

In summary, we report the second fully verified example of a “schizophrenic” diblock copolymer which can self-assemble to form either micelles or reverse micelles in aqueous solution. This new class of diblock copolymer surfactant is particularly easy to synthesize and its two micellar phase transitions are dictated solely by the solution temperature and the solution pH value. In view of this, we expect that the rich phase behavior of this new diblock copolymer will be of particular interest to theoreticians for testing the validity of the various theories of micellization.^[10]

Experimental Section

Synthesis of the PPO–DEA diblock copolymer: The diblock copolymer was synthesized by ATRP using a macro-initiator approach. A monohydroxy-capped poly(propylene oxide) (PPO–OH; mean degree of polymerization, $D_p = 33$ by ^1H NMR; $M_w/M_n = 1.06$ by gas-phase chromatography (GPC) with THF eluent) was kindly donated by Laporte Performance Chemicals (Hythe, UK). This PPO–OH was converted into an ATRP macro-initiator, PPO–Br, by allowing the terminal hydroxy group to react with 2-bromoisobutryl bromide in the presence of triethylamine in toluene. ^1H NMR spectroscopy confirmed that the degree of chain-end functionalization was 100%. The PPO macro-initiator (1.5 g, 0.75 mmol, 1 equiv), DEA (5.55 g, 30 mmol, 40 equiv), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 172 mg, 0.75 mmol, 1 equiv) and methanol (7 mL) were added to the reaction flask; the solution was degassed by two freeze–thaw cycles. After the solution temperature was increased to 55 °C, CuCl (74 mg, 0.75 mmol, 1 equiv) was introduced as a solid into the reaction flask to start polymerization at this temperature. The reaction solution became dark green and more viscous as polymerization proceeded. After about 3 h the conversion was close to 100% as judged by ^1H NMR spectroscopy; the reaction mixture was diluted with methanol and passed through a silica column to remove residual ATRP catalyst. After solvent evaporation, the products were extracted with ice-cold water (0 °C, pH 9) several times to remove any traces of unchanged PPO macro-initiator and then dried under vacuum at room temperature. The mean D_p of the DEA block was calculated to be 42 using ^1H NMR spectroscopy. The GPC studies (THF eluent, PMMA standards, refractive index detector) of the diblock copolymer indicated a relatively narrow polydispersity (M_w/M_n) of 1.20.

Dynamic light scattering (DLS) studies were conducted with a Brookhaven model BI-200SM and 9000AT correlator using a solid-state laser (50 mW, $\lambda = 532$ nm) at a fixed scattering angle (θ) of 15° with both cumulants and CONTIN software. The dn/dc of the PPO₃₃–DEA₄₂ diblock copolymer was determined to be 0.128 in aqueous solution at pH 6.5 and 20 °C, using an Optokem differential refractometer operating at $\lambda = 632.8$ nm. Static light scattering studies (SLS) were conducted at 5 °C (DEA cores) as well as 40 °C and 70 °C (PPO cores) using the same instrument at scattering angles ranging from 15° to 135°. The M_w and R_g data were obtained using standard Zimm plot analyses, assuming that the effects of temperature and pH on the dn/dc were negligible. Variable-temperature ^1H NMR spectra were recorded on 1.0 w/v % copolymer solutions in D₂O using a Bruker Avance DPX 300-MHz spectrometer. Transmission electron microscopy studies were conducted using a Hitachi 7100 instrument operating at 75 kV and employing OsO₄ as a staining agent.

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σ -Bond Metathesis of Alkanes on a Silica-Supported Tantalum(v) Alkyl Alkylidene Complex: First Evidence for Alkane Cross-Metathesis**

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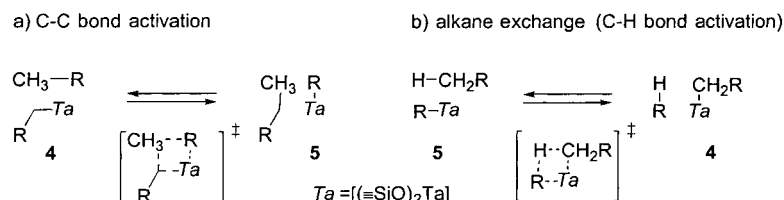
Here we report on direct evidence for the stoichiometric cross-metathesis of several alkanes (ethane, propane, and butanes) with the hydrocarbyl ligands of the surface complexes $[(\equiv\text{Si}-\text{O})_x\text{Ta}(\text{=CHCMe}_3)(\text{CH}_2\text{CMe}_3)_{(3-x)}]$ (**1**: $x = 1$, **2**: $x = 2$), and the catalytic activity of **1+2** in alkane metathesis.^[1]

We have shown that the silica-supported tantalum hydride $[(\equiv\text{SiO})_2\text{TaH}]$ (**3**) catalyzes the metathesis of alkanes (Scheme 1).^[2, 3] The key steps proposed for the reaction mechanism are: a) activation of the C–C bond of an incoming alkane on the surface Ta alkyl complex **4** leading to the evolution of an alkane and the formation of a new surface complex **5**; and b) regeneration of **4** in an alkyl-exchange reaction (C–H bond activation).^[4]

The related structures of **1+2** and **4/5**, the two key intermediates of the proposed mechanism for alkane metathesis, is noteworthy. This analogy led us to investigate the relative reactivity towards alkanes of **1+2**, a formal d⁰ 10-e metal center, and **3**, (the precursor of **4/5**) a formal d² 8-e metal center.

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Scheme 1. Alkane metathesis by a σ -bond metathesis mechanism.

After reaction of ethane with **1+2** (see Experimental Section), analysis of the gas phase showed the formation of methane, propane, and butanes, that is, the usual metathesis products of ethane. This demonstrates that Ta^V complexes can also act as precursors to the active species in alkane metathesis (Figure 1 and Table 1).^[5] In addition, other products that have so far not been observed in the metathesis of ethane in the presence of **3** were also obtained, namely, neopentane (NpH) and 2,2-dimethylbutane (NpMe), which are presumably derived from the neopentyl groups of **1+2** (Table 1, entry 1). The corresponding reaction of ¹³C-monolabeled ethane with **1+2** gave monolabeled NpMe^[6] and unlabeled neopentane, and thus provided clear evidence for a cross-metathesis process. Since **1+2** contains both neopentyl and neopentylidene ligands, two pathways can be considered (Scheme 2): a) a one-step mechanism involving activation of

the C-C bond by a Ta-C bond (σ -bond metathesis); b) a two-step process involving the Ta=C bond, that is, addition of a C-C bond to a Ta=C bond^[7] followed by an α -H abstraction,^[8] which is overall an apparent σ -bond metathesis process. Both processes can explain the formation of the observed products.

The reaction of **1+2** with ethane also gives neopentane, the formation of which does not

Table 1. Stoichiometric cross-metathesis of alkanes with silica-supported tantalum complexes **1+2**. Selectivity for neopentyl-containing compounds and catalytic activity in alkane metathesis.

Entry	Alkane	NpH	NpMe	NpEt	NpPr	Np/Pr	Total NpR in gas phase ^[a] [%]	TON ^[b]
1	ethane	76	24	< 1 ^[c]	— ^[d]	— ^[d]	37	25 (46)
2	propane	70	26	4	< 1 ^[c]	— ^[d]	48	58 (60)
3	butane	70	15	11	3	— ^[d]	48	55 (55)
4	isobutane	71	29	— ^[d]	— ^[d]	< 1 ^[c]	51	33 (40)

[a] Yield with respect to the amount of neopentyl and neopentylidene groups on the surface before reaction. [b] TON is defined as the number of cycles. Data in parentheses are for **3**. [c] These compounds were detected in amounts of about 0.1 % after concentration of the gas phase. [d] Not detected (< 0.1 % if any).

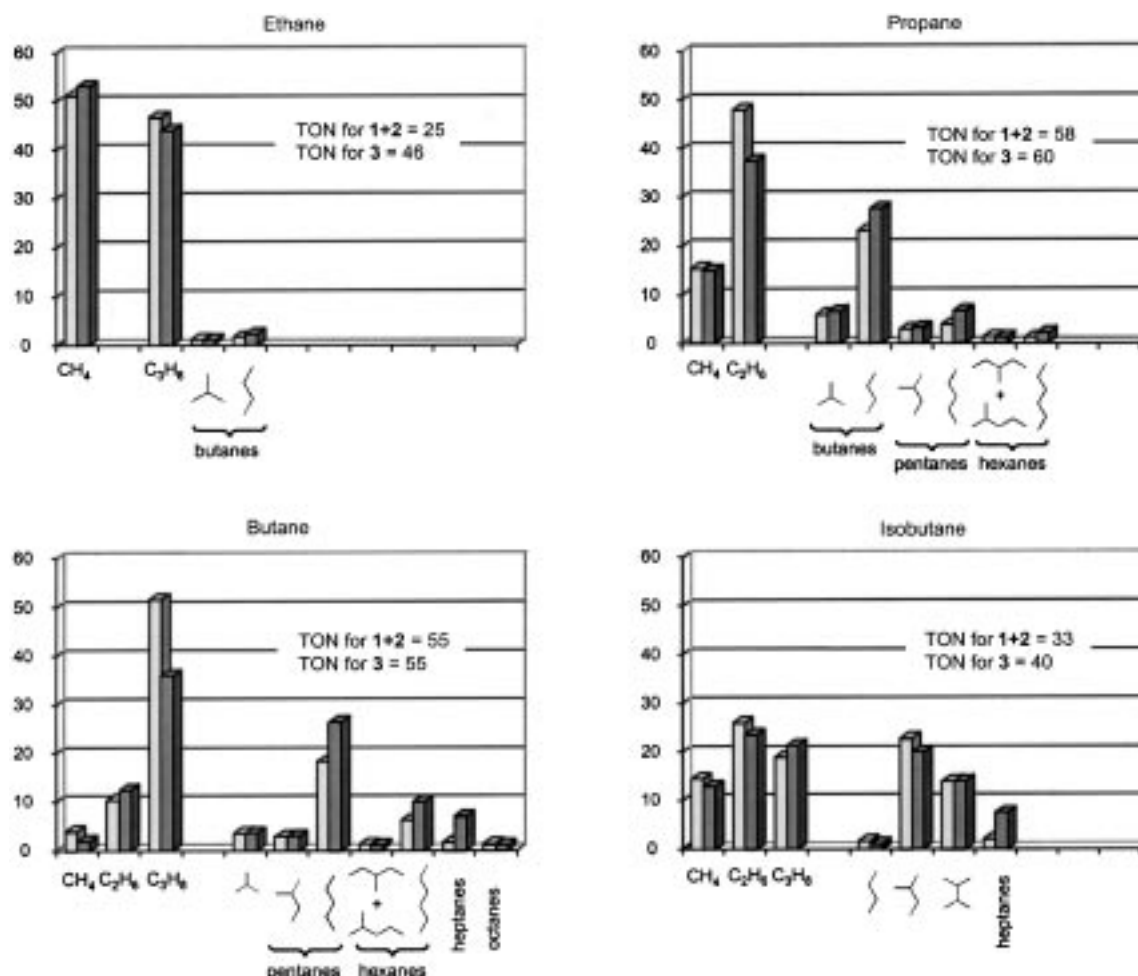


Figure 1. Percentage product distributions and turnover numbers (TONs) for the catalytic metathesis of various alkanes on **1+2** (light gray) and **3** (dark gray). Products of cross-metathesis in the case of **1+2** have been excluded for the sake of clarity; see Table 1 for details.

involve a C–C bond cleavage, but rather the activation of a C–H bond (Scheme 2). Since neopentane is the major product, C–H activation is kinetically favored over C–C activation. A C–H bond is in fact about three times easier to

In conclusion, the reaction of C–C σ bonds with a surface Ta complex containing both neopentyl and neopentylidene groups yields cross-metathesis products that were clearly identified by the *t*Bu “markers” and an active catalyst for σ -bond metathesis of alkanes. The surface complex **1+2** (Ta^{V} d^0 system) gives turnovers and selectivities comparable to those obtained with **3** (Ta^{III} d^2 system). This suggests that both systems probably lead to the same active catalyst. Since σ -bond metathesis has been mainly found for d^0 transition metals, that is, metals in their highest oxidation state, it suggests that the active species could be a Ta^{V} compound in both cases.^[10] However, we do not yet know which of the two oxidation states, if not both, is responsible for this unusual reactivity towards alkanes. Further studies are currently underway to clarify this matter.

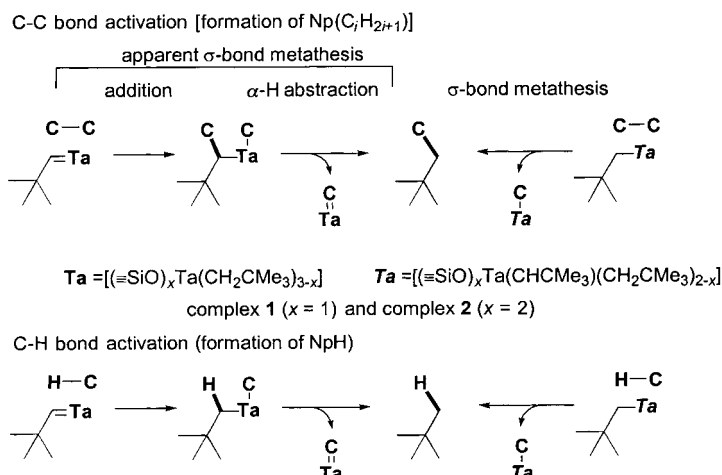
Experimental Section

The reactions were carried out with the same batch of catalyst in the strict absence of oxygen and water. **1+2** (50 mg, 0.013 mmol, 4.8% Ta) was introduced into a Pyrex batch reactor (300 mL) followed by an alkane (500–600 equiv), dried and deoxygenated over freshly regenerated molecular sieves (3 Å) and deoxo. The reaction mixture was then heated at 150 °C. Small-volume aliquots were removed, brought to atmospheric pressure, and analyzed by gas chromatography (HP 5890 apparatus, $\text{Al}_2\text{O}_3/\text{KCl}$ on fused silica column, 50 m $\times$ 0.32 mm) and GC-MS.

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Scheme 2. Carbon–carbon bond activation on **1+2**.

activate than a C–C bond of ethane under these conditions.^[9] Since the neopentyl and neopentylidene ligands were transformed by ethane into NpH and NpMe , the surface Ta complex now bears methyl (or methylidene) and ethyl (ethylidene) ligands;^[5] it is therefore similar to **4/5** or **1+2** and results in the subsequent catalytic metathesis of ethane (Table 1).

The reaction of other alkanes with **1+2** gave similar results, that is, catalytic alkane metathesis and formation of NpH and other neopentyl-containing products NpR (Table 1 and Figure 1). Propane gave NpMe and 2,2-dimethylpentane (NpEt , entry 2). Butane afforded NpMe , NpEt , and 2,2-dimethylhexane (NpPr), in contrast to isobutane, for which NpMe and only traces of 2,2,4-trimethylpentane ($\text{Np}i\text{Pr}$) were detected (entries 3 and 4). This clearly shows that each alkane gives specific products that depend on both its structure and the structure of the surface Ta alkyl complex (in the stoichiometric case: neopentyl). Moreover, the cross-metathesis leading to the transfer of one carbon atom from the incoming alkane to the surface alkyl fragment (NpMe) is favored over that of larger carbon fragments, as previously suggested by the observed selectivities for higher hydrocarbons in the catalytic reaction.^[2] The absence of reverse C–H activation products such as NpR for the reaction of RH on **1+2** is noteworthy. Hence, an order of reactivity can be proposed (Figure 2).

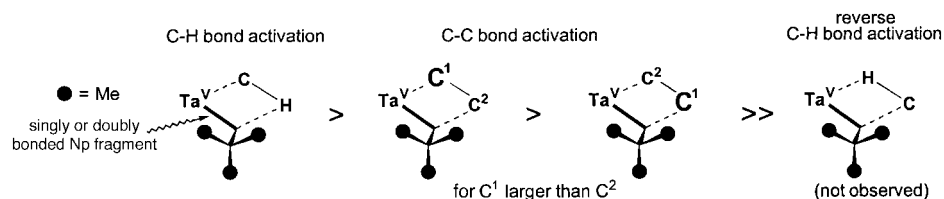


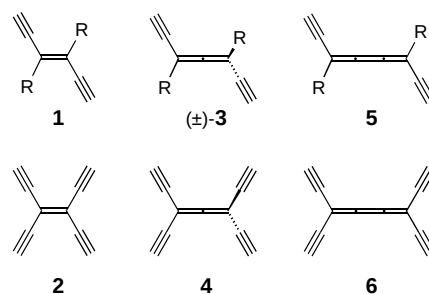
Figure 2. Order of reactivity in the reaction of alkanes with surface Ta hydrocarbyl complexes. C^1 and C^2 represent different alkyl groups.

- ment with the presence of methyldiene tantalum species. Determination of the exact structure of these surface complexes is underway.
- [6] The reaction of ^{13}C -monolabeled ethane on **1+2** gave the partially scrambled metathesis products of ethane along with unlabeled NpH and partially labeled NpMe (35% ^{13}C incorporated). This shows that at least 70% of this compound arises from cross-metathesis. The excess of unlabeled compound probably arises from rearrangement of **1+2**. Heating **1+2** under Ar at 150 °C for 15 h gives 0.25 equiv of NpH and 0.01 equiv of NpMe.
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1,3-Diethynylallenes: New Modules for Three-Dimensional Acetylenic Scaffolding**

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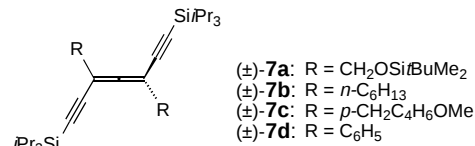
Oxidative coupling^[1] of multiply ethynylated building blocks has facilitated the assembly of well-defined molecular architecture that displays unusual electronic and optical properties.^[2] In particular, derivatives of (*E*)-1,2-diethynylethene (**1**, (*E*)-DEE, (*E*)-hex-3-ene-1,5-diyne) and tetraethynylethene (**2**, TEE, 3,4-diethynylhex-3-ene-1,5-diyne) have provided a unique class of π -conjugated precursors for the modular construction of one- and two-dimensional carbon-rich scaffolds (Scheme 1).^[3] They have provided access to monodisperse, linearly π -conjugated polytriacyetylene (PTA) oligomers that extend up to 18 nm in length,^[4] to perethynylated expanded radialenes that feature all-carbon cores (C_{30} to C_{60}), which undergo facile electrochemical reduction and



Scheme 1. Diethynyl- and tetraethynyl[n]cumulenes ($n = 1–3$) as carbon-rich modules for acetylenic scaffolding.

display low-energy electronic absorption bands with remarkably high molar extinction coefficients,^[5] and to photochromic molecules for photochemical switching without competing thermal isomerization pathways.^[6] Expansion of the central olefinic fragment in DEEs and TEEs leads to the di- and tetraethynylated allenes ($\pm$)-**3** and **4**, and butatrienes **5** and **6** (Scheme 1). Whereas silylated derivatives of peralkynylated butatriene **6** have been reported,^[7] 1,3-diethynyl- and tetraethynylallenes have remained elusive, despite intensive efforts aimed at their preparation.^[8] The major problems encountered in previous attempts to synthesize these novel building blocks for three-dimensional acetylenic scaffolding were their high tendency for rearrangement and facile [2+2] cycloaddition, which occurred readily even at room temperature or below.^[9]

Herein we describe the synthesis of the first 1,3-diethynylallenes ($\pm$)-**7a–d**. As a result of the inherent 90° twist of the



allene moiety, alkyne deprotection and oxidative acetylenic coupling of these compounds in enantiomerically pure form promises access to a fascinating new class of three-dimensional helical oligomers and polymers.^[10] Optically active helical polymers^[11] are attracting increasing interest as materials that exhibit circularly polarized electroluminescence^[12] or as dopants for cholesteric liquid-crystalline phases.^[13]

Palladium-catalyzed cross-coupling reactions have proven valuable in the preparation of alkynylallenes from substrates that bear propargylic leaving groups such as halides, epoxides, acetates, and carbonates.^[14] Given an appropriate regiochemical bias, application of these conditions to bispropargylic precursors should yield the corresponding 1,3-diethynylallenes. Thus, target compound ($\pm$)-**7a** was obtained from bispropargylic epoxide precursor ($\pm$)-**8**^[15] (prepared in five steps from but-2-yne-1,4-diol, Scheme 2) and $i\text{Pr}_3\text{SiCH}\equiv\text{CH}$ under standard palladium-catalyzed cross-coupling conditions ($[\text{Pd}(\text{PPh}_3)_4]$, CuI , HNiPr_2 , CH_2Cl_2). In situ protection of the primary alcohol that results from epoxide ring opening as the Si^tBuMe_2 ether gave 1,3-diethynylallene ($\pm$)-**7a** (Table 1)

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