreted on the assumption of a C_{2v} -symmetric structure with π -electron delocalization and equivalent bond lengths, as well as a rapid bond shift of the localized π -bonding isomers **3A** and **3B**. A ^{13}C NMR spectrum in $[\text{D}_8]\text{THF}$ recorded at 173 K shows no splitting of the signals by "freezing" a possible π -bond shift. The proton resonances of the azaindacene **3** experience a downfield shift of $\Delta\delta = 0.1$ for the 2-, 6-, and 8-H, compared with those of **2**. This small difference in chemical shift indicates the similarity between the electronic structures of both compounds.

The NMR spectra of the phosphaindacene **4** likewise show no signal splitting due to double bond localization, neither at room temperature nor at 173 K. The resonances in the ^1H NMR spectrum ($\Delta\delta = 0.25$ for 2-H and 6-H and 0.37 for 8-H) display a distinctly stronger downfield shift than those of **2**. The ^1H broadband decoupled ^{31}P NMR spectrum of **4** with a singlet at $\delta = 258.6$,^[16] indicates a comparatively strong deshielded phosphorus nucleus. This could be attributed to an appreciable contribution of dipolar resonance structures with a formal positive charge at the phosphorus atom, for example **4C**. An X-ray structure analysis of **4** did not furnish any reliable data regarding bond lengths and angles owing to statistical disorder of the molecules in the crystal.^[14]

The UV/Vis spectrum of **3** in dichloromethane shows an absorption maximum at $\lambda_{\text{max}} = 314$ nm with resolved vibrational fine structure and a further maximum at 564 nm (Fig. 1). In

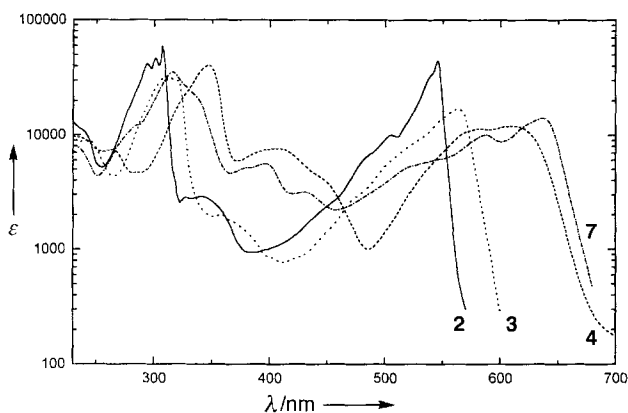
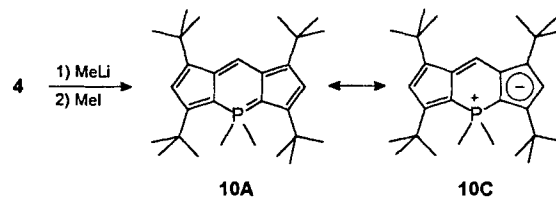


Fig. 1. UV/Vis spectra of the *s*-indacenes **2** and **3** in *n*-hexane, as well as those of **4** and **7** in CH_2Cl_2 .

comparison with the carbocyclic *s*-indacene **2**, the absorption bands of the 4-aza-indacene **3** are shifted bathochromically by 10–15 nm with a very similar fine structure. However, the extinction coefficients of the heterocycle **3** are comparable to those of the parent system **2**. The UV/Vis absorptions of the phosphaindacene **4** ($\lambda_{\text{max}} = 346, 582,$ and 610 nm) show a bathochromic shift of more than 30 nm relative to those of **2** (Fig. 1). The fact that these absorptions are shifted more bathochromically than

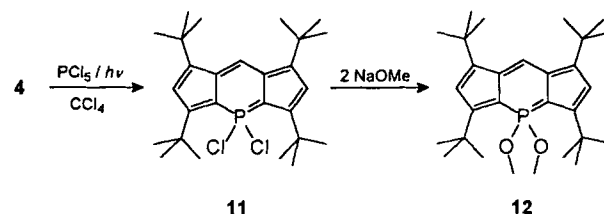
those of the azaindacene **3** may be, presumably, attributed to a resonance structure of type **4C**.

The reaction of the phosphaindacene **4** with methylolithium, followed by addition of methyl iodide led to 1,3,5,7-tetra-*tert*-butyl-4,4-dimethyl- $4\lambda^5$ -phospha-*s*-indacene (**10**), which was obtained as stable red needles (58% yield, sublimes ≥ 310 °C).



In an analogy to λ^5 -phosphinines,^[17] the cyclic π -conjugation is partially perturbed by the formally pentavalent phosphorus. The resulting decrease of the paramagnetic ring current effect leads to downfield shifts of $\Delta\delta = 0.59$ for 2-H and 6-H and 0.75 for 8-H in the ^1H NMR spectrum of **10**, relative to that of the λ^3 -phosphaindacene **4**. The ^{31}P resonance of **10** at $\delta = -16.7$ is in the range of usual values as expected for cyclic conjugated phosphorus ylides and suggests a substantial contribution of the resonance stabilized betaine structure of type **10C** to the ground state of the λ^5 -phospha-*s*-indacene **10**.

Upon irradiation (300 W, Osram Concentra), **4** reacts with phosphorus pentachloride under radical addition of one mole equivalent of chlorine at the phosphorus atom to give 1,3,5,7-tetra-*tert*-butyl-4,4-dichloro- $4\lambda^5$ -phospha-*s*-indacene (**11**) (43% yield, pale green needles, sublimes ≥ 235 °C). Double nucleophilic substitution in the 4-position of **11** with sodium methoxide affords the 4,4-dimethoxy derivative **12** (48% yield, black



crystals, m.p. 228–229 °C, soluble in organic solvents leading to an emerald green coloration).

Some spectroscopic data for the compounds **2–4**, **7**, **8**, and **10–12** [18].

2 [5]: ^1H NMR (300 MHz, CDCl_3): $\delta = 1.18$ (s, 36H; 1-, 3-, 5-, 7-*t*Bu), 5.29 (s, 2H; 2-, 6-H), 6.90 (s, 2H; 4-, 8-H); ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 31.2$ (C(CH_3)₃), 34.0 (C(CH_3)₃), 124.9 (C-2, C-6 or C-4, C-8), 129.1 (C-2, C-6 or C-4, C-8), 132.0 (C-3a, C-4a, C-7a, C-8a), 164.3 (C-1, C-3, C-5, C-7); UV/Vis (*n*-hexane): λ_{max} (lg ϵ) = 224 (4.10), 234 (4.03) (sh), 278 (4.23) (sh), 284 (4.37) (sh), 289 (4.48) (sh), 294 (4.61), 301 (4.66), 307 (4.77), 330 (3.45) (sh), 340 (3.48), 451 (3.41) (sh), 486 (3.83) (sh), 500 (3.96) (sh), 505 (4.01), 519 (4.11) (sh), 527 (4.26) (sh), 539 (4.51) (sh), 545 nm (4.64)

3: MS (70 eV): m/z (%): 377 (33) [M^+], 362 (100) [$M^+ - \text{Me}$], 332 (17) [$M^+ - 3\text{Me}$], 320 (12) [$M^+ - t\text{Bu}$], 57 (34) [$t\text{Bu}^+$]; ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 1.16$ (s, 18H; 1-, 7-*t*Bu), 1.22 (s, 18H; 3-, 5-*t*Bu), 5.41 (s, 2H; 2-, 6-H), 6.81 (s, 1H; 8-H); ^{13}C NMR (75.5 MHz, CD_2Cl_2): $\delta = 29.96$ (3-, 5-C(CH_3)₃), 30.50 (1-, 7-C(CH_3)₃), 33.85 (1-, 7- or 3-, 5-C(CH_3)₃), 34.49 (1-, 7- or 3-, 5-C(CH_3)₃), 126.58 (C-2, C-6), 126.96 (C-7a, C-8a), 128.71 (C-8), 153.44 (C-3a, C-4a), 163.21 (C-1, C-7 or C-3, C-5), 163.78 (C-1, C-7 or C-3, C-5); UV/Vis (CH_2Cl_2): λ_{max} (lg ϵ) = 236 (3.94), 301 (4.41) (sh), 307 (4.49), 314 (4.51), 320 (4.47), 355 (3.29) (sh), 505 (3.78) (sh), 527 (3.95) (sh), 564 nm (4.24)

4: MS (70 eV): m/z (%): 394 (47) [M^+], 379 (100) [$M^+ - \text{Me}$], 364 (25) [$M^+ - 2\text{Me}$], 337 (28) [$M^+ - t\text{Bu}$], 57 (34) [$t\text{Bu}^+$]; ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 1.24$ (s, 18H; 1-, 7-*t*Bu), 1.34 (s, 18H; 3-, 5-*t*Bu), 5.54 (d, $^1J(\text{P,H}) = 3.7$ Hz, 2H;

2-, 6-H), 7.27 (s, 1H; 8-H); ^{13}C NMR (75.5 MHz, CD_2Cl_2): $\delta = 31.70$ (s, 1-, 7- $\text{C}(\text{CH}_3)_3$), 33.25 (d, $^1J(\text{P},\text{C}) = 9.1$ Hz, 3-, 5- $\text{C}(\text{CH}_3)_3$), 34.00 (s, 1-, 7- or 3-, 5- $\text{C}(\text{CH}_3)_3$), 35.49 (s, 1-, 7- or 3-, 5- $\text{C}(\text{CH}_3)_3$), 125.63 (d, $^2J(\text{P},\text{C}) = 9.8$ Hz, C-2, C-6), 131.50 (s, C-7a, C-8a), 132.15 (s, C-8), 149.19 (d, $^1J(\text{P},\text{C}) = 47.4$ Hz, C-3a, C-4a), 165.16 (d, $^2J(\text{P},\text{C}) = 9.9$ Hz, C-1, C-7 or C-3, C-5), 173.18 (d, $^2J(\text{P},\text{C}) = 23.7$ Hz, C-1, C-7 or C-3, C-5); ^{31}P NMR (121.5 MHz, CDCl_3): $\delta = 258.6$; UV/Vis (CH_2Cl_2): λ_{max} (lg ϵ) = 240 (3.96) (sh), 262 (3.87), 346 (4.61), 407 (3.88), 443 (3.64) (sh), 582 (4.06), 610 (4.08), 864 (2.30), 984 (2.23) (sh), 1120 nm (1.79) (sh)

7: MS (70 eV): m/z (%): 393 (42) [M^+], 378 (23) [$M^+ - \text{Me}$], 57 (36) [$t\text{Bu}^+$]; ^1H NMR (300 MHz, CDCl_3): $\delta = 1.21$ (s, 18H; 1-, 7- $t\text{Bu}$), 1.27 (s, 18H; 3-, 5- $t\text{Bu}$), 5.47 (s, 2H; 2-, 6-H), 6.98 (s, 1H; 8-H); ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 27.32$ (3-, 5- $\text{C}(\text{CH}_3)_3$), 31.24 (1-, 7- $\text{C}(\text{CH}_3)_3$), 33.74 (1-, 7- or 3-, 5- $\text{C}(\text{CH}_3)_3$), 33.87 (1-, 7- or 3-, 5- $\text{C}(\text{CH}_3)_3$), 124.95 (C-2, C-6), 127.29 (C-8), 128.84 (C-7a, C-8a), 141.77 (C-3a, C-4a), 157.96 (C-1, C-7 or C-3, C-5), 158.99 (C-1, C-7 or C-3, C-5); UV/Vis (CH_2Cl_2): λ_{max} (lg ϵ) = 239 (3.85) (sh), 288 (4.09) (sh), 316 (4.55), 334 (4.36) (sh), 380 (3.71), 396 (3.74), 432 (3.49), 528 (3.72) (sh), 547 (3.77), 587 (4.00), 627 (4.11) (sh), 637 nm (4.15)

8: MS (70 eV): m/z (%): 486 (6) [$M^+ - \text{OMe}$], 377 (42) [$M^+ - \text{OP}(\text{OMe})_3$], 362 (100) [$M^+ - \text{OP}(\text{OMe})_3 - \text{Me}$], 57 (34) [$t\text{Bu}^+$]; ^1H NMR (300 MHz, CDCl_3): $\delta = 1.02$ (br.s, 9H; 2a- $t\text{Bu}$), 1.25 (s, 9H; $t\text{Bu}$), 1.27 (s, 9H; $t\text{Bu}$), 1.30 (s, 9H; $t\text{Bu}$), 3.54 (d, $^3J(\text{P},\text{H}) = 12.9$ Hz, 9H; $\text{P}(\text{OCH}_3)_3$), 5.99 (d, $^2J(\text{P},\text{H}) = 7.3$ Hz, 1H; 3-H), 6.30 (s, 1H; 5-H or 7-H), 6.91 (s, 1H; 5-H or 7-H), ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 26.83$ (br.s, 2a- $\text{C}(\text{CH}_3)_3$), 29.47 (s, $\text{C}(\text{CH}_3)_3$), 29.92 (s, $\text{C}(\text{CH}_3)_3$), 30.00 (s, $\text{C}(\text{CH}_3)_3$), 32.55 (s, $\text{C}(\text{CH}_3)_3$), 33.16 (d, $^1J(\text{P},\text{C}) = 2.0$ Hz, $\text{C}(\text{CH}_3)_3$), 34.60 (s, $\text{C}(\text{CH}_3)_3$), 35.78 (d, $^2J(\text{P},\text{C}) = 5.9$ Hz, 2a- $\text{C}(\text{CH}_3)_3$), 53.50 (d, $^2J(\text{P},\text{C}) = 10.7$ Hz, OCH_3), 87.57 (d, $^1J(\text{P},\text{C}) = 152.4$ Hz, C-2a), 89.16 (d, $^2J(\text{P},\text{C}) = 16.8$ Hz, C-9a), 113.09 (s, C_{quat}), 117.10 (d, $^4J(\text{P},\text{C}) = 4.3$ Hz, C-5), 129.70 (d, $^2J(\text{P},\text{C}) = 14.3$ Hz, C-3), 135.26 (s, C-7), 143.99 (d, $^2J(\text{P},\text{C}) = 13.4$ Hz, C_{quat}), 145.14 (s, C_{quat}), 150.04 (d, $^2J(\text{P},\text{C}) = 15.7$ Hz, C_{quat}), 151.52 (s, C_{quat}), 175.45 (s, C-8a); ^{31}P NMR (121.5 MHz, CDCl_3): $\delta = -29.4$; UV/Vis (*n*-hexane): λ_{max} (lg ϵ) = 250 (4.24), 303 (3.89), 493 nm (3.34)

10: MS (70 eV): m/z (%): 424 (93) [M^+], 409 (100) [$M^+ - \text{Me}$], 394 (4) [$M^+ - 2\text{Me}$], 379 (9) [$M^+ - 3\text{Me}$], 57 (13) [$t\text{Bu}^+$]; ^1H NMR (300 MHz, CDCl_3): $\delta = 1.39$ (s, 18H; 1-, 7- or 3-, 5- $t\text{Bu}$), 1.40 (s, 18H; 1-, 7- or 3-, 5- $t\text{Bu}$), 2.23 (d, $^2J(\text{P},\text{H}) = 12.9$ Hz, 6H; $\text{P}(\text{CH}_3)_3$), 6.13 (d, $^4J(\text{P},\text{H}) = 6.9$ Hz, 2H; 2-, 6-H), 8.02 (d, $^4J(\text{P},\text{H}) = 2.8$ Hz, 1H; 8-H); ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 22.04$ (d, $^1J(\text{P},\text{C}) = 58.1$ Hz, $\text{P}(\text{CH}_3)_3$), 33.19 (s, 1-, 7- or 3-, 5- $\text{C}(\text{CH}_3)_3$), 33.25 (s, 1-, 7- or 3-, 5- $\text{C}(\text{CH}_3)_3$), 34.14 (s, 1-, 3-, 5- and 7- $\text{C}(\text{CH}_3)_3$), 91.00 (d, $^1J(\text{P},\text{C}) = 100.0$ Hz, C-3a, C-4a), 119.39 (d, $^2J(\text{P},\text{C}) = 17.0$ Hz, C-2, C-6), 124.27 (d, $^2J(\text{P},\text{C}) = 12.1$ Hz, C-7a, C-8a), 135.07 (s, C-8), 149.08 (d, $^2J(\text{P},\text{C}) = 9.3$ Hz, C-1, C-7 or C-3, C-5), 154.13 (d, $^2J(\text{P},\text{C}) = 10.6$ Hz, C-1, C-7 or C-3, C-5); ^{31}P NMR (121.5 MHz, CDCl_3): $\delta = -16.7$; UV/Vis (CH_2Cl_2): λ_{max} (lg ϵ) = 234 (4.36), 303 (3.33), 318 (3.30), 457 (4.01), 575 nm (4.40)

11: MS (70 eV): m/z (%): 464, 466 (81, 55) [M^+], 449, 451 (100, 67) [$M^+ - \text{Me}$], 434, 436 (7, 6) [$M^+ - 2\text{Me}$], 394 (39) [$M^+ - 2\text{Cl}$], 379 (75) [$M^+ - 2\text{Cl} - \text{Me}$], 364 (25) [$M^+ - 2\text{Cl} - 2\text{Me}$], 337 (19) [$M^+ - 2\text{Cl} - t\text{Bu}$], 57 (96) [$t\text{Bu}^+$]; ^1H NMR (300 MHz, C_6D_6): $\delta = 1.36$ (s, 18H; 1-, 7- or 3-, 5- $t\text{Bu}$), 1.49 (s, 18H; 1-, 7- or 3-, 5- $t\text{Bu}$), 6.30 (d, $^4J(\text{P},\text{H}) = 9.1$ Hz, 2H; 2-, 6-H), 8.03 (d, $^4J(\text{P},\text{H}) = 2.4$ Hz, 1H; 8-H); ^{13}C NMR (75.5 MHz, C_6D_6): $\delta = 32.43$ (s, 1-, 7- or 3-, 5- $\text{C}(\text{CH}_3)_3$), 32.96 (s, 1-, 7- or 3-, 5- $\text{C}(\text{CH}_3)_3$), 33.77 (s, 1-, 7- or 3-, 5- $\text{C}(\text{CH}_3)_3$), 35.27 (s, 1-, 7- or 3-, 5- $\text{C}(\text{CH}_3)_3$), 96.88 (d, $^1J(\text{P},\text{C}) = 119.9$ Hz, C-3a, C-4a), 122.91 (d, $^3J(\text{P},\text{C}) = 23.0$ Hz, C-2, C-6), 129.61 (d, $^2J(\text{P},\text{C}) = 18.9$ Hz, C-7a, C-8a), 133.47 (s, C-8), 156.78 (d, $^2J(\text{P},\text{C}) = 17.3$ Hz, C-1, C-7 or C-3, C-5), 164.10 (d, $^2J(\text{P},\text{C}) = 12.1$ Hz, C-1, C-7 or C-3, C-5); ^{31}P NMR (121.5 MHz, C_6D_6): $\delta = 25.3$; UV/Vis (CH_2Cl_2): λ_{max} (lg ϵ) = 262 (4.55), 303 (3.74), 353 (3.48), 415 (3.68) (sh), 443 (3.93) (sh), 474 (4.24) (sh), 492 (4.40), 682 nm (3.85)

12: MS (70 eV): m/z (%): 456 (61) [M^+], 441 (100) [$M^+ - \text{Me}$], 426 (15) [$M^+ - 2\text{Me}$], 411 (7) [$M^+ - 3\text{Me}$], 57 (60) [$t\text{Bu}^+$]; ^1H NMR (300 MHz, CDCl_3): $\delta = 1.32$ (s, 18H; 1-, 7- or 3-, 5- $t\text{Bu}$), 1.36 (s, 18H; 1-, 7- or 3-, 5- $t\text{Bu}$), 3.58 (d, $^3J(\text{P},\text{H}) = 13.8$ Hz, 6H; $\text{P}(\text{OCH}_3)_3$), 5.95 (d, $^4J(\text{P},\text{H}) = 6.7$ Hz, 2H; 2-, 6-H), 7.68 (d, $^4J(\text{P},\text{H}) = 3.2$ Hz, 1H; 8-H); ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 31.82$ (s, 1-, 7- or 3-, 5- $\text{C}(\text{CH}_3)_3$), 33.15 (s, 1-, 7- or 3-, 5- $\text{C}(\text{CH}_3)_3$), 33.50 (s, 1-, 7- or 3-, 5- $\text{C}(\text{CH}_3)_3$), 34.34 (s, 1-, 7- or 3-, 5- $\text{C}(\text{CH}_3)_3$), 52.43 (s, OCH_3), 88.81 (d, $^1J(\text{P},\text{C}) = 140.6$ Hz, C-3a, C-4a), 120.31 (d, $^3J(\text{P},\text{C}) = 18.3$ Hz, C-2, C-6), 130.51 (d, $^2J(\text{P},\text{C}) = 17.9$ Hz, C-7a, C-8a), 133.33 (s, C-8), 154.38 (d, $^2J(\text{P},\text{C}) = 13.5$ Hz, C-1, C-7 or C-3, C-5), 161.46 (d, $^2J(\text{P},\text{C}) = 9.9$ Hz, C-1, C-7 or C-3, C-5); ^{31}P NMR (121.5 MHz, CDCl_3): $\delta = 56.1$; UV/Vis (CH_2Cl_2): λ_{max} (lg ϵ) = 240 (4.47), 275 (3.75) (sh), 328 (3.26) (sh), 338 (3.39), 472 (4.22), 482 (4.32), 638 nm (4.00)

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Surprising Formation of a Carborane-Substituted Digallane**

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Dedicated to Professor M. Frederick Hawthorne on the occasion of his 65th birthday

Classical inorganic compounds with Ga–Ga bonds such as Ga_2Br_3 ^[1] have been known for several years. However, organometallic derivatives with Ga–Ga bonds are of newer vintage,^[2] and structurally characterized examples are restricted to the Ga^I and Ga^{II} compounds [$\text{GaC}(\text{SiMe}_3)_3$]₄^[3] and Ga_2R_4 (R = $(\text{Me}_3\text{Si})_2\text{CH}$,^[4] 2,4,6-*i*Pr₃C₆H₂,^[5] and 2,4,6-(CF₃)₃C₆H₂^[6]). We report a new class of compound in which the Ga–Ga bond is supported by 2,4-dicarba-*nido*-hexaborate(2⁻) carborane ligands.

The reaction of one equivalent of $[\text{Ga}(t\text{Bu})\text{Cl}]_2$ with two equivalents of the disodium compound of *closo-exo-5,6-Na*(thf)₂-1-*Na*(thf)₂-2,4-(SiMe₃)₂-2,4-C₂B₄H₄^[7] afforded a mixture of two products, 1 and 2 (Scheme 1), which were separated by fractional distillation and sublimation. Compound 1 is an air- and moisture-sensitive colorless oil for which the overall

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