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Quest for Even Higher Stabilized Foiled Carbenes†

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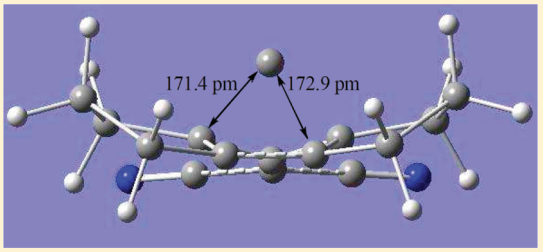
Supporting Information

ABSTRACT: Foiled carbene structures comprising strong stabilizing interactions between the divalent carbon and the intramolecular double bond have been located by DFT calculations. These tetracyclic species bearing fused five-membered rings impeding intramolecular rearrangements are theoretically predicted to lie in a deep potential energy well. A suitable dibromocyclopropane precursor for this type of foiled carbene has been prepared in 12 steps. Its treatment with methyllithium led to the isolation of a product of a formal carbene dimerization, a bicyclopropylidene.



INTRODUCTION

According to the definition of Gleiter and Hoffmann, foiled carbenes[1] are special carbenes in which an artificial energy minimum is created as a result of initial stabilization due to the inhibition of a typical facile carbene reaction, that is, an intramolecular addition to its double bond. This concept is attractive because it provides an opportunity to generate stabilized carbenes with a reduced reactivity. As a consequence, one may expect that this type of carbenes will react more selectively than the usual ones. Foiled carbenes are appealing also for another reason: the interaction between the divalent carbon atom and the double bond causes impressive changes in the geometry of the molecule, leading to highly unusual structures. Experimentally, norbornenylidene and derivatives thereof belong to the best studied examples of foiled carbenes.[2] During the last years, their reduced electrophilicity and their lower reactivity toward intermolecular reactions have been revealed. This results in a high reluctance toward addition to electron-rich alkenes[3] and the absence of insertion into nonacidic CH-bonds.[4] Still, this has opened up the possibility to perform clean reactions, such as cyclopropanation of electron-deficient alkenes[5] and formal insertion into the N−H bond of diethylamine[6] and into protic bonds.[4,7] Thus, the classification of norbornenylidene as a foiled carbene and, therefore, as a stabilized nucleophilic carbene has been confirmed.[8] However, all of these studies have shown that the double bond exerts a strong influence on the stereochemical outcome of the reaction and the geometry of the carbene.[2−7]

Since then, we have started a search for carbenes in which interactions with the double bond are even stronger.[9] This should result in a still greater stabilization of the carbenic center and a more pronounced distortion of the molecule. A logical candidate is bicyclo[2.1.1]hex-2-en-5-ylidene (**1**), a transient species also called "homopyramidane." Its properties have been investigated previously at the theoretical level.[9]

RESULTS AND DISCUSSION

B3LYP calculations have predicted that foiled carbene **1** lies indeed in a deep potential well if one considers only the most classical reactions, that is, vinyl shift, cyclobutylidene-methylenecyclopropane rearrangement, C−H insertion to a bicyclobutane, and 1,2-hydride shift to a strained alkene.[9] However, one pathway to bicyclo[3.1.0]hex-2-en-6-ylidene (**2**) still remains open and allows very easily a rearrangement with a calculated transition state of 3.4 kcal/mol. This pathway represents the first example of a retro-Skattebøl rearrangement, that is, the back reaction of the vinylcyclopylidene-cyclopentenylidene rearrangement.[10] Cyclopropylidene **2** easily undergoes ring expansion to the energetically favored allene 1,2,4-cyclohexatriene (**3**) (Figure 1).

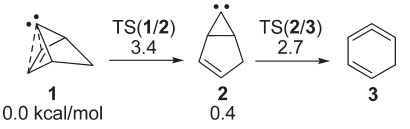


Figure 1. Rearrangements of homopyramidane **1** (B3LYP/6-31G(d): E + ZPVE).[9]

Experimentally, starting from **2**, it has already been shown that this cyclopropylidene-allene rearrangement to **3** is the main pathway in aprotic solvents.[11] In water/dioxane, probably through a cationic pathway, the Skattebøl rearrangement to **1** occurs, leading to *exo*-bicyclo[2.1.1]hex-2-en-5-ol.[12]

To inhibit pathway **2** → **3**, it was planned to attach two cyclopentane rings to the central five-membered ring. Indeed,

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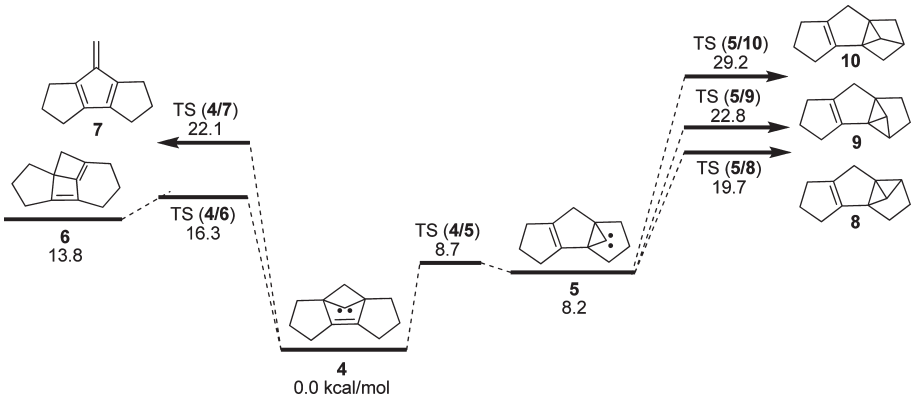
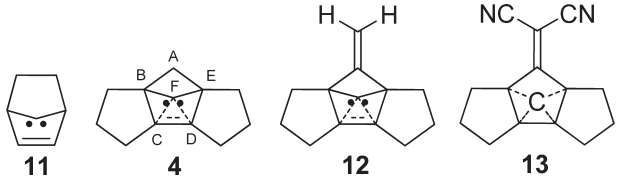


Figure 2. Stability of foiled carbene **4** (B3LYP/6-31G(d): E + ZPVE).

Table 1. Bond Lengths and Stabilization Energies of Foiled Carbenes 11, 4, 12, and 13



compound	d(C_B−C_C) (pm)	d(C_C−C_D) (pm)	d(C_B−C_F) (pm)	d(C_C−C_F) (pm)	SE (kcal/mol)
11[9]	148.5	137.4	155.9	189.3	39.3
4	147.0	138.9	162.4	177.7	59.3
12	146.5	139.5	166.5	174.4	64.0
13	145.4	140.1	171.4	172.9	69.2

computations predict a considerable kinetic stability for foiled carbene **4** (Figure 2). The rearrangement of lowest energy, that is, formation of highly strained diene **6** through a vinyl shift, requires 16.3 kcal/mol.

In addition to the effect caused by the attached rings, different substituents at C_A influence the stabilization of the foiled carbene intermediate (Table 1). The affinity of the carbene center toward the double bond can be observed as a change in bond lengths. Moreover, a substantial increase of the stabilization energy[13] (SE) and the distortion is obtained in comparison to the well-investigated norbornenylidene (**11**), the stabilization energy of **13** (69.2 kcal/mol) surpassing even the SE of difluorocarbene (65.4 kcal/mol).

To illustrate this enormous effect, the calculated structure of foiled carbene **13** is presented in the graphical abstract comprising almost equivalent bond lengths of 171.4 pm (C_B−C_F) and 172.9 pm (C_C−C_F) (Table 1). The apical carbon in species **13** can be considered a new kind of pyramidally coordinated carbon atom,[14] which reminds us of the one found in pyramidane (bond lengths of about 167 pm depending on the level of theory).[15]

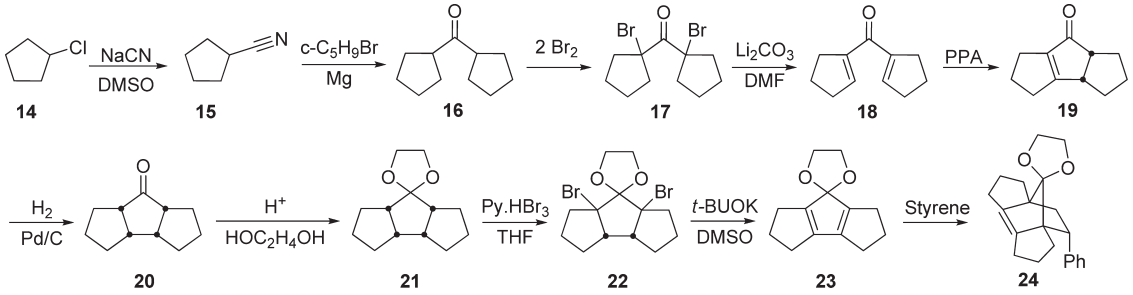
Synthesis of Precursors. To experimentally examine the theoretical calculations, different precursors for the generation of the theoretically predicted pyramidally coordinated carbene center have to be synthesized. At this point, one can choose between two options. First, to construct directly the tetracyclo-[8.1.1.0^{1,5}.0^{6,10}]dodec-5-ene skeleton of **4**. However, this pathway experimentally is relatively lengthy in comparison to the preparation of a tetracyclo[6.3.1.0^{1,8}.0^{2,6}]dodec-2(6)-ene scaffold as found in **5**. Therefore, this second approach was chosen. Carbene **5** contains a vinylcyclopropylidene,[10] which is expected to undergo the Skattebøl rearrangement to **4**. Additionally, this approach allows checking to see if the Skattebøl reaction in **5** takes place at all.

A nine-step synthesis[16,17] of the tetracyclic ketal **23** was carried out starting with chlorocyclopentane (Scheme 1). The outlined preparation of **23** was reported by Eaton et al.[17] and could be reproduced without difficulty. The single modification to the synthesis was the replacement of cyclopentyl lithium by the Grignard compound cyclopentyl magnesium bromide, which was prepared in situ. Structure **23** was verified by a single crystal X-ray analysis (Figure 3).

Dibromocarbene addition[18] with cyclopentadienone ketal **23** led directly to a suitable precursor, dibromocyclopropane **25** (Scheme 2). This reaction was performed by addition of bromoform to a mixture of ketal **23** with potassium *tert*-butoxide in hexane yielding 75% of **25**. Chemical modification at the spiro carbon atom allowed for the preparation of further derivatives. Still, it was better to perform these modifications with the dibromocarbene adduct **25**, because cyclopentadiene derivatives may be too reactive. For example, ketal cleavage of **23** to the corresponding ketone immediately[19] led to a Diels−Alder dimerization. We were able to confirm the high propensity toward a Diels−Alder reaction of compound **23** by stirring it with styrene at room temperature. Adduct **24** was cleanly formed in 52% yield.

The first step in the chemical modification of precursor **25** had to be the removal of the ethylene ketal protecting group[20] (Scheme 2). This could be realized classically by stirring of the compound overnight in aqueous acetone in the presence of a catalytic amount of *p*-toluenesulfonic acid. This acidic hydrolysis gave ketone **26** in 78% yield. The replacement of the carbonyl

Scheme 1. Synthesis of Tetracyclic Ketal 23



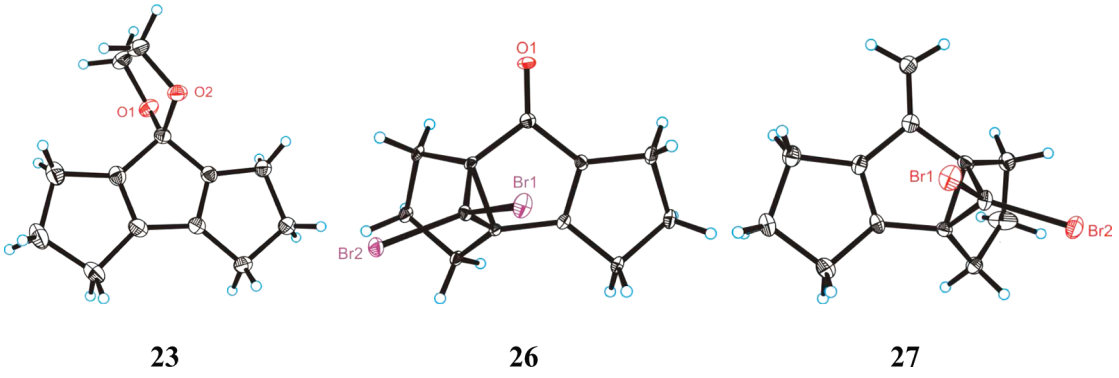
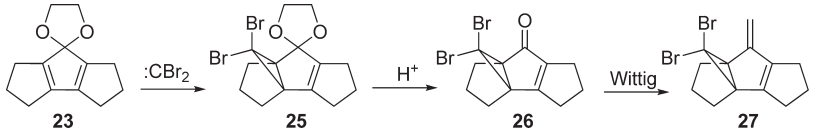


Figure 3. ORTEP representation of single crystal X-ray diffraction structures of **23**, **26**, and **27**.

Scheme 2. Synthesis of Precursors 25 and 27

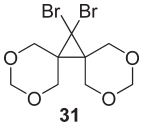


group by a new double bond was most conveniently performed via a Wittig reaction.[21] Thus, treatment of ketone **26** with methylenetriphenylphosphorane generated in situ by deprotonation of methyltriphenylphosphonium bromide with *n*-butyllithium in THF yielded 44% of diene **27**. The structures of compounds **26** and **27** were also confirmed by X-ray analysis (Figure 3). The geminal dibromide group was tolerated under the reaction conditions for conversions **25** → **26** and **26** → **27**.

Further attempts were made to obtain an oxygen−free dibromocyclopropane precursor by removing the carbonyl group of **26** under mild conditions. The two standard methods for this deoxygenation are the Wolff−Kishner[22] and the Clemmensen[23] reduction, respectively. In the case of the Wolff−Kishner method, a hydrazone derivate is generated with hydrazine. Even with the Huang−Minlon modification of this reduction, temperatures over 100 °C and application of a strong base are necessary to afford the corresponding hydrocarbon. The alternative Clemmensen reduction involves heating in the presence of amalgamated zinc. Additionally, a strong mineral acid such as HCl is required. Both methods include treatment with a strong base or acid and fairly high reaction temperatures. Under these conditions, the weak dibromocyclopropyl group probably would not be stable at all. Therefore, we decided to run a two-step reaction sequence involving a thioacetal formation followed by hydrogenolysis.[24]

The first step was to convert ketone **20**[25] into the thioacetal. Afterward, a subsequent reductive hydrogenolysis with catalytic Raney nickel[26] was planned. The thioketalization of **20** yielded **28**, which was not purified and directly used for the next step. However, the bromination of **28** (Scheme 3) to give **29** failed. Instead, unexpected product **30** was obtained and characterized. To account for this finding, we propose an addition elimination-mechanism with 1,2-sulfur migration[27] yielding **30**.

Carbenoid Generations. Dibromocyclopropane **25** comprising a 1,3-dioxolane ring was particularly resistant toward carbenoid generation and formation of rearrangement products, even when the reaction was performed with methyllithium in boiling ether. Instead, brominated or methylated products were obtained. A similar outcome was independently observed with the related 13,13-dibromo-2,4,9,11-tetraoxadispiro[5.0.5.1]tridecane (**31**).[28] This behavior can be attributed to the inductive effect of the oxygen atoms resulting in a more electrophilic character of the carbenoid to be generated.



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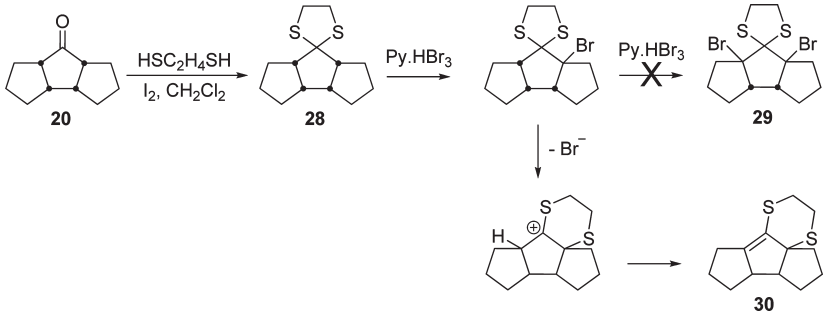
Scheme 3. Thioketalization and Bromination of Ketone 20



Scheme 4. Treatment of 27 with Methyllithium

Similarly, it was expected that during treatment of dibromide **26** with methyllithium, the lithium ion may coordinate with the lone pair of the carbonyl group, thereby affecting the carbenoid generation. Thus, to avoid this adverse interaction, most of the experiments were performed with dibromocyclopropane **27**.

While debromination of dibromide **27** with MeLi or BuLi was successful, it was not possible to isolate any product(s) originating from foiled carbene **12** as a result of a Skattebøl rearrangement. One reason is that the intramolecular products are expected to be highly strained. In fact, usually and with the exception of monobrominated, methylated or butylated derivatives, no low molecular compounds could be localized in the crude mixture using GC-MS analysis. Moreover, foiled carbenes, due to their reduced reactivity, are relatively difficult to trap intermolecularly. This has already been demonstrated with norbornen-7-ylidene derivatives.[3−7] Indeed, most of the compounds that may react with a foiled carbene contain slightly acidic bonds or functional groups that would rapidly react with the alkyllithium used for the generation of the carbenoid. The most interesting result from the reaction of **27** was obtained with 1,1-diethoxyethene, a polar alkene that was proven to be an efficient trap for the nucleophilic 2-cyclohexylidenecyclobutylidene.[29] In our hands, for the generation of carbenoid **12**, methyllithium was added to a solution of dibromide **27** with 1,1-diethoxyethene in dry diethyl ether. After 1 h of continuous stirring at 0 °C, the reaction mixture was allowed to warm to room temperature and **32**, a formal dimerization product, could be isolated (Scheme 4). The structure of dimer **32** was verified by mass spectroscopy and various 2D NMR measurements. It came out that two isomers of compound **32** are formed in a 4:1 ratio according to the proton NMR spectra of the product. The exact configurations of both isomers cannot be determined by NMR, as there are no NOEs detectable between indicative protons. The spatial distance between the two halves of the molecules, which are connected via the central double bond and the two cyclopropane rings, is too large for measurable dipolar interactions. Furthermore, dihedral angles between indicative nuclei are very similar in all possible isomers. Hence, long-range proton−proton or proton-carbon couplings do also not allow a discrimination between the possible isomers and a determination of the exact molecular structures.

CONCLUSION

In this study, guided by calculations, we were able to identify a promising structure of a foiled carbene for which the interactions between the divalent carbon and the double bond are particularly strong, leading to a high stabilization and a pronounced distortion of the molecule. In the tetracyclic species **13**, the carbenic carbon even adopts a pyramidal coordination. Still, because the central foiled carbene structure is fused with further five-membered rings, intramolecular reactions are impeded and these reactive compounds lie in a deep potential energy well. Moreover, with species **27** we were able to prepare a suitable precursor for the generation of this kind of foiled carbene. However, identification of the resulting products proved to be difficult, probably because the expected main product is a highly strained diene. Thus, with formal dimer **32**, only one low-molecular weight compound was obtained.

COMPUTATIONAL METHODS

The Gaussian 03 program[30] was used for DFT calculations, employing Becke's[31] three-parameter hybrid method and the exchange functional of Lee, Yang, and Parr (B3LYP).[32] Geometries were optimized at the B3LYP/6-31G(d) level of theory. The stationary points were characterized by vibrational analysis. All reported energies include zero-point corrections. The zero-point vibrational energies (ZPE) were scaled by a factor of 0.9806 for B3LYP/6-31G(d).[33]

EXPERIMENTAL SECTION

The ^{1}H NMR and ^{13}C NMR spectra were recorded under conditions as indicated. Chemical shifts are reported in ppm. The NMR solvent used was $CDCl_3$ and the residual solvent peak was used as an internal standard (δ_H = 7.24 ppm (s), δ_C = 77.0 ppm (t)). Abbreviations used: s (singlet), d (doublet), t (triplet), m (multiplet), m_c (centered multiplet). For all compounds, the structure was determined by 2D NMR experiments, namely COSY, NOESY, HMBC, and HMQC. GC-MS data were obtained on a 30 m × 250 μm HP-5MS, 0.25-μm film thickness, poly(methylphenylsiloxane) capillary column employing He as the carrier gas. IR spectra were recorded on a FT-IR spectrophotometer equipped with an ATR sampling unit. Melting points are uncorrected and were measured on a Kofler-type melting point microscope. All common solvents were distilled before use. All starting compounds were purchased from commercial sources and used without purification. For chromatography, silica gel 60 (230−400 mesh) was used.

Spiro[1,3-dioxolane-2,7′-tricyclo[6.3.0.0^{2,6}]undeca-1(8),2(6)-diene] (23). The ketal **23** was prepared according to the literature.[17b] GC-MS t_R: 18.66 min; ^{1}H NMR (400.1 MHz, $CDCl_3$) δ = 2.16−2.39 (m, 12H), 4.05 (s, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ = 27.0, 27.47, 27.53, 65.2, 108.2, 147.5, 150.4; *m*/*z* 204 (M^+, 100), 175 (27), 148 (73),

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131 (21), 117 (36), 104 (21), 91 (44), 77 (20), 65 (11), 51 (11). For X-ray structure verification of **23**, see the Supporting Information.

***endo*-11′-Phenylspiro[1,3-dioxolane-2,13′-tetracyclo-[8.2.1.0^{1,5}.0^{6,10}]tridec-5-ene] (24).** Ketal **23** (70 mg, 0.343 mmol) was stirred overnight with styrene (0.384 mL, 3.43 mmol) in 3 mL of ether. The solvent was removed and the residue submitted to column chromatography with hexane/ethyl acetate 19:1. Fifty-five milligrams (0.18 mmol, 52%) of **24** were obtained as an oil. GC-MS t_R: 25.60 min; ^{1}H NMR (400.1 MHz, $CDCl_3$) δ = 1.09−1.20 (m, 1H), 1.27−1.44 (m, 2H), 1.45−1.54 (m, 1H), 1.56−1.67 (m, 3H), 1.75−1.83 (m, 1H), 1.93−2.09 (m, 3H), 2.18−2.29 (m, 1H), 2.30−2.41 (m, 2H), 3.37 (dd, J = 9.4 + 4.9 Hz, 1H), 3.88−3.92 (m, 2H), 3.98−4.03 (m, 2H), 7.12−7.22 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ = 23.2, 25.0, 25.3, 25.9, 28.8, 29.6, 38.7, 45.9, 65.1, 65.4, 66.1, 72.9, 125.9, 126.1, 127.7, 129.0, 139.0, 141.9, 143.9; m/z 308 (M$^+$, 1), 236 (10), 86 (16), 57 (100); HRMS (ESI) calcd for $C_{21}H_{24}O_2$ 308.1776, found 308.1762.

12,12′-Dibromospiro[1,3-dioxolane-2,7′-tetracyclo[6.3.1.0^{1,8}.0^{2,6}]dodec-2(6)-ene] (25). To a mixture of ketal **23** (2.85 g, 13.97 mmol) and potassium *tert*-butoxide (2.19 g, 1.4 equiv) in 100 mL of dry hexane, while cooling with an ice/salt mixture at −10 °C, bromoform (4.19 g, 1.2 equiv) in 40 mL of hexane were added over 1 h. The stirring was continued overnight, while the reaction mixture was allowed to warm to room temperature. Then 40 mL of water were added, the organic layer was separated, and the aqueous layer was treated with hexane (3 × 20 mL). The combined organic phases were then washed with water, brine, and dried over $MgSO_4$. After removal of all solvents, product **25** was obtained as an oil. Yield: 3.94 g (10.48 mmol, 75%). GC-MS t_R: 24.03 min; IR (neat) 2941, 2885, 1440, 1194, 1135, 1097, 1022, 988, 947, 775 cm^{-1}; ^{1}H NMR (600.1 MHz, $CDCl_3$) δ = 1.76−1.82 (m, 1H), 1.92−2.00 (m, 2H), 2.09−2.32 (m, 8H), 2.51−2.58 (m, 1H), 3.89−4.05 (m, 4H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ = 24.9, 27.9, 28.15, 28.23, 28.4, 34.9, 51.6, 56.7, 58.2, 65.1, 65.7, 113.3, 151.8, 154.3; m/z 378 (M$^+$, <1), 376 (M$^+$, <1), 297 (2), 295 (2), 269 (5), 267 (5), 253 (5), 251 (5), 216 (100), 188 (9), 172 (9), 144 (9), 128 (15); HRMS (ESI) calcd for $C_{14}H_{16}Br_2O_2$ 375.9498, found 375.9492.

12,12-Dibromotetracyclo[6.3.1.0^{1,8}.0^{2,6}]dodec-2(6)-en-7-one (26). Dibromide **25** (5.05 g, 13.4 mmol) was dissolved in a mixture of 460 mL of acetone and 230 mL of H_2O. After addition of a catalytic amount of *p*-toluenesulfonic acid, the mixture was stirred overnight. Then 50 mL of hexane were added, the organic layer was separated, and the aqueous layer was treated with hexane (3 × 20 mL). The combined organic phases were washed with water, brine, and dried over $MgSO_4$. After removal of the solvent, 3.46 g of **26** (78%) were obtained. Chromatographic purification (hexane/ethyl acetate = 9:1) provided product **26**, which turned out to be unstable toward silica gel. Yield: 2.83 g (7.52 mmol, 56%); mp = 72−73 °C. GC-MS t_R: 21.97 min; IR (neat) 2941, 1693, 1611, 1441, 1377, 1225, 1173, 1098, 1023 cm^{-1}; ^{1}H NMR (600.1 MHz, $CDCl_3$) δ = 2.00−2.06 (m, 1H), 2.06−2.13 (m, 2H), 2.16−2.23 (m, 1H), 2.23−2.30 (m, 2H), 2.30−2.46 (m, 5H), 2.51−2.60 (m, 1H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ = 24.3, 27.0, 27.8, 28.1, 30.5, 34.4, 49.7, 60.1, 60.2, 153.5, 182.9, 195.9; m/z (EI) 253 (M-Br$^+$, 84), 251 (M-Br$^+$, 91), 225 (6), 223 (6), 172 (100), 144 (96), 128 (53), 113 (47), 91 (9), 51 (9). See also the X-ray structure in the Supporting Information. HRMS (ESI) calcd for $C_{12}H_{12}BrO$ 251.0066, found 251.0065.

12,12-Dibromo-7-methylenetetracyclo[6.3.1.0^{1,8}.0^{2,6}]dodec-2(6)-ene (27). Via syringe, *n*-BuLi (3 eq., 0.29 mL of the 1.6 M solution) was added to methyltriphenylphosphonium bromide (Ph_3-PMeBr, 3 equiv (293.92 mg) in 10 mL of dry THF. After 3 h of stirring, ketone **26** (90.5 mg, 0.272 mmol) dissolved in 1 mL of dry THF was added. The color of the reaction mixture turned immediately from yellow to orange. After continuous stirring overnight, water and dichloromethane were added for work up. The organic layer was separated and the aqueous layer was treated with dichloromethane (3 × 20 mL). The combined organic phases then were washed with water, brine, and dried over $MgSO_4$. Chromatographic purification with hexane/ethyl acetate 19:1 provided product **27**, which turned out to be unstable on silica gel. Yield: 39.5 mg (0.120 mmol, 44%). GC-MS t_R: 20.38 min; IR (neat) 3085, 2929, 2843, 1702, 1632, 1441, 1377, 875 cm^{-1}; ^{1}H NMR (600.1 MHz, $CDCl_3$) δ = 1.93−2.04 (m, 3H), 2.08−2.34 (m, 7H), 2.75−2.79 (m, 2H), 4.96 (s, 1H), 4.99 (s, 1H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ = 21.3, 28.6, 31.5, 34.3, 37.5, 47.9, 67.2, 106.7, 128.4, 154.5, 157.1; m/z (EI) 332 (M$^+$, 4), 330 (M$^+$, 9), 328 (4), 251 (M-Br$^+$, 100), 249 (M-Br$^+$, 96), 173 (45), 155 (61), 139 (36), 115 (33), 91 (14), 63 (9); HRMS (ESI) calcd for $C_{13}H_{14}Br_2$ 329.9442, found 329.9434. See also the X-ray structure in the Supporting Information.

Spiro[1,3-dithiolane-2,7′-tricyclo[6.3.0.0^{2,6}]undecane] (28). 1,2-Ethanedithiol (0.52 mL, 6 mmol) and iodine (17.3 mg, 10 mol %) were added to a stirred solution of ketone **20**[17b] (100 mg, 0.61 mmol) in dry CH_2Cl_2 (0.35 mL). After 1 h of continuous stirring at room temperature, a $Na_2S_2O_3$ solution (1 M, 1 mL) followed by a NaOH solution (10%, 5 mL) were added. The reaction mixture was stirred for an additional 5 min and afterward was worked up with water and dichloromethane to afford 219 mg of an oil. GC-MS measurement ensured a purity of 91% for **28**. The crude product was chromatographied with hexane/ethyl acetate 19:1. Yield: 118 mg (0.49 mmol, 80%). GC-MS t_R: 23.23 min; IR (neat) 2943, 2864, 1470, 1446, 1421, 1275, 976 cm^{-1}; ^{1}H NMR (400.1 MHz, $CDCl_3$) δ = 1.42−1.55 (m, 4H), 1.57−1.87 (m, 8H), 2.60−2.70 (m, 2H), 2.84−2.92 (m, 2H), 3.20−3.29 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ = 27.5, 28.8, 32.5, 38.2, 39.8, 45.7, 61.6, 76.9; GC-MS t_R: 22.39 min; m/z 240 (M$^+$, 47), 212 (100), 179 (83), 171 (47), 147 (22), 131 (21), 111 (13), 91 (18), 67 (13); HRMS (ESI) calcd for $C_{13}H_{20}S_2$ 240.1006, found 240.1008.

12,15-Dithiatetracyclo[9.4.0.0^{1,5}.0^{6,10}]pentadec-10-ene (30). Pyridinium hydrobromide perbromide (629 mg, 1.83 mmol) was added in two portions to a stirred solution of **28** (219 mg, 0.91 mmol) in 5 mL of dry THF at 5 °C. After 1 h of continuous stirring at 5−10 °C, first pyridine (0.15 mL) and then Na_2CO_3 (10%, 5 mL) were added. Work up with hexane, aqueous $NaHCO_3$ (saturated), and brine yielded 145 mg of the crude mixture. For identification of **30**, a small amount of the mixture (24 mg, 0.10 mmol) was purified using a thin layer chromatography plate (silica gel) with hexane/ethyl acetate = 1:1 as eluent. Yield: 2.6 mg, 11%. GC-MS t_R: 22.02 min; ^{1}H NMR (400.1 MHz, $CDCl_3$) δ = 1.23 (m$_c$, 1H), 1.47 (m$_c$, 1H), 1.53 (m$_c$, 1H), 1.64 (m$_c$, 3H), 1.83−2.24 (m, 5H,), 2.36 (m$_c$, 2H), 2.76 (m$_c$, 2H), 2.97 (m$_c$, 1H), 3.11 (m$_c$, 1H), 3.29 (m$_c$, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ = 22.9, 26.1, 26.5, 27.4, 29.0, 29.4, 32.4, 40.8, 49.8, 52.8, 67.9, 121.0, 153.4; m/z 238 (M$^+$, 100), 210 (86), 195 (9), 177 (45), 150 (27), 134 (8), 117 (10), 91 (14), 67 (7), 51 (3); HRMS (ESI) calcd for $C_{13}H_{18}S_2$ 238.0850, found 238.0848.

12,12′-Bi(7-methylenetetracyclo[6.3.1.0^{1,8}.0^{2,6}]dodec-2(6)-ene) (32). Dibromide **27** (111.8 mg) and 1,1-diethoxyethylene (4 equiv, 157.2 mg) were dissolved in dry diethyl ether. While cooling at 0 °C, methyllithium (4 equiv, 0.85 mL of a 1.6 M solution) was added via a syringe. The reaction mixture was stirred at 0 °C for 1 h and then allowed to warm up to room temperature. Work up with water and dichloromethane afforded 111.8 mg of a crude mixture. Recrystallization in hexane yielded dimerization product **32**. Yield: 1.9 mg (3.3%). GC-MS t_R: 27.72 min; ^{1}H NMR (600.1 MHz, $CDCl_3$) δ = 1.29−1.39 (m, 2H), 1.56−1.63 (m, 2H), 1.67−1.74 (m, 2H), 1.78−1.84 (m, 2H), 1.84−1.89 (m, 2H), 1.91−1.96 (m, 2H), 1.97−2.07 (m, 2H), 2.11−2.30 (m, 8H), 2.33−2.40 (m, 2H), 4.67 (s, 2H), 4.85 (s, 2H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ = 25.8, 27.9, 28.2, 28.6, 29.5, 30.0, 42.4, 50.1, 102.4, 129.5, 148.2, 150.9, 156.5; m/z 340 (M$^+$, 55), 325 (64), 311 (52), 297 (100), 282 (70), 267 (45), 252 (62), 239 (42), 219 (21), 203 (26), 187 (14), 165 (27), 128 (34); HRMS (ESI) calcd for $C_{26}H_{28}$ 340.2191, found 340.2178.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. NMR spectra of all new compounds and crystallographic data in CIF format for **23**, **26**, and

27. This material is available free of charge via the Internet at http://pubs.acs.org.

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