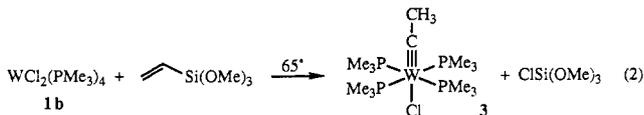


structures in solution.¹⁶ The analogous 2-methylallyl complex is formed slowly from **1a** and $\text{CH}_2=\text{CMeCH}_2\text{OSiMe}_3$.

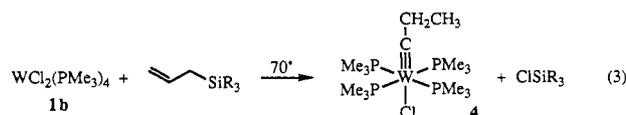
Since $\text{CH}_2=\text{CRCH}_2\text{OSiMe}_3$ delivers an allyloxy fragment to tungsten, we investigated whether $\text{CH}_2=\text{CHSi(OMe)}_3$ would transfer a methoxy group, with the vinyl acting as the tether. A clean reaction is observed with **1b**, but the product is the carbyne complex $\text{W}(\equiv\text{CCH}_3)(\text{PMe}_3)_4\text{Cl}$ (**3**) (eq 2).¹⁷ Thus vinyl is transferred instead of methoxy, with rearrangement of $\text{CH}_2=\text{CH}-$ to $\text{CH}_3\text{C}\equiv$. The carbyne complex **3** has been charac-



terized by NMR¹⁶ and an X-ray crystal structure,¹³ which is quite similar to the structures of $\text{W}(\equiv\text{CCH}_3)(\text{PMe}_3)_4\text{Me}$ and $\text{W}(\equiv\text{CH})(\text{PMe}_3)_4\text{Cl}$.¹⁸ An intermediate is observed in the formation of **3**, believed to be the vinylsilane complex $\text{WCl}_2[\text{CH}_2=\text{CHSi(OMe)}_3](\text{PMe}_3)_3$ on the basis of its paramagnetic NMR spectrum,¹⁹ consistent with the vinyl acting as a tether. Vinylsilanes $\text{CH}_2=\text{CHSiMe}_3$ and $\text{CH}_2=\text{CHSi(OEt)Me}_2$ also react with **1b** to give **3**, but carbyne products have not been observed starting from **1a**.

Kinetic and mechanistic studies are in progress to map out this transformation in detail. Labeling studies indicate that the formal vinyl to methylcarbyne rearrangement (eq 2) involves net movement of the methine hydrogen to the methylene group. Reaction of $^{13}\text{C}_2\text{H}_2=\text{CHSiMe}_3$ gives $\text{W}(\equiv\text{C}^{13}\text{CH}_3)(\text{PMe}_3)_4\text{Cl}$ with <1% label at the carbyne carbon, and $\text{CH}_2=\text{CDSiMe}_3$ gives $\text{W}(\equiv\text{CCH}_2\text{D})(\text{PMe}_3)_4\text{Cl}$, with $\leq 5\%$ CHD_2 product (by ^{13}C NMR). A crossover experiment using a 50:50 mixture of $^{13}\text{C}_2\text{H}_2=\text{CHSiMe}_3$ and $\text{CH}_2=\text{CDSiMe}_3$ shows that the reaction is not intramolecular: both $\text{W}(\equiv\text{C}^{13}\text{CH}_3)$ and $\text{W}(\equiv\text{C}^{13}\text{CH}_2\text{D})$ (60:40) are observed by ^{13}C NMR. These data are consistent with the mechanism proposed by Green for the other reported vinyl to carbyne rearrangement:²⁰ deprotonation of the vinyl complex gives a vinylidene, which protonates to form the carbyne.

Allylsilanes also react with **1b** to give a carbyne complex, in this case the ethylcarbyne $\text{W}(\equiv\text{CCH}_2\text{CH}_3)(\text{PMe}_3)_4\text{Cl}$ (**4**) (eq 3). A remarkable amount of hydrogen migration has to occur to complete this allyl to ethylcarbyne transformation. The ^1H , ^{31}P , and ^{13}C NMR spectra of **4** are very similar to those of **3**,



indicating the same basic structure. Reactions of **1b** with allylsilanes are slower than reactions of **1b** with vinylsilanes. Equations 2 and 3 are a new and quite convenient route to tungsten-carbon multiple bonds.

Three unusual transformations are reported here: formally allyloxy to oxo-allyl, vinyl to methylcarbyne, and allyl to ethylcarbyne. These reactions support the idea that the alkene function acts as a "tether" in the activation of silyl ethers, with the silicon acting as the organic fragment donor and as chloride acceptor. Once a substrate is bound to the tungsten, the formation of a very strong metal-ligand multiple bond, $\text{W}=\text{O}$ or $\text{W}=\text{C}$, provides the driving force for cleavage of the Si-O bond and for the unusual rearrangements.

Acknowledgment. We thank the National Science Foundation for financial support.

Supplementary Material Available: Synthetic procedures and spectral data for **2-4** and crystallographic tables for **2b** and **3** (16 pages); listing of observed and calculated structure factors for **2b** and **3** (8 pages). Ordering information is given on any current masthead page.

Synthesis and Characterization of a Branched-Chain Hexacarbene in a Tridecet Ground State. An Approach to Superparamagnetic Polycarbenes

Nobuo Nakamura, Katsuya Inoue, and Hiizu Iwamura*

The Department of Chemistry
Faculty of Science, The University of Tokyo
7-3-1 Hongo, Tokyo 113, Japan

Toshio Fujioka and Yasuhiko Sawaki

Department of Applied Chemistry
Faculty of Engineering, Nagoya University
Chikusa, Nagoya 464, Japan

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Design and synthesis of organic molecules in very high-spin ground states are current subjects of great importance.¹ The basic principle underlying the design is the desire to endow organic molecules with many half-filled orthogonal orbitals. Their presence is dictated by symmetry and can be achieved in two ways: orthogonality in space and topological symmetry. Carbenes in triplet ground states are examples of the former. In π -diradicals, parallel alignment of the two spins can become favored if the radical centers are placed in phase with the spin polarization of the intervening π -bonds. A Schlenk hydrocarbon in the triplet ground state is such an example.² Poly(*m*-phenylenecarbenes) **1**³ combine these two concepts in the construction of higher spin organic molecules.^{1,4} The spin alignment in **1** is, however, one-dimen-

(15) Alt, H. G.; Engelhardt, H. E.; Wrackmeyer, B.; Rogers, R. D. *J. Organomet. Chem.* **1989**, *379*, 289. Boyer, M.; Daran, J. C.; Jeannin, Y. *Inorg. Chim. Acta* **1981**, *47*, 191-195. Boyer, M.; Daran, J. C.; Jeannin, Y. *J. Organomet. Chem.* **1980**, *190*, 177-186. Dawans, F.; Dewailly, J.; Meunier-Piret, J.; Piret, P. *J. Organomet. Chem.* **1974**, *76*, 53-63. Greenhough, T. J.; Legzdins, P.; Martin, D. T.; Trotter, J. *Inorg. Chem.* **1979**, *18*, 3268-3270. Gourdon, A.; Prout, K. *Acta Crystallogr.*, Sect C **1983**, *39*, 865-868. Prout, K.; Gourdon, A.; Couldwell, C.; Meunier, B.; Miao, F. M.; Woolcock, J. *Acta Crystallogr.*, Sect. B **1982**, *38*, 456-462.

(16) Selected NMR data (C_6D_6): δ (multiplicity, *J*, number of hydrogen atoms, type). For **2b**, ^1H : 1.49 (d, 9, 9 H, PMe_3), 2.01 (dd, 6, 15, 2H, $\text{CH}_2\text{H}_5\text{CHH}_5\text{H}_5$), 3.28 (m, 1 H, CH_2CHCH_2), 4.23 (m, 2 H, $\text{CH}_2\text{H}_5\text{CHCH}_2\text{H}_5$). For **2b**, $^{31}\text{P}\{^1\text{H}\}$: -26.8 (s, $J_{\text{WP}} = 428$). For **2b**, ^{13}C : 58.8 (t, 154, CH_2CHCH_2), 19.6 (quartet, 130 PMe_3), 82.5 (d, 154, CH_2CHCH_2). For **3**, ^1H : 1.50 (s, 36 H, PMe_3), 1.58 (quintet, 5, 3 H, $\equiv\text{CCH}_3$). For **3**, $^{31}\text{P}\{^1\text{H}\}$: -20.8 (s, $J_{\text{WP}} = 285$). For **3**, ^{13}C : 253.3 (t, $J_{\text{CP}} = 13$, $\equiv\text{CCH}_3$), 23.2 (quartet, 128, PMe_3), 35.6 (quartet, 124, $\equiv\text{CCH}_3$).

(17) A THF solution (60 mL) of 1.00 g of **1b** and 0.55 mL of vinyltrimethoxysilane was refluxed at 65 °C for 2 days. The volatiles were removed, PMe_3 (0.18 mL) and THF (50 mL) were added, and the yellow solution was stirred at 25 °C overnight. The volatiles were removed, and the residue was recrystallized from 20 mL of pentane to give 0.75 g of bright yellow solids of **3**. Second and third crops were obtained from the filtrate to give a 93% yield. Anal. Calcd for $\text{WClP}_4\text{C}_4\text{H}_9$: C, 30.54; H, 7.15. Found: C, 30.53; H, 7.07.

(18) Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1981**, 1204-1211. Churchill, M. R.; Rheingold, A. L.; Wasserman, H. *J. Inorg. Chem.* **1981**, *20*, 3392-3399.

(19) ^1H NMR (C_6D_6 ; all singlets): δ 2.71, 1.35, -15.18 (PMe_3), 6.38 [$\text{CH}_2=\text{CHSi(OMe)}_3$]; assignments confirmed by ^1H and ^2H NMR of $\text{WCl}_2[\text{P}(\text{CD}_3)_3]_4 + \text{CH}_2=\text{CHSi(OMe)}_3$.

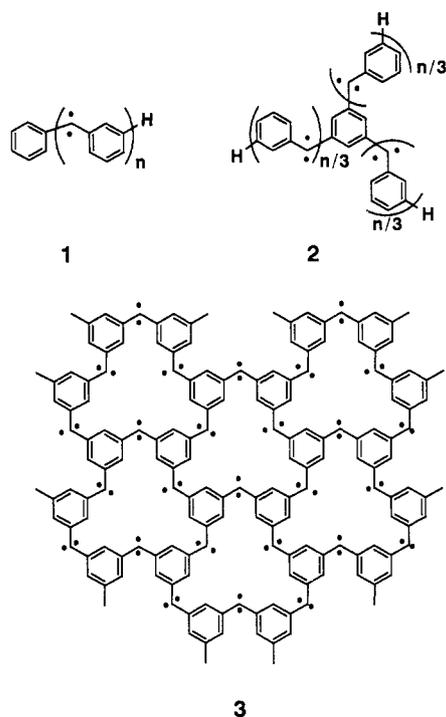
(20) Green, M. *J. Organomet. Chem.* **1984**, *300*, 93-109 and references therein. See also: Allen; S. R.; Beevor, R. G.; Green, M.; Orpen, A. G.; Paddick, K. E.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1987**, 591-604.

(1) Iwamura, H. *Adv. Phys. Org. Chem.* **1990**, *26*, 179.

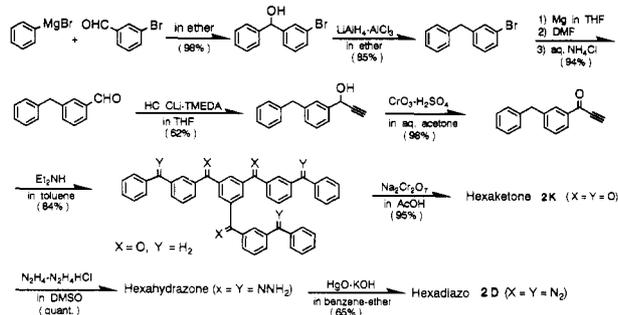
(2) Kothe, G.; Denkel, K.-H.; Summermann, W. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 906.

(3) Teki, Y.; Takui, T.; Itoh, K.; Iwamura, H.; Kobayashi, K. *J. Am. Chem. Soc.* **1983**, *105*, 3722. Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Itoh, K. *J. Am. Chem. Soc.* **1984**, *106*, 6449. Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Itoh, K. *J. Am. Chem. Soc.* **1986**, *108*, 368. Teki, Y.; Takui, T.; Itoh, K.; Iwamura, H.; Kobayashi, K. *J. Am. Chem. Soc.* **1986**, *108*, 2147. Fujita, I.; Teki, Y.; Takui, T.; Kinoshita, Y.; Itoh, K.; Miko, F.; Sawaki, Y.; Izuoka, A.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1990**, *112*, 4074.

Chart I



Scheme I



sional. In order to realize the long-range order at finite temperatures, increasing the dimension of the aligned spins is imperative. This can be achieved either by imposing the proper stacking orientation and therefore magnetic interaction between the molecular chains of **1** as in crystals⁵ or by increasing the dimension of **1** itself. We have now introduced a branched-chain pseudo-two-dimensional structure **2** to achieve the latter possibility,⁶ although the two-dimensional honeycomb-like π -system **3** would be ideal (Chart I).

The synthetic route employed for the precursor **2D** is outlined in Scheme I.⁷ One of the key steps in this reaction sequence is the secondary-amine-catalyzed trimerization of the ethynyl aryl ketones to give 1,3,5-tris(substituted aryl)benzenes,⁸ a method also applicable to the higher analogues of **2**.⁹ **2D** was purified by chromatography (Woelm neutral alumina, activity IV, hex-

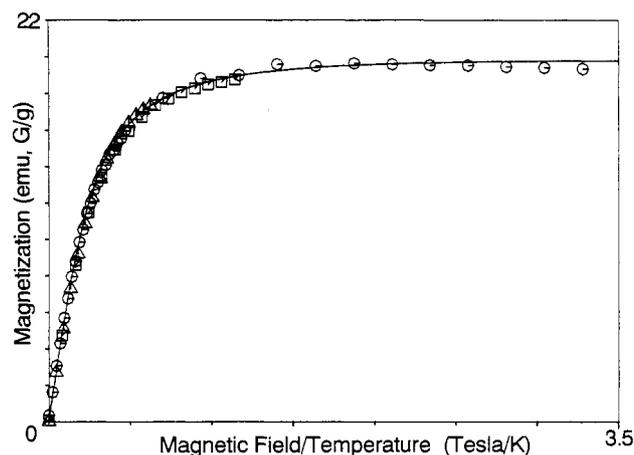


Figure 1. Field dependence of the magnetization of hexacarbene **2** ($n = 6$) at 2.1 (○), 4.8 (□), and 10.0 (Δ) K.

ane/benzene, 0 °C) and confirmed by IR (2060 cm^{-1}), UV-vis (λ_{max} (ϵ) 291 (1.35×10^5), 520 nm (510)), and NMR spectra, including HH- and CH-COSY data.

Photolysis of **2D** in 2-methyltetrahydrofuran (MTHF) glasses at 10 K in an X-band ESR cavity resulted in the appearance of strong, complex ESR signals centered at ca. 3300 G and characteristic of high-spin states; signals attributable to triplet carbenes and quintet dicarbenes were very weak if not undetected.

An Oxford Faraday balance was installed with a quartz light guide through which the UV light ($480 > \lambda > 400$ nm obtained by the combined use of a Kenko B-390 band-pass filter and an OCLI type B cold mirror) was introduced into ca. 0.08 mg of **2D** in 25 μL of MTHF in a quartz sample basket suspended in the superconducting solenoid (≤ 7 T). The magnetic measurements of **2** ($n = 6$) thus produced at ca. 2 K were carried out in situ. The plots of the magnetization vs the applied magnetic field strength at 2.1, 4.8, and 10.0 K were analyzed in terms of the Brillouin function to give $S = 6.0_0$ for **2** ($n = 6$), the highest spin ever reported for a purely organic molecule (Figure 1).

Thus, the branched-chain pseudo-two-dimensional topology of the framework in **2** was demonstrated to be appropriate for controlling its high-spin ground state. It is not clear at this stage if structure **2** has the merit of stabilizing its highest spin ground state relative to lower spin states better than **1**. According to a statistical-mechanical theory on the high-spin chain molecules in a helical conformation,¹⁰ the dipole-dipole interaction between the nearest spins on the neighboring loops can be ferromagnetic and might contribute further in stabilizing the spins aligned within the chain by exchange coupling through bonds. NMR chemical shift data on the series **2D** and **2K** suggest an increase in spatial overlapping of the phenyl rings at higher unit number n .

Since the magnetization data at the three different temperatures were fit to the same Brillouin function, the sample is considered to be free from ferro- or antiferromagnetic intermolecular interactions. When the sample concentration was high (> 6.7 mmol/L), the antiferromagnetic interaction between the molecules was revealed by an ca. 15% lowering of the effective magnetic moment at 1.9 K relative to 20 K. Similar behavior was observed for partially photolyzed neat samples of **2D**. The exchange interaction between the tridecet molecules in fortuitously formed clusters is suggested to be antiferromagnetic. Additional designs of molecular stacking should be made for establishing the order extending among the molecules.

Once a molecular assembly of super-high-spin **1** and **2** acquires magnetocrystalline or shape anisotropy and the relaxation time for reorientation of a principal axis of the magnetization becomes longer than the measuring time, it will have a chance of developing residual magnetization which might be used as magnetic memory at temperatures lower than the blocking temperature.

(4) Mataga, N. *Theor. Chim. Acta* **1968**, *10*, 372. Itoh, K. *Bussei* (in Japanese) **1971**, *12*, 635. Iwamura, H.; Izuoka, A. *Nippon Kagaku Kaishi* (in Japanese) **1987**, 595. Iwamura, H. *J. Phys. (Paris)* **1988**, *49*, C8 813.

(5) Izuoka, A.; Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1985**, *107*, 1786. Sugawara, T.; Murata, S.; Kimura, K.; Iwamura, H.; Sugawara, Y.; Iwasaki, H. *J. Am. Chem. Soc.* **1985**, *107*, 5293. Izuoka, A.; Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1987**, *109*, 2631.

(6) A similar branched-chain polyradical having a triarylmethyl group as the spin carrier has been reported: Rajca, A. *J. Am. Chem. Soc.* **1990**, *112*, 5890.

(7) Fujioka, T. M.S. Dissertation, Nagoya University, Nagoya, Japan, 1985.

(8) Balasubramanian, K.; Selvaraj, S.; Venkataramani, P. S. *Synthesis* **1980**, 29.

(9) Nakamura, N.; Inoue, K.; Iwamura, H. To be published.

(10) Nath, K.; Taylor, P. L. *Mol. Cryst. Liq. Cryst.* **1991**, *205*, 87.