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Received: July 31, 2000 [Z15561]

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Isolation of Dinuclear (μ-Silylene)(silyl)nickel Complexes and Si–Si Bond Formation on a Dinuclear Nickel Framework[**]

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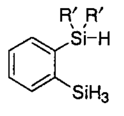
Teruyuki Hayashi, and Masato Tanaka[*]

Palladium and platinum complexes are versatile catalysts for the transformation of organosilicon compounds.[1] However, the utility of nickel complexes has not been as well established.[2] The understanding of the structure and the reactivity of silylnickel species[3] is indispensable for the development of new catalytic methodologies. Although a number of mononuclear silylmetal complexes are known for all Group 10 metals, structurally characterized silylene-bridged dinuclear complexes have been reported only for platinum[4] and palladium.[5, 6] These dinuclear species are considered to play important roles in catalytic processes. For example, silylene-bridged Pt_2Si_2 rings are potential key intermediates in the platinum-catalyzed dehydrocoupling of hydrosilanes.[4b–d] Here we report on the reaction of 1,2-disilylbenzene (**1**) with nickel(0) complexes, which led to the isolation of the dinuclear (μ-silylene)(silyl)nickel(III) complexes $[\{1,2\text{-}C_6H_4(SiH_2)(SiH)\}_2Ni_2(R_2PCH_2CH_2PR_2)_2]$ (R = Me or Et), which contain the first structurally characterized four-membered Ni_2Si_2 rings. The short contact between the SiH_2 and μ-SiH moieties revealed by X-ray crystallography suggests the possibility of Si–Si bond formation, which indeed takes place in a similar reaction of 1-(dimethylsilyl)-2-silylbenzene (**2**) with $[Ni(dmpe)_2]$ (dmpe = 1,2-bis(dimethylphosphanyl)ethane).



1: R′ = H
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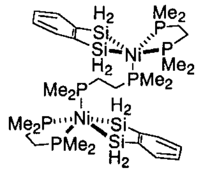

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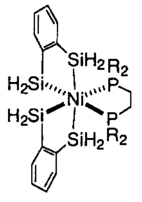
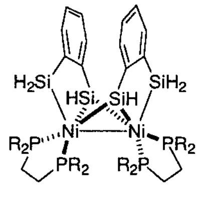
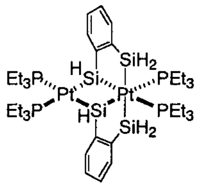


4a: R = Me
4b: R = Et

Previously, we reported that treatment of **1** with $[Ni(dmpe)_2]$ results in the dimeric bis(silyl)nickel(II) complex **3** and the first tetrakis(silyl)nickel(IV) complex **4a**.[7] A similar reaction under somewhat different conditions led to the formation of a new dimeric Ni^{III} complex. While studying **3** by variable-temperature NMR spectroscopy in $[D_8]$toluene, we observed, upon heating the solution to 80 °C, a color change from pale yellow to orange and the emergence of new weak signals in the ^1H and ^{31}P NMR spectra. Further heating at 110 °C for 30 min gave a new complex **5a**, which could be isolated as orange crystals (34%) by crystallization from benzene. The similar complex **5b**, ligated by 1,2-bis(diethylphosphanyl)ethane (depe), was also obtained directly from **1** and $[Ni(PEt_3)_2(depe)]$ (**1**:Ni = 1:1.05); the reaction proceeded even at room temperature and gave **5b** as the main product (49% yield). The ^{29}Si NMR spectrum of the crude mixture showed the presence of the tetrakis(silyl)nickel(IV) complex **4b** as a side product [$\delta = -2.11$ (dd, $^2J(Si,P_{cis}) = 20$, $^2J(Si,P_{trans}) = 101$ Hz), 3.03 (t, $^2J(Si,P) = 16$ Hz)].



5a: R = Me
5b: R = Et



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[**] We are grateful to the Japan Science and Technology Corporation (JST) for financial support through the CREST (Core Research for Evolutional Science and Technology) program and for a postdoctoral fellowship to M.L.N.R.

Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

The structures of **5a** and **5b** were established by X-ray diffraction as dinuclear (μ-silylene)(silyl)nickel complexes (Figure 1).[8] In sharp contrast to the case of platinum, which forms complex **6** with a mixed valent $Pt^{II}Pt^{IV}Si_2$ four-membered ring,[4f] **5a** and **5b** have symmetric structures with $Ni_2^{III}Si_2$ four-membered rings. Most of the complexes containing four-membered Pt_2Si_2 rings so far reported have short diagonal Si···Si distances (2.55–2.88 Å) and long Pt···Pt distances (3.66–4.05 Å).[4b–f] In contrast, **5a** and **5b** have long diagonal Si···Si distances (2.980(1) Å for **5a** and 2.998(1) Å for **5b**) and short Ni···Ni distances (2.6658(7) Å for **5a** and 2.7201(7) Å for **5b**). The Ni···Ni distances are longer than the usual Ni–Ni single bonds but still within the range of known Ni–Ni bond lengths; this suggests a bonding interaction.[9] The Ni–Si distances range from 2.210(1) to 2.304(1) Å for **5a** and from 2.2098(6) to 2.2976(6) Å for **5b**, and 2.304(1) Å is the longest Ni–Si bond so far reported. In contrast to the diagonal Si···Si distances, the Si1···Si4 and Si2···Si3 distances (2.693(2) Å and 2.685(1) Å for **5a** and 2.7049(9) for **5b**) are short and nearly the same as the value for the longest Si–Si single bond.[10] Complexes **5a** and **5b** are envisioned to be formed by the dehydrogenative dimerization of bis(silyl)nickel(II) complexes **7a** and **7b**, respectively. In the reaction of **1** with [Ni(dmpe)$_2$], the sterically less demanding dmpe easily intercepts **7a** to form stable pentacoordinate species such as **3**, while in the reaction of **1** with [Ni(PEt$_3$)$_2$(depe)], the bulkier depe and PEt$_3$ ligands probably prevent the formation of analogous pentacoordinate nickel species and allow **7b** to dimerize even at room temperature.

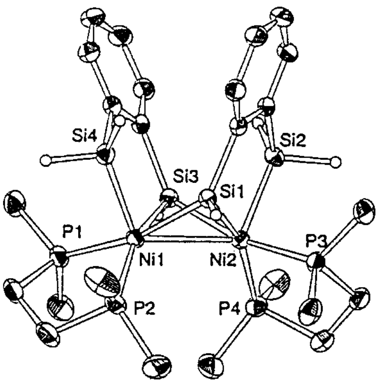
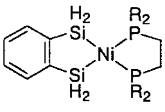


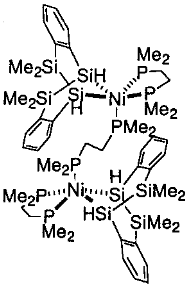
Figure 1. Molecular structure of **5a** (30% probability thermal ellipsoids).



7a: R = Me
7b: R = Et

Solid-state CP/MAS NMR spectra of **5b** displayed ^{31}P signals at $\delta = 48.6$ and 52.0, reasonable for the structure, and ^{29}Si signals at $\delta = -48.5$ and 79.9, which can be assigned to SiH$_2$ and μ-SiH, respectively. A solution of **5b** in [D$_8$]THF at $-40\,^{\circ}C$ also displayed signals similar to those found in the solid-state NMR spectrum; a pair of triplets at $\delta = 47.4$ and 50.1 in the $^{31}P\{^1H\}$ NMR spectrum and two signals at $\delta = -52.0$ (ddd, $J = 6$, 13, 55 Hz, *Si*H$_2$) and 92.2 (quasi dt, $J = 6$, 67 Hz, *Si*H) in the $^{29}Si\{^1H\}$ spectrum.[11] However, these signals became broad and/or weak at higher temperatures, and a number of other signals were observed.[12] These results suggest that **5b** is in equilibrium between several species in solution, although their structures are unknown at the moment.

The short Si1···Si4 and Si2···Si3 distances in **5a** and **5b** suggest that and Si–Si bond-forming reaction can possibly take place in these complexes to form an eight-membered cyclic dimer of **1**. Attempted thermal reactions of **5a** or **5b** did not provide any clear evidence for Si–Si bond formation. However, Si–Si bond formation did take place upon treatment of **2**[13] with [Ni(dmpe)$_2$] to generate the dimeric complex **8**. Heating a mixture of **2** and [Ni(dmpe)$_2$] (**2**:[Ni(dmpe)$_2$] = 2:1) in benzene at 55–80 °C for 4 d resulted in the spontaneous separation of yellow crystals of **8** (21% yield) from the solution. ^1H, ^{31}P, and ^{29}Si NMR spectroscopy on the solution part of the reaction mixture revealed that a large amount of [Ni(dmpe)$_2$] still remained, while **2** was completely consumed to give a mixture of silicon-containing compounds. Crystalline **8** is virtually insoluble in benzene. The structure determined by X-ray diffraction unequivocally verifies that the silyl ligand originated from Si–Si bond formation through dehydrocoupling (Figure 2).[8]



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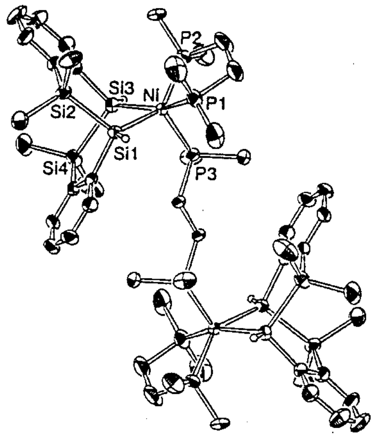
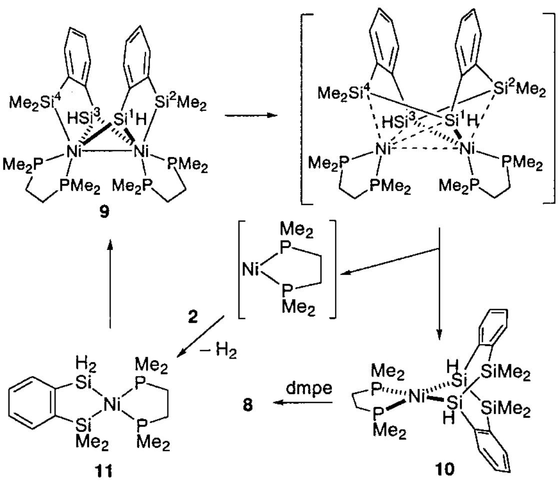


Figure 2. Molecular structure of **8** (30% probability thermal ellipsoids). Selected bond lengths [Å] and angles [°]: Ni1–Si1 2.263(2), Ni1–Si3 2.257(2), Ni1–P1 2.160(2), Ni1–P2 2.182(2), Ni1–P3 2.236(2), Si1–Si2 2.357(2), Si3–Si4 2.361(2); Si1-Ni1-Si3 76.83(6), P1-Ni1-P2 86.81(8), P1-Ni1-Si1 90.24(7), P2-Ni1-Si3 90.89(7), P1-Ni1-P3 103.53(8), Ni1-Si1-Si2 116.48(8), Ni1-Si1-C1 124.1(2), Si2-Si1-C1 102.3(2), Ni1-Si3-Si4 119.82(8), Ni1-Si3-C2 121.5(2), Si4-Si3-C2 101.1(2).

Although further studies are necessary to clarify the reaction mechanism, an assumption of the intermediacy of a dinuclear species **9** similar to **5** appears to rationalize the formation of **8** (Scheme 1). Formation of Si^1–Si^4 and Si^2–Si^3 bonds on the dimeric nickel framework in **9** and the release of a [Ni(dmpe)] fragment generate a monomeric product **10**, which readily dimerizes by coordination of dmpe to form **8**. The release of Ni(dmpe) fragment is likely to be assisted by the simultaneous attack of **2** to regenerate **11**. The successful Si–Si bond formation observed for **2**, but not for **1**, is presumably



Scheme 1. A possible mechanism for the formation of **8**.

associated with the low stability of organosilicon to transition metal bonds relative to that of hydridosilicon to transition metal bonds.[14] Further mechanistic studies and catalytic dimerization of **1** and **2**[15] are now underway.

Experimental Section

5a: A solution of **3** (160 mg, 0.19 mmol) in toluene (8 mL) was heated at 110 °C for 30 min under N_2. During heating, the color of the mixture turned from yellow to red. After removal of volatile substances under vacuum (10^{-4} Torr), the residue was dissolved in hot benzene (2 mL), from which remaining **3** crystallized (10 mg). After collection of the crystals by filtration, the filtrate was concentrated and the residue was dissolved in hot benzene (1 mL). A few seed crystals of **5a** were added, and the hot benzene solution was slowly cooled to room temperature. During the cooling process, orange prismatic crystals of **5a** grew initially, and then a small amount of crystalline **3** precipitated. After removal of the liquid portion with a syringe, washing the solid with benzene (1 mL) and diethyl ether (2 × 2 mL), and drying under vacuum, the solids were manually separated under a microscope to give pure **5a** (50 mg, 34 % yield) and a mixture of **3** and **5a** (18 mg). **5a**: M.p. 134–152 °C (decomp); IR (KBr): $\tilde{\nu} = 3088$, 3033, 2962, 2896, 2799, 2022, 1989, 1415, 1293, 1278, 1123, 1097, 931, 891, 819, 745, 701, 673, 632, 478, 459 cm^{-1}. X-ray diffraction showed the presence of one molecule of benzene per molecule of **5a** in the crystal; elemental analysis calcd for $C_{24}H_{46}Ni_2P_4Si_4 \cdot C_6H_6$: C 47.02, H 6.84; found: C 46.78, H 6.85.

5b: $[Ni(PEt_3)_4]$ (505 mg, 0.95 mmol) was dissolved in toluene (3 mL) and depe (222 µL, 0.95 mmol) added at room temperature. After 20 min of stirring, volatile substances were removed under vacuum to give $[Ni(PEt_3)_2(depe)]$ (^{31}P NMR ([D$_8$]toluene, 202 MHz): $\delta = 16.25$ (t, $J = 28$ Hz), 30.98 (t, $J = 28$ Hz)). **1** (124 mg, 0.90 mmol) was added to a solution of crude $[Ni(PEt_3)_2(depe)]$ in hexane (4 mL) at 0 °C. During the addition of **1**, the color of the mixture changed from light purple to light brown with evolution of a small amount of H_2. After the addition of **1**, the mixture was stirred at 30 °C for 44 h and then at 50 °C for 9 h to give a deep brown solution. Removal of volatile substances under vacuum left a brown oil, from which **5b** crystallized. Washing the solid with diethyl ether (1 × 15 mL, 2 × 3 mL) followed by drying under vacuum afforded analytically pure **5b** as orange crystals (120 mg). Another crop (55 mg) of **5b** was obtained by evaporation of the diethyl ether washings and crystallization of the residue from diethyl ether/hexane. Total yield based on **1** was 49 %. M.p. 150–157 °C (decomp); ^{31}P CP/MAS NMR (121.5 MHz): $\delta = 48.6$, 52.0; ^{29}Si CP/MAS NMR (59.6 MHz): $\delta = -48.5$, 79.8; IR (KBr): $\tilde{\nu} = 3034$, 2961, 2932, 2902, 2028, 1456, 1416, 1376, 1240, 1097, 1026, 950, 867, 816, 762, 677, 622 cm^{-1}; elemental analysis calcd for $C_{32}H_{62}Ni_2P_4Si_4$: C 48.02, H 7.81; found: C 48.33, H 7.75.

8: A solution of **2** (0.332 g, 2 mmol) and $[Ni(dmpe)_2]$ (0.358 g, 1 mmol) in benzene (4 mL) was heated at 55 °C for 24 h and at 80 °C for 3 d. Yellow crystals precipitated and were collected by filtration, washed with benzene (3 × 1 mL), and dried under vacuum to give **8** (125 mg, 20.5 %). M.p. 178–183 °C (decomp); IR (KBr): $\tilde{\nu} = 3033$, 2963, 2903, 1958, 1637, 1420, 1295, 1248, 1139, 933, 892, 830, 804, 746, 717, 657, 635, 440 cm^{-1}; elemental analysis calcd for $C_{50}H_{92}Ni_2P_6Si_8$: C 49.18, H 7.59; found: C 48.95, H 7.77.

Received: July 19, 2000 [Z15488]

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[8] Crystal structure analysis of $\mathbf{5a} \cdot C_6H_6$: $C_{24}H_{46}Ni_2P_4Si_4 \cdot C_6H_6$, $M_r = 766.38$, monoclinic, space group $P2_1/c$, $a = 11.412(3)$, $b = 16.510(3)$, $c = 20.489(4)$ Å, $\beta = 91.03(2)°$, $V = 3859(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.32$ g cm^{-3}, $R = 0.038$, $R_w = 0.047$. Crystal structure analysis of **5b**: $C_{32}H_{62}Ni_2P_4Si_4$, $M_r = 800.48$, monoclinic, space group $C2/c$, $a = 20.222(3)$, $b = 10.974(4)$, $c = 19.785(4)$ Å, $\beta = 115.45(1)°$, $V = 3964(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.34$ g cm^{-3}, $R = 0.029$, $R_w = 0.039$. Crystal structure analysis of **8**: $C_{50}H_{92}Ni_2P_6Si_8$, $M_r = 1221.20$, triclinic, space group $P\bar{1}$, $a = 9.488(3)$, $b = 11.327(3)$, $c = 16.766(3)$ Å, $\alpha = 88.92(2)$, $\beta = 81.06(2)$, $\gamma = 68.25(2)°$, $V = 1651.7(9)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.23$ g cm^{-3}, $R = 0.046$, $R_w = 0.054$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-138595 (**5a**), -138596 (**5b**) and -138597 (**8**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[11] See the Supporting Information for the variable-temperature ^1H, ^{31}P, and ^{29}Si NMR spectra of **5b**.

[12] ^1H and ^{31}P NMR spectra of **5a** in C_6D_6 were also complex at room temperature.

[13] Preparation of compound **2** was based on Tamao's method: K. Tamao, H. Yao, Y. Tsutsumi, H. Abe, T. Hayashi, Y. Ito, *Tetrahedron Lett.* **1990**, *31*, 2925–2928.

[14] It is known that M–SiH_3 bonds are shorter than M–$SiMe_3$ bonds (M = $(CO)_5Mn$ or $(CO)_5Re$): L. Manojlovic-Muir, K. W. Muir, J. A. Ibers, *Inorg. Chem.* **1970**, *9*, 447–452; D. W. H. Rankin, A. Robertson, *J. Organomet. Chem.* **1975**, *85*, 225–235; D. W. H. Rankin, A. Robertson, *J. Organomet. Chem.* **1976**, *105*, 331–340; M. C. Couldwell, J. Simpson, W. T. Robinson, *J. Organomet. Chem.* **1976**, *107*, 323–339.

[15] A preliminary study showed that nickel complexes catalyze the dehydrogenative dimerization of **2**.

A Mass Spectrometric Labeling Strategy for High-Throughput Reaction Evaluation and Optimization: Exploring C–H Activation**

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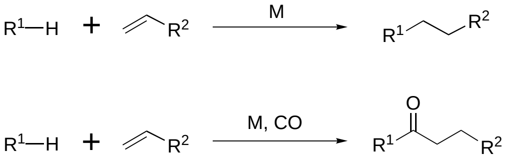
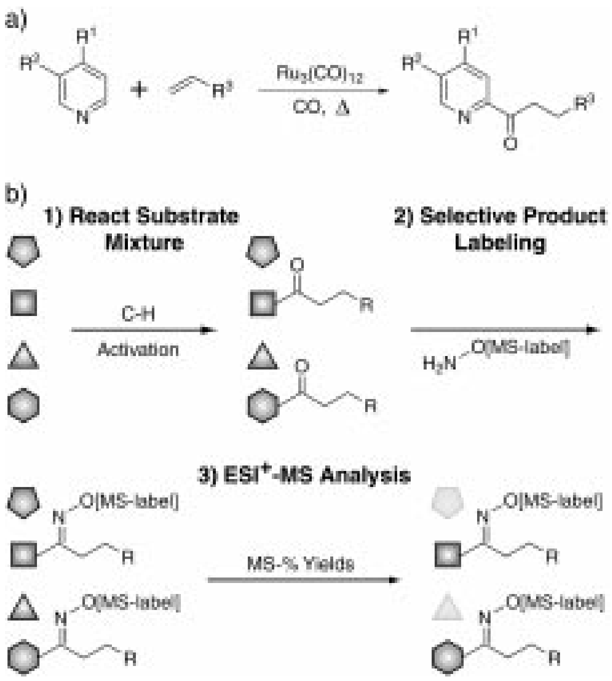
Chemical transformations that combine C–H activation[1] and olefin insertion[2] present attractive opportunities for the rapid assembly of complex structures from unexploited classes of building blocks through carbon–carbon bond formation (Scheme 1).[3] Controlling the site of activation is one of the key challenges of this chemistry. Moore et al. first demonstrated that $[Ru_3(CO)_{12}]$ catalytically activates the *ortho* positions of pyridine toward acylation with CO and olefins (Scheme 2a).[4] They proposed that the aromatic nitrogen atom coordinates the ruthenium catalyst, and directs activation specifically to the *ortho* sp^2 C–H bonds. More recently, Murai and co-workers have extended this reaction to several different aromatic heterocycles and olefin substrates.[5] A better understanding of the rules for functional group compatibility and substrate generality demands that a large number of heterocyclic classes be investigated, yet current approaches cannot efficiently provide this information because of the large number of compounds that require testing.



Scheme 1. The generality of C–H activation allows, in principle, the combination of aromatic heterocycles with alkenes to rapidly assemble diverse structures using unexploited classes of building blocks.



Scheme 2. a) A mixture of diverse pyridines is C–H activated to provide a mixture of products each bearing a ketone group. b) A schematic representation summarizing the high-throughput strategy for the optimization of the reaction and discovery of new products.

Combinatorial methods have made a major impact on new catalyst discovery, but the development of rapid and efficient analyses remains a challenge.[7] Several recent high-throughput methods monitor reactions through the catalyst turnover and/or reaction conversion by IR thermography,[8] the formation of UV-active products,[9] or the production of acid[10] or carbon dioxide.[11] Although, these techniques are powerful, they cannot distinguish between products, by-products, and decomposition. Alternatively, serial methods (TLC, GC, and HPLC) have been employed to identify products and/or quantify yields,[12] but these methods severely limit the number of reactions that can be analyzed in a short period of time. In addition, fluorescent-labeled substrates have been used in the rapid monitoring of reactions.[13] Unfortunately, each substrate under investigation must be individually synthesized as a specifically labeled compound prior to reaction and analysis; thus experimental effort increases linearly with the number of different substrates to be evaluated. We report here the first optimization strategy that enables efficient quantitation of product yields at multiple time points for large numbers of substrates, thereby establishing structure–reactivity relationships and reaction compatibility of functional groups (Scheme 2b).

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[**] This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, U.S. Department of Energy, under contract No. DE-AC03-76SF00098. We are grateful to the National Institutes of Health for support (GM-50353) and for a Postdoctoral Fellowship to J.W.S.

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