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[6 + 2] CYCLOADDITIONS CATALYZED BY TITANIUM COMPLEXES

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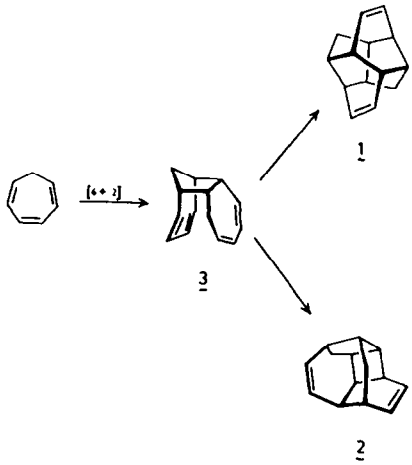
Abstract—The Ziegler catalyst $TiCl_4$-Et_2AlCl and the arenetitanium(II) complex $(\eta^6\text{-}C_6H_6)Ti(II)(AlCl_4)_2$ induce [6 + 2] cycloaddition reactions of cycloheptatriene with dienes and acetylenes. Addition to 1,3-butadiene affords 7 - *endo* - vinyl - bicyclo[4.2.1]nona - 2,4 - diene (main product) and bicyclo[4.4.1]-undeca - 2,4,8 - triene, a product of [6 + 4] cycloaddition. Isoprene reacts similarly, yielding mainly 7-*endo* - isopropenyl - bicyclo[4.2.1]nona - 2,4 - diene. 2,3 - Dimethyl - 1,3 - butadiene gives 8,9 - dimethylbicyclo[4.4.1]undeca - 2,4,8 - triene, a product of [6 + 4] cycloaddition, while [6 + 2] cross-adducts are minor products. The reaction of cycloheptatriene with norbornadiene gives mainly hexacyclo[6.5.1.$0^{2,7}$.$0^{3,12}$.$0^{6,10}$.$0^{9,13}$]tetradec - 4 - ene *via* [6 + 2] cycloaddition followed by intramolecular Diels-Alder reaction. As a by-product, pentacyclo[7.5.0.$0^{2,7}$.$0^{3,5}$.$0^{4,8}$] tetradeca - 10,12 - diene is formed by a [2 + 2 + 2] mechanism. Addition of cycloheptatriene to diphenylacetylene and bis - (trimethylsilyl)acetylene furnishes sustituted bicyclo[4.2.1]nona - 2,4,7 - trienes. Alkenes, *E,E* - 2,4 - hexadiene and 1,3 - cyclooctadiene are unreactive. The [6 + 2] cycloaddition is made possible by coordination of cycloheptatriene to titanium, which changes the symmetry of the frontier orbitals in the triene. The reactivity of the trienophile is also enhanced by coordination to the catalyst.

The reactions of cycloheptatriene (CHT) with nitrosobenzene,[1,2] benzyne,[3] chlorosulfonylisocyanate,[4] propenonitrile and methyl propenoate[5] and photochemical addition to quinones[6] represent a few known cases of [6 + 2] cycloadditions. Besides this, $(\eta^7$-cycloheptatriene)$Fe(CO)_3$ was found to enter [6 + 2] cycloaddition with some acetylenes[7] and a similar mechanism was found for the reaction of CHT with $(\eta^4$ - cyclobutadiene)$Fe(CO)_3$.[8]

Recently we have found that titanium complexes, e.g. $(\eta^6$ - $C_6H_6)$ - bis - (dichloroalane - di - μ - chloro)titanium(II), itself or in combination with Et_2AlCl, and the Ziegler catalyst $TiCl_4$–Et_2AlCl, induced dimerization of CHT, yielding two pentacyclic dienes **1** and **2** (Scheme 1).[9,10] Based on the structure of the products, the reaction has been postulated as proceeding *via* tandem [6 + 2] and [4 + 2] cycloadditions, although the intermediate **3** (Scheme 1) could be neither isolated, nor detected due to its high propensity for intramolecular Diels–Alder reaction.[10] It therefore appeared useful to explore other trienophiles in order to trap the products of the initial [6 + 2] step and thus bring support for the postulated mechanism.[11] From a synthetic point of view, the [6 + 2] reaction of CHT with olefins would give access to cyclopentane derivatives with well defined relative configuration on the 5-membered ring,[5] a topic of current interest.



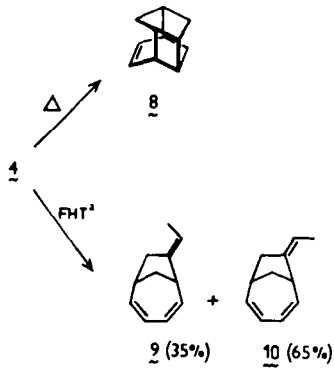
Scheme 1.

RESULTS

Catalysts. Two types of catalysts, i.e. $(\eta^6\text{-}C_6H_6)Ti(II)(AlCl_4)_2$ **(A)**[12] and $TiCl_4$–Et_2AlCl **(B)** have been examined in cross-additions of CHT to unsaturated hydrocarbons. The system **A**, while being much more active than **B**, was found to induce mainly the dimerization of CHT. On the other hand, the system **B** exhibited a negligible catalytic activity in dimerization at ambient temperature, but showed specific activity in catalyzing cross-additions of CHT to dienes and acetylenes at increased temperature. Hence, all cross-adducts were prepared using the catalyst **B** at 60°. The system **B** in benzene (Al : Ti = 6–20) forms a rusty precipitate that partially dissolves upon addition of hydrocarbons capable of complexation (CHT, 1,3-butadiene, isoprene, 2,3 - dimethyl - 1,3 - butadiene, norbornadiene,

acetylenes). The same solutions are obtained when the catalyst components are mixed in the presence of the above-mentioned hydrocarbons. The ESR spectra of these solutions showed a series of signals in the range $g = 1.973–1.943$, depending on the nature of the hydrocarbon. However, intensities of these signals corresponded to only 5–10% of the Ti content. Hence, a major part of Ti(III) formed from $TiCl_4$ under the reductive action of Et_2AlCl must be in the form of cluster compounds with paired electron spins. Further information was obtained from the electronic absorption spectra of the reacting systems. The $(\eta^6\text{-}C_6H_6)Ti(II)(AlCl_4)_2$ complex reacts quantitatively with CHT in excess to give a green species, characterized by a strong absorption band at 625 nm ($\epsilon \approx 250$). The interaction of **B** with CHT gave rise to another green complex ($\lambda_{max} = 675$ nm) which was unstable and gradually decomposed to a new species showing a band at 475 nm. Formation of the latter coincided with the cycloaddition reaction. The final, catalytically inactive organometallic product is common for **A** and **B**. It precipitates from the reaction mixture as light-green crystalline agglomerates that cannot be recrystallized from aromatic solvents due to their insolubility. The inactive reaction solution gave no ESR signal and its electronic absorption spectrum ($\lambda_{max} = 720 - 740$ nm) resembled the spectra of η^5-cyclopentadienyl binuclear Ti(III)–Al complexes.[12] The absence of ESR signals indicates that the product contains Ti(III) centers bound in strong electron-exchange interaction. The mass spectrum, obtained under simultaneous decomposition, revealed that the complex contained a multinuclear Ti–Al core with chlorine and η^7-cycloheptatrienyl ligands at both Ti and Al ($C_{14}H_{14}{}^{35}ClAl^+$ Calc: 244.0596, Found: 244.0596; $C_7H_7{}^{35}ClAl^+$ Calc: 187.9740, Found: 187.9732; $C_7H_7{}^{35}Cl^{48}Ti$ Calc: 147.9559, Found: 147.9560).

Cycloadditions. The catalytic reaction of CHT with 1,3-butadiene afforded 7 - *endo* - vinylbicyclo [4.2.1]nona - 2,4 - diene **4** as the main product, accompanied by bicyclo[4.4.1]undeca - 2,4,8 - triene **5**, *Z*, *E*, *E*- and *E*, *E*, *E*-1,5,9-cyclododecatrienes **6** and **7** and CHT dimers **1** and **2** (Scheme 2). The formation of **4** gave conclusive evidence for the overall [6 + 2] course of the catalyzed cycloaddition, as assumed earlier.[10] The structure of **4** was deduced from the spectral data. The mass spectrum showed molecular ions $C_{11}H_{14}^+$ and $C_7H_8^+$ ion as the base peak corresponding to a retro-[6 + 2] fragmentation of M^+. The ^{13}C-NMR spectrum displayed five sp^2 methines, one sp^2 methylene, three sp^3 methines and two sp^3 methylenes in accordance with the structure **4**. A careful decoupling in the ^{1}H-NMR spectrum made it possible to assign the proton signals in **4** (Experimental). On heating **4** underwent an intramolecular Diels–Alder reaction to give tetracyclo[5.4.0.0^{2,6}.0^{4,10}]undec - 8 - ene **8** (Scheme 3).

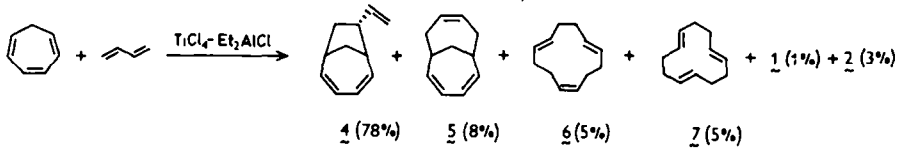


Scheme 3. *FHT = (η^5 : η^5 - fulvalene) - di - μ - hydrido - bis - (η^5 - cyclopentadienyltitanium).

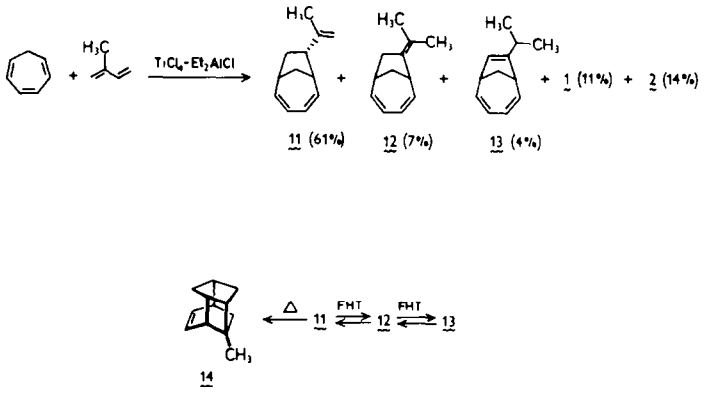
This intramolecular cyclization is possible only in *endo*-configuration of the vinyl group. The structure of **8** followed again from the spectral data; the assignment of proton signals (Experimental) was achieved through decoupling experiments. A further proof for the presence of the vinyl group in **4** stemmed from isomerization to a mixture of *E*- and *Z*-7-ethylidene-bicyclo[4.2.1]nona - 2,4 - dienes **9** and **10**, catalyzed by a double-bond shifting complex[13] (η^5: η^5 - fulvalene) - di - μ - hydrido - bis - (η^5 - cyclopentadienyltitanium) (Scheme 3, FHT). The optimum yield of the cross-adduct **4** was achieved by using the catalyst **B** at Ti : Al = 20. At lower molar ratios the yield of homoadducts was slightly enhanced (see Table 1, entries 1–3). The inevitable formation of **1** and **2** can be minimized by adjusting the ratio CHT: butadiene (Table 1, entries 1,4,5). Comparison of entries 4 and 6 (Table 1) indicates that a slightly higher proportion of CHT dimers is formed in the initial stage of the reaction. The catalyst **A** (Et_2AlCl : Ti(II) = 12) yielded mainly the homoadducts **1**, **2**, **6** and **7**. Measurements of the ESR and electronic absorption spectra during the cross-addition catalyzed by **B** revealed only the features characteristic of the interaction of **B** with CHT.

The minor product **5** arose by a symmetry-allowed [6 + 4] cycloaddition which, nevertheless, was promoted by the Ti catalyst. Analogous thermal [6 + 4] reactions require more vigorous conditions to occur.[14] The structure of **5** followed directly from the mass ($C_{11}H_{14}M^+$, $C_7H_8{}^+$ base peak) and ^{13}C-NMR spectra (three different sp^2 methines, two sp^3 methylenes (2 : 1) and one sp^3 methine), which indicated a symmetry plane bisecting the diene system, the double bond and apical methylene group.

The cycloaddition of CHT to isoprene is a straightforward process, yielding 7 - *endo* - isopropenylbicyclo[4.2.1]nona - 2,4 - diene **11** as the main cross-adduct (Scheme 4). The structure of **11** followed from the mass ($C_{12}H_{16}$, M^+, $C_7H_8{}^+$), ^{1}H- and ^{13}C-NMR



Scheme 2.



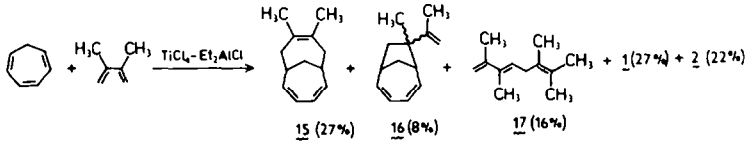
Scheme 4.

spectra, the latter showing one sp^2 methylene, four sp^2 methines, one sp^2 quarternary carbon, two sp^3 methylenes, three sp^3 methines and a methyl group on the double bond. The *endo*-configuration of the side chain in **11** was confirmed by intramolecular Diels–Alder cyclization yielding 1 - methyltetracyclo[5.4.0.$0^{2,6}$.$0^{4,10}$]undec - 8 - ene **14**. In contrast to **4**, the isopropenyl group in **11** is much more sensitive to acid-catalyzed double-bond shifts. Even on acidic work-up, **11** yields the 7-isopropylidene derivative **12** accompanied by a minor amount of 7 - isopropylbicyclo[4.2.1]nona - 2,4,7 - triene **13** (Scheme 4). The structure of **12** followed from the ^{13}C-NMR spectrum (two different Me groups on the double bond, two quarternary sp^2 carbons, four sp^2 methines, two sp^3 methines and two sp^3 methlyenes). The ^{13}C-NMR spectrum of **13** showed two aliphatic Me groups, five sp^2 methines, one sp^2 quarternary carbon, two sp^3 methines and one sp^3 methylene. A trace amount of another $C_{12}H_{16}$ isomer was also detected (mass spectrum, m/z 160; ^{13}C-NMR, six sp^2 carbons, five sp^3 methines and methylenes, one Me group), which may correspond to 8 - methylbicyclo[4.4.1]undeca - 2,4,8-triene, but a firm proof of the structure was impossible in this case. The by-products of the catalyzed cycloaddition consisted mainly of the dimers **1** and **2** (Scheme 4) and trace amounts of isoprene dimers, 1,4-dimethyl - 4 - vinylcyclohexene and dimethylcycloocta - 1,5 - dienes, which were identified by gas chromatography-mass spectrometry.

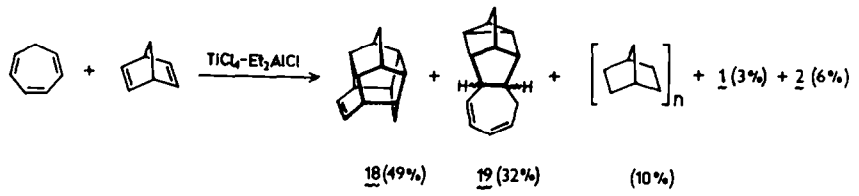
Catalyzed isomerization[13] of **11** *via* FHT-induced double bond shifts eventually yielded the tetracyclic compound **14** and the same result was obtained for catalyzed isomerization of a mixture of **11**, **12** and **13**. To account for this, we assume that the latter isomers are interconvertible under FHT catalysis, while **11** is perpetually consumed by intramolecular Diels–Alder reaction (Scheme 4).

In contrast to 1,3-butadiene and isoprene, 2,3 - dimethyl - 1,3 - butadiene afforded mainly 8,9 - dimethylbicyclo[4.4.1]undeca - 2,4,8 - triene **15** (27%), a product of the symmetry-allowed [6 + 4] cycloaddition. The structure for **15** was inferred from the ^{13}C-NMR spectrum that reflects the molecular symmetry, showing two sp^2 methines, one sp^2 quarternary carbon, one sp^3 methine, two different sp^3 methylenes (2 : 1) and one Me group. The minor fraction from the catalyzed cycloaddition consisted of two inseparable $C_{13}H_{20}$ isomers, each showing an aliphatic Me group in the ^{13}C-NMR spectrum. These minor products probably correspond to [6 + 2] cycloadducts **16** with different configuration at C-7 (Scheme 5). The overall reactivity for the catalyzed cross-addition of 2,3 - dimethyl - 1,3 - butadiene is much lower than that of 1,3 - butadiene and isoprene. This is reflected by a higher fraction of homoadducts **1**, **2** and **17** isolated from the reaction mixture.

Two cross-adducts, hexacyclo[6.5.1.$0^{2,7}$.$0^{3,12}$.$0^{6,10}$.$0^{9,13}$] tetradec - 4 - ene **18** and pentacyclo [7.5.0.$0^{2,7}$.$0^{3,5}$.$0^{4,8}$] tetradeca - 10,12 - diene **19** (Scheme 6) were obtained from norbornadiene and CHT (molar ratio 1 : 1), together with small amounts of **1**, **2** and a norbornadiene polymer. We suggest that **18** arises by the [6 + 2] cycloaddition followed by intramolecular Diels–Alder reaction, although an alternative [2 + 2 + 2 + 2] mechanism could not be excluded. The structure of **18** was determined from spectral data. The ^{13}C-NMR spectrum displayed eight distinct carbon signals (one sp^2 methine, five sp^3 methines and two sp^3 methylenes), the intensities of which in the NOE-suppressed spectrum (2 : 2 : 2 : 2 : 2 : 2 : 1 : 1, respectively) indicated a symmetry plane bisecting the double bond and both methylene groups. This, together with the mass spectral ($C_{14}H_{16}$,$M^{+\cdot}$, $C_7H_8^{+\cdot}$ base peak) and fully assigned ^{1}H-NMR data (Experimental) rendered support for the structure **18**. The minor product **19**, the formation of which may be visualized as a [2 + 2 + 2] process, was characterized through mass ($C_{14}H_{16}$, $M^{+\cdot}$) and ^{13}C-NMR spectra (four sp^2 methines, two sp^3 methylenes, five sp^3



Scheme 5.



Scheme 6.

methines and three cyclopropane methines), although the relative orientation (*syn* or *anti*) of the cycloheptatriene and norbornadiene subunits was not established. In contrast to other dienes, norbornadiene and the catalyst **B** form a red, transient complex ($\lambda_{max} = 520$ nm) which, in the absence of CHT, induces polymerization of the diene. This red complex was also formed at the onset of the CHT-norbornadiene co-dimerization; however, it was rapidly converted to a green complex that showed a similar electronic absorption spectrum as the product from CHT dimerizataion.

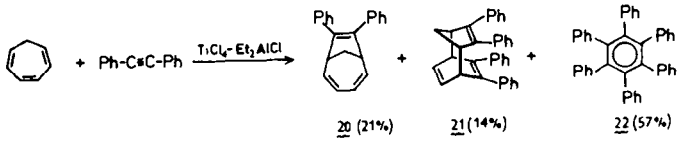
Introduction of substituents onto the terminal carbons of the 1,3-diene system in the trienophile has a deleterious effect on the reactivity. The catalyzed reaction of *E*, *E* - 2,4 - hexadiene and 1,3 - cyclooctadiene with CHT gave only the dimers **1** and **2**. 1,5 - Cyclootadiene and 5-ethylidenenorbornene were also found to be unreactive. Simple alkenes and cycloalkenes (1 - hexene, 3,3 - dimethyl - 1 - butene, 2,3 - dimethyl - 2 - butene, allylbenzene and cyclohexene) turned out to be unreactive towards CHT and the dominating products of the catalytic reaction were the dimers **1** and **2**. A trace amount of a cross-adduct from CHT and norbornene was detected by gas chromatography-mass spectrometry (M^+, m/z 186).

The catalyzed reaction of CHT with acetylenes competed with cyclotrimerization of the trienophile. With 2-butyne, the catalyzed trimerization was very rapid, giving hexamethylbenzene as the single product. Diphenylacetylene afforded, beside an appreciable amount of hexaphenylbenzene **22**, two cross-adducts, 7,8 - diphenylbicyclo[4.2.1]nona-2,4,7-triene **20** and 3,4,7,8 - tetraphenyltricyclo[4.2.2.$1^{2,5}$]-undeca - 3,7,9 - triene **21** (Scheme 7). The compound **20** was identified through the ^{1}H-NMR spectrum[8] and the structure was further confirmed by ^{13}C-NMR and mass spectra. On the other hand, the spectral methods gave no definite clue for *syn* or *anti* orientation of the diphenylacetylene subunits in **21**. The ^{13}C-NMR spectrum showed one signal for each methylene group and skeletal sp^3 and sp^2 methines, while the signals of the quarternary sp^2 carbons appeared as a series of four doublets and also the number of aromatic methines was higher than expected from the molecular symmetry. This may be due to a close spacing of the phenyl groups in **21**, which would result in hindered rotation of the phenyls and local disturbance of the symmetry. Since the phenyl groups in **20** behave as freely rotating (four ^{13}C signals for both phenyls) we assume that the hindered rotation in **21** is due to an *endo*-configuration.

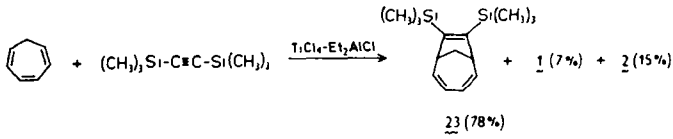
The catalyzed reaction of CHT with bis - (trimethylsilyl)acetylene gave 7,8 - bis - (trimethylsilyl)bicyclo[4.2.1]nona - 2,4,7 - triene **23** as the main product, accompanied by **1** and **2** (Scheme 8). Bis - (trimethylsilyl)acetylene and the catalyst **B** form a soluble, green complex ($\lambda_{max} = 675$ nm), stable for several weeks at room temperature. This organometallic species is catalytically active, for admission of CHT brings about the cycloaddition reaction yielding **23**, **1** and **2**. The absence of acetylene trimerization makes this [6 + 2] cycloaddition a convenient synthetic way to functionalized bicyclo[4.2.1]-nonanes, as the vinylsilane moiety has a considerable potential for further selective transformations.[15]

DISCUSSION

According to the orbital-symmetry rules,[16] the [6 + 2] cycloaddition is symmetry-forbidden and therefore should be associated with a high activation barrier.[3] The non-catalyzed [6 + 2] additions of CHT to highly polarized trienophiles were experimentally shown[4] or postulated[5] to proceed in two steps to avoid the symmetry restrictions. The catalyzed reaction of CHT with dienes and acetylenes effectively competes with parallel reactions of low activation



Scheme 7.



Scheme 8.

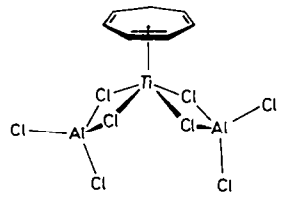


Fig. 1. The most stable complex of CHT with $Ti(II)(AlCl_4)_2$.

energy, namely, cyclotrimerization of butadiene with $E_a = 5$–7 kcal.mol^{-1},[17] and therefore it should have a very low activation energy, as well. The role of the titanium catalyst then could be either to remove the symmetry restrictions in a pericyclic [6 + 2] process, or to enhance the rate of the multistep reaction.[18] The interaction between CHT and the catalyst probably takes place in a transient complex which, after having reacted with a trienophile, releases the catalytic species for further complexation with CHT. Although the complexation of CHT with the catalytic systems **A** and **B** was proven by spectral means, the active complexes resisted all attempts at isolation, which precluded structure elucidation. The interaction between CHT and the catalyst of type **A** was therefore modelled using a $Ti(II)(AlCl_4)_2$ complex of known geometry.[19] Preliminary calculations,[20] performed at the extended-Hückel-theory level, showed that the complexation of CHT with the titanium species was generally associated with a decrease in the total energy. Since the mutual orientation of the CHT ligand and the Ti atom was unknown, the calculations were performed for a number of geometries in which CHT faced the titanium center while moving and twisting about the apex of the $Ti(AlCl_4)_2$ pyramid. As expected, the π-orbitals of CHT and d-orbitals of Ti mixed considerably upon complexation and the shapes of the newly formed HOMO and LUMO in the CHT-Ti-$(AlCl_4)_2$ complex strongly depended on the arrangement of the CHT ligand and the Ti atom.[20] However, in the complex of the lowest calculated energy (Fig. 1) the symmetry of the frontier MO's of CHT was perturbed in such a way that the HOMO became unsymmetrical with respect to the CHT symmetry plane. This means that the ligand can enter a [6 + 2] cycloaddition with a suitable trienophile, for the reaction is no longer precluded on symmetry grounds. Although these results do not rule out a step-wise mechanism,[18] they show that the pericyclic reaction is possible, at least in principle. It should be noted that the calculations disclosed more CHT-$Ti(AlCl_4)_2$ geometries that exhibited similar changes in the shape of the frontier MO's and the total energy of which was less than 3 kcal.mol^{-1} higher than that of the most stable form. This suggests that the CHT ligand can move on a relatively flat energy surface, while still retaining its reactivity for the [6 + 2] cycloaddition.

In order to observe the cross-addition, the reactivity of the trienophile must be comparable to that of CHT. The results showed, however, that even reactive alkenes such as norbornene[21] and 5-ethylidenenorbornene were inefficient trienophiles if compared with CHT. Also the high reactivity for the [6 + 2] cycloaddition of 1,3–butadiene vs 2,4-hexadiene and 2,3 - dimethyl - 1,3 - butadiene is unusual and contrasts the reactivity order known from other cycloaddition reactions.[22,23] From the properties of the trienophiles examined it appears that only those capable of coordination to the catalyst, e.g. 1,3-butadiene, isoprene, norbornadiene and acetylenes, are efficient $_{\pi}2$ components. The interaction between the trienophile and the catalyst must be different for the systems **A** and **B**. The catalyst **A** is much more active and induces mainly the [6 + 2] dimerization of CHT, whereas other trienophiles are less active. On the other hand, the system **B** strongly favours cross-additions. As a possible rationalization of this difference we suggest that in **A** the coordinated CHT molecule is attacked by a free, uncoordinated CHT. This would mean that the Ti(II) complex with CHT (Fig. 1) does not dissociate to provide a new coordination site and that the propensity of CHT to serve as a trienophile exceeds that of most dienes. In contrast, we assume that in **B** both CHT and the trienophile are coordinated to the catalyst[18] and the reaction occurs between the ligands. This would account for the exclusive reactivity of those trienophiles which are able to form complexes with **B**. The enhanced reactivity of some dienes and acetylenes in cycloadditions catalyzed by **B** may be due to steric and/or electronic factors, but in the light of our limited knowledge of the catalyst structure these remain unspecified.

Table 1. Products of titanium-catalyzed cross-addition of CHT with butadiene

entry	catalyst molar ratio Al:Ti	butadiene mmol	products (%) 4	5	6	7	1	2
1	20	10	78	8	5	5	1	3
2	8	10	67	10	8	7	2	6
3	5	10	47	8	18	7	6	14
4	20	8	70	11	7	6	2	4
5	20	13	60	6	16	15	1	2
6	20	8[b]	70	10	5	4	5	6
7	12[c]	10	14	2	10	0	10	64

[a]Reaction conditions: $TiCl_4$ 0.012 mmol, CHT 5 mmol, benzene 3 ml, 60°C, 8 hours; 100% conversion of CHT in all entries.

[b]Experimental conditions as in entry 4; stopped after 45 minutes.

[c](η^6 - C_6H_6)$Ti(AlCl_4)_2$ (0.012 mmol) used instead of $TiCl_4$.

EXPERIMENTAL

The mass spectra were recorded on a Jeol D-100 instrument (75 eV, 300 μA) using either a direct inlet or coupled to a gas chromatograph (column SE-30, 3% on Chromosorb W). The ^{1}H- and ^{13}C-NMR spectra were measured on Varian XL-200 (200.058 MHz for ^{1}H, 50.309 MHz for ^{13}C, FT-mode) and Jeol FX-60 (59.797 MHz for ^{1}H, 15.036 MHz for ^{13}C, FT-mode) instruments in $CDCl_3$ with TMS as internal reference. The ^{1}H–^{1}H coupling constants were obtained from the second-order analysis and checked by simulating the spectra. The ^{13}C–^{1}H coupling constants (^{1}J and ^{3}J) were obtained from proton coupled ^{13}C-NMR spectra. The IR spectra were taken on a UR-75 Zeiss (Jena) grating spectrometer. The ESR spectra were measured on an ERS-220 spectrometer in X-band using a variable temperature unit. The UV spectra were measured on a Cary 17 spectrometer in all-sealed quartz cuvettes (Hellma).

Chemicals. Benzene, CHT, norbornadiene, 1,3- and 1,5-cyclooctadiene and 5-ethylidenenorbornene (all Fluka) were distilled from $LiAlH_4$ and then heated repeatedly with fresh portions of FHT at 120° in sealed ampoules until the soln remained green. The purified olefins were distilled off *in vacuo* and stored in ampoules with breakable seals. Butadiene, isoprene, 2,3 - dimethyl - 1,3 - butadiene, 2,4 - hexadiene, 1 - hexene, 3,3 - dimethyl - 1 - butene, 2,3 - dimethyl - 2 - butene, cyclohexene, allylbenzene and 2-butyne were degassed and then purified by standing with a titanocene hydride complex[24] prepared from $(\eta^5\text{-}C_5H_5)TiCl_2$ and $LiAlH_4$ in benzene. Bis - (trimethylsilyl)acetylene and 2 - norbornene were degassed during vacuum distillation and stored under vacuum. Diphenylacetylene (Fluka) was evacuated and dissolved in benzene *in vacuo*. Diethylaluminum chloride (Fluka) and $TiCl_4$ (Enzymes Int,) were distilled *in vacuo* and dissolved in benzene. (η^6 - Benzene) - bis - (dichloroalan - di - μ - chloro(-titanium(II) was prepared and purified as described earlier.[25]

Catalytic cross-additions

General procedure. Cycloheptatriene (10 mmol), an olefin or acetylene (10 mmol), a soln of Et_2AlCl (2 mmol in 1 ml of benzene) and benzene (3 ml) were mixed in a reaction ampoule. All components were dosed *in vacuo* from ampoules with breakable seals. A soln of $TiCl_4$ (0.1 mmol in 1 ml of benzene) was added to the mixture, the ampoule was cooled to 77 K and sealed off. After heating to 60° for 8 hr the ampoule was opened, the mixture diluted with CH_2Cl_2 and poured into water. The organic layer was washed with $NaHCO_3$, dried over $NaSO_4$ and the solvents were distilled off *in vacuo*. The products were separated on a silica gel column (elution with *n*-hexane or hexane-benzene, 3 : 1) or purified by preparative gas chromatography (column SE-30, 5 m, 10% on Chromosorb). The yields of pure isolated products are based on cycloheptatriene.

Compound **4** was prepared from CHT and butadiene in 78% yield. IR(neat): 3075, 3056, 3023, 3016, 2976, 2952, 2932, 2864, 1639, 1595, 1445, 1423, 1392, 1020, 998, 911, 870, 833, 790, 713, 630, 481 cm^{-1}; ^{1}H-NMR (δ, ppm): 6.12 (H_3, m, $J_{2,3}$ = 10.8, $J_{3,4}$ = 8.2, $J_{3,5}$ = 2.0, $J_{1,3}$ = 1.2 Hz), 6.02 (H_{10}, m, $J_{10,11}$ = 17.2, $J_{10,11'}$ = 10.1, $J_{7,10}$ = 8.2 Hz), 5.84 (H_4, m, $J_{4,5}$ = 11.6, $J_{2,4}$ = 0.7 Hz), 5.75 (H_5, m, $J_{5,6}$ = 6.4 Hz), 5.59 (H_2, m, $J_{1,2}$ = 6.8 Hz), 5.04 (H_{11}, m, $J_{11,11'}$ = 2.2, $J_{7,11}$ = 0.8 Hz), 4.97 ($H_{11'}$, m, $J_{7,11'}$ = 0.8 Hz), 2.87 (H_7, m), 2.70 (H_1, m), 2.65 (H_6, m), 2.18 (H_9, m, $J_{9,9'}$ = 11.8, $J_{1,9}$, $J_{6,9}$ = 7.6, 4.8 Hz), 2.02 (H_8, m), 1.91 ($H_{9'}$, d), 1.65 ($H_{8'}$, ddd, $J_{8,8'}$ = 13.6, $J_{7,8'}$, $J_{1,8'}$ = 10.2, 3.8 Hz); ^{13}C-NMR (δ, ppm): 141.0 d, 139.4 d, 135.1 d, 126.1 d, 123.3 d, 114.5 t, 61.3 d, 46.4 d, 41.5 t, 36.8 d, 33.5 t; UV (λ_{max}): 262 nm, shoulders at 252 and 272 nm; mass spectrum (*m/z*, %): 146(7), 131(4), 128(2), 118(3), 117(8), 105(7), 104(6), 92(100), 91(89), 80(10), 79(20), 77(10), 68(21), 65(12), 51(6), 41(6), 39(14).

Compound **5** was obtained from CHT and butadiene in 8% yield. IR(neat): 3015, 3007, 2922, 2883, 2859, 2837, 1688, 1653, 1637, 1613, 1449, 1434, 1394, 1266, 1258, 1202, 1054, 1045, 968, 958, 920, 906, 887, 880, 824, 815, 717, 695, 665, 515 cm^{-1}; ^{1}H-NMR (δ, ppm): 5.76 (4H, m), 5.68 (2H, m), 2.75 (2H, m), 2.42 (4H, m), 2.18 (2H, t, J = 3.6 Hz); ^{13}C-NMR (δ, ppm): 132.11 (dm, ^{1}J = 157 Hz, ^{3}J = 15.2, 7.0, 0.3, 0.3 Hz), 124.79 (dm, ^{1}J = 152 Hz, ^{3}J = 11.6, 6.6, 1.5, 1.5 Hz), 138.24 (dm, ^{1}J = 152 Hz, W(^{3}J) = 22 Hz), 38.30 (dm, ^{1}J = 131 Hz), 37.00 (tm, ^{1}J = 131 Hz), 32.15 (tm, ^{1}J = 129 Hz, W(^{3}J) = 16 Hz); UV (λ_{max}) 256 nm; mass spectrum (*m/z*, %): 146(9), 131(8), 128(3), 118(4), 117(9), 115(5), 105(9), 104(16), 92(100), 91(95), 80(16), 79(19), 77(12), 68(18), 65(14), 51(8), 41(7), 39(16).

Tetracyclo[5.4.0.0^{2,6}.0^{4,10}]*undec* - 8 - *ene* **8**. Triene **4** (1 g) was placed in an ampoule which was evacuated, sealed and heated to 190–200° for 6 hr. The semicrystalline product (a single peak by gas chromatography) was sublimed to afford 880 mg (88%) of **8**, m.p. 149–151° (sealed capillary). IR (nujol mull): 3033, 2937, 2867, 1613, 1453, 1367, 1311, 1297, 1293, 1280, 1273, 1254, 1246, 1225, 1180, 1137, 1127, 1104, 1073, 1039, 1017, 1010, 1000, 971, 960, 932, 919, 907, 865, 849, 830, 813, 781, 767, 747, 727, 714, 697, 680, 663, 590, 559, 530, 503 cm^{-1}; ^{1}H-NMR (δ, ppm): 6.21 (H_9, m, $J_{8,9}$ = 8.3, $J_{9,10}$ = 7.2, $J_{7,9}$ = 1.2 Hz), 5.56 (H_8, m, $J_{7,8}$ = 6.3, $J_{8,10}$ = 1.0 Hz), 2.59 (H_{10}, m), 2.51 (H_7, m), 2.18 (H_2, m), 2.07 (H_6, m), 1.96 (H_1, m), 1.85 (H_4, m), 1.48 (H_3, m), 1.43 (H_{11}, m), 1.35 (H_5, ddd, $J_{5,5'}$ = 10.0, J = 2.4, 2.2 Hz), 1.19 ($H_{3'}$, ddd, $J_{3,3'}$ = 9.5, J = 1.6, 1.6 Hz), 0.95 ($H_{11'}$, dm, J_d = 10.0 Hz), 0.91 ($H_{5'}$, dm, J_d = 10.0 Hz); ^{13}C-NMR (δ, ppm): 136.72 (dm, ^{1}J = 159.4 Hz, W(^{3}J) = 23 Hz), 126.45 (dm, ^{1}J = 159.2 Hz), 47.95 (dm, ^{1}J = 140.0 Hz), 41.68 (dm, ^{1}J = 130.0 Hz), 40.80 (dm, ^{1}J = 136 Hz), 40.16 (d, ^{1}J = 136 Hz), 36.82 (d, ^{1}J = 136 Hz), 36.67 (d, ^{1}J = 131 Hz), 36.67 (t, ^{1}J = 132 Hz), 34.49 (t, ^{1}J = 122 Hz), 34.28 (t, ^{1}J = 124 Hz); mass spectrum (*m/z*, %): 146(29), 131(8), 118(11), 117(22), 115(6), 105(22), 104(20), 92(51), 91(31), 80(54), 79(100), 78(27), 77(25), 67(99), 66(13), 65(10), 51(7), 41(10), 39(16).

E,Z-7-*Ethylidenebicyclo*[4.2.1]*nona* - 2,4 - *dienes* **9**, **10**. A mesitylene soln of FHT (0.05 mmol of the complex) was placed in a bulb sealed to a vacuum line. Mesitylene was distilled off *in vacuo* and **4** (1 ml) was distilled to the solid catalyst. The bulb was sealed off and heated to 170° for 4 hr. Then it was opened to air and **9** and **10** were isolated in a quantitative yield by vacuum distillation. IR (**9** + **10**, neat): 3017, 2957, 2926, 2880, 2857, 2828, 1723, 1673, 1598, 1480, 1450, 1389, 1376, 1010, 981, 970, 901, 834, 782, 758, 703 cm^{-1}; ^{1}H-NMR (**9**, δ, ppm): 6.10 (1H, m), 5.97 (1H, m), 5.64 (1H, m), 5.20 (2H, m), 3.41 (1H, dd, J = 8.0, 8.0 Hz), 2.73 (1H, m), 2.56 (1H, broad d), 2.48 (1H, m), 2.25 (1H, dd, J = 6.6, 6.3 Hz), 1.89 (1H, dd, J = 4.2, 1.2 Hz), 1.60 (3H, broad d, J = 6.8 Hz); ^{13}C-NMR (**9**, δ, ppm): 150.55 s, 137.81 d, 136.24 d, 123.64 d, 123.19 d, 114.74 d, 47.35 t, 41.19 d, 39.41 d, 32.90 t, 16.37 q; ^{1}H-NMR (**10**, δ, ppm): 6.10 (1H, m), 5.97 (1H, m), 5.64 (1H, m), 5.20 (2H, m), 3.26 (1H, dd, J = 8.0, 8.0 Hz), 2.73 (1H, m), 2.56 (1H, m), 2.48 (1H, m), 2.19 (1H, dd, J = 6.4, 6.4 Hz), 1.95 (1H, dd, J = 4.0, 1.2 Hz), 1.53 (3H, ddd, J = 6.8, 1.3, 0.8 Hz); ^{13}C-NMR (**10**, δ, ppm): 152.26 s, 138.82 d, 137.96 d, 123.64 d, 123.45 d, 114.69 d, 42.17 t, 45.50 d, 38.57 d, 32.45 t, 14.66 q; UV (**9** + **10**, λ_{max}): 263 nm; mass spectrum (**9** + **10**, *m/z*, %): 146(74), 145(11), 131(88), 129(13), 117(66), 116(19), 115(26), 105(7), 104(6), 92(42), 91(100), 79(24), 77(22), 68(16), 67(17), 65(19), 53(13), 51(14), 41(14), 39(28).

Compound **11** was prepared from CHT and isoprene (molar ratio 1 : 2) in 61% yield. IR(neat): 3086, 3013, 2923, 2858, 1643, 1595, 1443, 1373, 886, 831, 724, 688, 561, 546, 513 cm^{-1}; ^{1}H-NMR (δ, ppm): 6.15 (H_2, m, $J_{1,2}$ = 8.2, $J_{2,3}$ = 10.4, $J_{2,4}$ = 0.9 Hz), 5.79 (H_4, m, $J_{3,4}$ = 6.4, $J_{4,5}$ = 11.2 Hz), 5.66 (H_5, m, $J_{5,6}$ = 6.4, $J_{3,5}$ = 0.9 Hz), 5.57 (H_3, m), 4.80 (H_{11}, m, $J_{7,11}$ = 1.2, $J_{11,11'}$ = 3, $J_{11,12}$ = 1.5 Hz), 4.74 ($H_{11'}$, m, $J_{7,11'}$ = 0.6, $J_{11',12}$ = 0.6 Hz), 2.79 (H_7, m), 2.70, 2.66 (H_1, H_6, m), 2.20 (H_9, m), 1.92 ($H_{9'}$, m), 1.85 (H_8, $H_{8'}$, m), 1.80 ($3H_{12}$, ddd); ^{13}C-NMR (δ, ppm): 144.07 s, 141.57 d, 134.87 d, 126.13 d, 123.35 d, 109.72 t, 63.24 d, 44.14 d, 37.38 t, 35.67 d, 33.35 t, 23.91 q.

7 - *Isopropylidenebicyclo*[4.2.1]*nona* - 2,4 - *diene* **12**. The mixture containing **11** and the catalyst **B** was heated at 100° and the products were slowly distilled off *in vacuo*. Preparative gas chromatography furnished **12** in 40% yield. ^{1}H-NMR (δ, ppm): 5.99 (2H, m), 5.60 (2H, m), 3.38 (H_6, m), 2.71 (H_1, m), 2.54 (H_8, m), 2.21 (H_9, m), 1.93 ($H_{8'}$, d, J = 11.6 Hz), 1.925 ($H_{9'}$, d, J = 11.6 Hz), 1.66 (11-CH_3, dd, J = 1.8, 1.8 Hz), 1.56 (12-CH_3, dd, J = 1.0, 0.4 Hz); ^{13}C-NMR (δ, ppm): 143.92 s, 138.37 d, 136.77 d, 123.24 d, 123.21 d, 121.14 s, 44.84 t, 42.70 d, 39.42 d, 32.85 t, 22.59 q, 20.64 q; mass spectrum (*m/z*, %): 160(73), 145(75), 130(14), 119(19), 117(76), 115(22), 106(21), 105(20), 92(34), 91(100), 79(19), 77(19), 67(22), 65(20), 41(24), 39(20).

Compound **13** was prepared as described for **12**. Yield 15%; ^{1}H-NMR (δ, ppm): 6.13 (2H, m), 5.78 (2H, m), 5.02 (H_8, m, $J_{1,8}$ = 2.8, $J_{8,10}$ = 0.8 Hz), 3.20 (H_6, dd, $J_{5,6} = J_{6,9}$ = 7.2 Hz), 2.97 (H_1, m, $J_{1,9} = J_{1,2}$ = 6.9 Hz), 2.45 (H_{10}, hp(dd), J_{hp} = 6.8 Hz), 2.13 (H_9, m, $J_{9,9'}$ = 10.8 Hz), 1.48 ($H_{9'}$, d), 1.03 (11-CH_3, d, $J_{10,11}$ = 6.8 Hz), 1.02 (12-CH_3, d); ^{13}C-NMR (δ, ppm): 148.08 s, 139.39 d, 138.97 d, 123.92 d, 124.40 d, 117.16 d, 44.63 d, 42.90 d, 31.73 t, 27.76 d, 22.90 q, 22.47 q; mass spectrum (*m/z*, %): 160(27), 145(22), 130(5), 129(5), 128(6), 117(100), 115(35), 91(33).

1 - *Methyltetracyclo*[5.4.0.0^{2,6}.0^{4,10}]*undec* - 8 - *ene* **14**. The crude triene **11** (1 g) was heated with FHT (0.05 mmol) in an evacuated sealed bulb at 270° for 5 hr. The cooled bulb was open and the semicrystalline product purified by crystallization from MeOH to give 760 mg (76%) of **14**, m.p. 99–101° (sealed capillary). IR(nujol mull): 3030, 2924, 2858, 1614, 1473, 1452, 1372, 1363, 1330, 1303, 820, 756, 703, 675, 620, 590, 518 cm^{-1}; ^{1}H-NMR (δ, ppm): 6.16 (H_9, m, $J_{8,9}$ = 8.2, $J_{9,10}$ = 6.9, $J_{7,9}$ = 1.1 Hz), 5.60 (H_8, m, $J_{7,8}$ = 6.2, $J_{8,10}$ = 1.3 Hz), 2.48 (H_{10}, m), 2.06 (H_7, m, $J_{6,7}$ = 5.7 Hz), 1.83 (2H, m), 1.58 (1H, m), 1.54 (1H, m), 1.39 (H_{11}, dd, J = 10.1, 5.6 Hz), 1.33 (H_3, m, J = 10.4, 1.8, 1.6 Hz), 1.08 ($H_{11'}$, m, J = 10, 2, 1.6 Hz), 1.04 (12-CH_3, s), 0.93 ($H_{5'}$, d, J = 9.9 Hz), 0.92 ($H_{3'}$, d, J = 10 Hz); ^{13}C-NMR (δ, ppm): 136.10 (C_9, dddd, ^{1}J = 159.3 Hz, ^{3}J = 7.8, 7.0, 7.0 Hz), 127.48 (C_8, ddd, ^{1}J = 159 Hz, ^{3}J = 5.2, 4.7 Hz), 52.41 (C_7, dm, ^{1}J = 142 Hz, W(^{3}J) = 20 Hz), 48.68 (C_{10}, dm, ^{1}J = 135 Hz, W(^{3}J) = 25 Hz), 46.30 (C_1, sm, W(^{3}J) = 20 Hz), 45.43 (C_{11}, tm, ^{1}J = 132 Hz, W(^{3}J) = 10 Hz), 38.69 (C_4, dm, ^{1}J = 138 Hz), 38.32 (C_2, dm, ^{1}J = 138 Hz), 37.16 (C_6, dm ^{1}J = 143.5 Hz, W(^{3}J) = 18 Hz), 33.91 (C_5, tm, ^{1}J = 133 Hz, W(^{3}J) = 20 Hz), 31.71 (C_3, tdd, ^{1}J = 133 Hz, ^{3}J = 9.8, 3.0 Hz), 23.14 (C_{12}, Qd, ^{1}J = 123 Hz, ^{3}J = 5.2 Hz); mass spectrum (*m/z*, %): 160(30), 145(30), 121(25), 119(15), 118(17), 117(16), 105(18), 94(47), 93(97), 92(100), 91(86), 79(38), 77(40), 67(17), 65(15), 41(18), 39(22).

Compound **15** was prepared according to the general procedure, using a four-fold excess of 2,3 - dimethyl - 1,3 - butadiene. The products were separated by preparative gas chromatography. **15**: IR(neat): 3060, 2996, 2890, 1666, 1608, 1440, 1434, 1373, 1168, 942, 885, 866, 827, 696, 571 cm^{-1}; ^{1}H-NMR (δ, ppm): 5.74 (4H, m), 2.71 (2H, m), 2.65 (2H, m), 2.10 (2H, m), 1.95 (2H, dm, J_d = 13.4 Hz), 1.53 (6H, d, J = 1.0 Hz); ^{13}C-NMR (δ, ppm): 136.71 (C_2, C_5, dm, ^{1}J = 150.5 Hz, W(^{3}J) = 21 Hz), 130.03 (C_8, C_9, sm), 124.78 (C_3, C_4, ddd, ^{1}J = 150.6 Hz, ^{3}J = 8.6, 9.3 Hz), 39.64 (C_7, C_{10}, tm, ^{1}J = 127 Hz), 37.87 (C_1, C_6, dm, ^{1}J = 126 Hz), 36.20 (C_{11}, tm, ^{1}J = 128 Hz), 22.32 (8-CH_3, 9-CH_3, qdd, ^{1}J = 125.6 Hz, ^{3}J = 4.3, 4.2 Hz); mass spectrum (*m/z*, %): 174(20), 159(12), 145(6), 131(7), 119(9), 107(12), 106(9), 105(9), 92(100), 91(100), 77(14), 41(16), 39(17). **16** (mixture of isomers): ^{13}C-NMR (δ, ppm): 136.56, 132.75, 132.34, 131.26, 129.48, 125.46, 124.41, 124.09, 122.04, 118.41, 110.74, 44.45, 42.24, 41.64, 41.08, 40.18, 37.75, 37.26, 34.28, 33.84, 32.40, 27.32, 26.64, 19.10, 18.95; mass spectrum (*m/z*, %): 174(58), 159(40), 132(19), 131(22), 129(18), 128(15), 119(29), 117(22), 115(18), 107(34), 105(42), 92(58), 91(100), 79(23), 77(31), 67(18), 65(20), 41(32), 39(30). **17**: ^{1}H-NMR (δ, ppm): 5.51 (1H, tq, J = 7.3, 1.0 Hz), 4.97 (1H, s), 4.87 (1H, broad s), 2.87 (2H, dm, J_d = 7.3 Hz), 1.88 (3H, broad s), 1.85 (3H, br s), 1.65 (9H, s); ^{13}C-NMR (δ, ppm): 144.8 s, 134.8 s, 126.8 s, 126.7 d, 124.5 s, 110.8 t, 33.9 t, 21.0 q, 20.6 q, 20.3 q, 18.4 q, 13.7 q.

Compound **18** was obtained from CHT and norbornadiene in 30% yield, m.p. 168–169° (sealed capillary). IR(KBr pellet): 3035, 2940, 2865, 1624, 1455, 1444, 1384, 1374, 1326, 1313, 1287, 1246, 1087, 938, 912, 858, 837, 812, 782, 766, 758, 734, 692, 525 cm^{-1}; ^{1}H-NMR (δ, ppm): 5.99 (H_4, H_5, m, J = 8.5, 6.7, 0.4 Hz), 2.63 (H_3, H_6, m), 2.48 (H_9, H_{13}, m), 2.12 (H_{10}, H_{12}, m), 2.07 (H_1, H_8, m), 1.90 (H_2, H_7, m), 1.79, 1.69 (H_{14}, $H_{14'}$, AB, J_{AB} = 10.3 Hz), 1.49 (H_{11}, t(AB), J_{AB} = 12.2 Hz, J_t = 3.3 Hz), 1.21 ($H_{11'}$, AB, J_{AB} = 12.2 Hz); ^{13}C-NMR (δ, ppm): 130.8 (2C, d), 53.7 (2C, d), 47.0 (2C, d), 43.1 (2C, d), 42.9 (2C, d), 41.8 (2C, d), 39.5 (1C, t), 35.4 (1C, t); mass spectrum (*m/z*, %): 184(30), 169(17), 156(12), 155(18), 143(23), 142(17), 141(30), 130(23), 129(35), 128(32), 118(45), 117(83), 116(23), 115(38), 106(23), 105(25), 104(14), 93(28), 92(46), 91(100), 80(16), 79(26), 78(22), 77(33), 66(13), 65(21), 63(10), 51(15), 41(13), 39(24).

Compound **19** was obtained from CHT and norbornadiene in 20% yield. IR(neat): 3056, 3017, 3000, 2920, 2860, 2840, 1759, 1740, 1598, 1452, 1436, 1340, 1316, 1306, 1246, 1200, 959, 851, 824, 795, 785, 723, 681, 606, 578, 506 cm^{-1}; ^{1}H-NMR (δ, ppm): 6.17–6.03 (2H, m), 5.95–5.72 (2H, m), 2.73 (1H, t, J = 3.4 Hz), 2.68 (1H, m), 2.30–2.09 (2H, m), 2.07 (1H, m), 1.90 (1H, m), 1.68 (1H, m), 1.47 (2H, t, J = 1.5 Hz). 0.99–0.88 (2H, m); ^{13}C-NMR (δ, ppm): 137.0 d, 133.8 d, 128.1 d, 125.6 d, 56.0 d, 49.9 d, 49.2 d, 42.6 d, 40.0 d, 31.4 t, 30.7 t, 14.3 d, 11.6 d, 10.8 d; mass spectrum (*m/z*, %): 184(38), 169(19), 156(10), 155(15), 143(23), 142(18), 141(23), 130(22), 129(34), 128(31), 118(45), 117(81), 116(21), 115(38), 106(21), 105(25), 104(15), 103(9), 93(32), 92(42), 91(100), 80(18), 79(27), 78(25), 77(33), 66(13), 65(21), 63(9), 51(14), 41(12), 39(23).

Compound **20** was obtained from CHT and diphenylacetylene in 16% yield, m.p. 53–55°. IR (nujol mull): 3080, 3064, 3059, 3047, 3030, 3018, 1600, 1578, 1495, 1486, 1443, 1384, 1377, 1070, 1025, 1017, 962, 912, 850, 842, 756, 720, 702, 698, 691, 670, 651, 586, 569, 536, 529, 509 cm^{-1}; ^{1}H-NMR (δ, ppm): 7.18 (10H, m), 6.26 (2H, m, J = 7 Hz), 5.88 (2H, m), 3.62 (2H, dd, J = 7 Hz), 2.58 (1H, m), 1.81 (1H, d, J = 11.3 Hz); ^{13}C-NMR (δ, ppm): 139.23 (2C, dm, ^{1}J = 157.1 Hz, W(^{3}J) = 22 Hz), 136.65 (2C, sdd, ^{3}J = 6.0, 6.0 Hz), 135.93 (2C, sm, W(^{3}J) = 16 Hz), 129.11 (4C, ddd, ^{1}J = 162 Hz), 127.97 (4C, ddd, ^{1}J = 162 Hz), 126.51 (2C, ddd, ^{1}J = 160.5 Hz), 124.62 (2C, ddd, ^{1}J = 160 Hz, ^{3}J = 12.0, 8.0 Hz), 49.23 (2C, dm, ^{1}J = 133.8 Hz, W(^{3}J) = 19 Hz), 30.50 (1C, tdd, ^{1}J = 133 Hz, ^{3}J = 5.0, 3.0 Hz); mass spectrum (*m/z*, %): 270(2), 255(0.6), 239(0.3), 192(0.8), 178(100), 177(12), 176(18), 165(4), 152(13), 151(8), 139(3), 126(5), 115(2), 102(2), 98(2), 89(11), 76(6), 63(6), 51(5), 39(4).

Compound **21** was obtained from diphenylacetylene and CHT in 11% yield, m.p. 175–177°. IR(KBr pellet): 3016, 2952, 2932, 1585, 1512, 1441, 1405, 1384, 1249, 990, 911, 864, 839, 820, 756, 745, 704, 637, 623, 550, 473, 434, 390, 375 cm^{-1}; ^{1}H-NMR (δ, ppm): 7.04 (10H, s), 6.78 (10H, s), 5.82 (2H, br s), 4.10 (2H, m), 3.26 (2H, dd, J = 8.5, 4.9 Hz), 2.82 (1H, dm, J_d = 8.5 Hz), 2.57 (1H, m); ^{13}C-NMR (δ, ppm): 141.6 s, 141.0 s, 140.8 s, 140.3 s, 139.6 s, 139.4 s, 133.7 s, 133.5 s, 130.9 (4C, d), 129.6 (2C, d), 129.5 (2C, d), 127.4 (2C, d), 127.2 (2C, d), 126.8 (4C, d) 126. 1 (2C, d), 125.8 (2C, d), 125.3 (2C, d), 46.8 (2C, d), 44.0 (2C, d), 30.1 (1C, t); mass spectrum (*m/z*, %) : 488 (100).

Compound **23** was prepared from CHT and bis - (trimethylsilyl)acetylene in 61% yield, m.p. −3–0°. IR(neat): 3016, 2952, 2932, 1585, 1512, 1441, 1405, 1384, 1249, 990, 911, 864, 839, 820, 756, 745, 704, 637, 623, 550, 473, 434, 390, 375 cm^{-1}; ^{1}H-NMR (δ, ppm): 6.22–5.61 (4H, m), 3.31 (2H, dd, J = 7.3, 6.1 Hz), 1.94 (1H, dd, J = 11.0, 6.1 Hz), 1.42 (1H, d, J = 11.0 Hz), 0.16 (18H, s); ^{13}C-NMR (δ, ppm): 146.5 (2C, s), 137.8 (2C, d), 123.9 (2C, d), 51.9 (2C, d), 30.1 (1C, t), 1.79 (6C, q); UV(λ_{max}): 226, 244, 270 nm; mass spectrum (*m/z*, %): 262(14), 247(3), 189(3),

188(2), 174(5), 173(5), 171(6), 159(9), 145(14), 131(3), 97(5), 92(100), 91(27), 83(5), 73(67), 59(12), 45(13), 43(6).

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