

Photoinduced Reactions of Cr(CO)₃-Coordinated 1,3,5-Cycloheptatriene: [6 + 2] Cycloaddition with an Alkyne and Catalytic 1,6-Hydrogenation[☆]

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Irradiation of Cr(CO)₃(η⁶-1,3,5-cycloheptatriene) (**1**) in the presence of bis(trimethylsilyl)ethyne results in [6 + 2] cycloaddition of the alkyne to the cycloheptatriene ligand, yielding Cr(CO)₃{η^{4:2}-7,8-bis(trimethylsilyl)bicyclo[4.2.1]nona-2,4,7-triene} (**2**, 60% yield, Φ = 0.08), which upon oxidative decom-

position with Ce(IV) releases the organic cycloadduct, 7,8-bis(trimethylsilyl)bicyclo[4.2.1]nona-2,4,7-triene (**3**). Photocatalytic hydrogenation of 1,3,5-cycloheptatriene in the presence of complex **1** affords 1,3-cycloheptadiene. This process involves 1,6-addition of hydrogen, as demonstrated by using D₂.

Transition metal-mediated cycloaddition of unsaturated organic substrates to coordinated cyclopolyenes is of potential synthetic value as it provides access to oligocyclic adducts, which may be difficult to produce by using conventional multistep syntheses. Thus, in the presence of a Ziegler-type catalyst 1,3,5-cycloheptatriene (CHT) forms mixtures of various cycloadducts with alkynes and with dienes as well¹⁾. By contrast, a single product results from the photoreaction of Cr(CO)₃(η⁶-CHT) (**1**) with a conjugated diene (Scheme 1), which involves selective coupling between the terminal carbon atoms of the cycloheptatriene and the diene component. Following the pioneering work by Kreiter et al.²⁾ this process meanwhile has been exploited for the syntheses of a series of bicyclo[4.4.1]undecatriene derivatives with a wide range of different substituents on both of the two organic substrates^{3–6)}. A similar photoinitiated [6 + 2] cycloaddition to cycloheptatriene, but using a carbonyliron group as the metal template, has been observed with alkyne reactants⁷⁾.

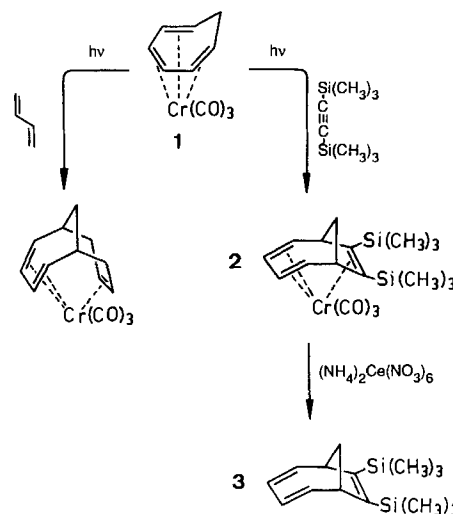
In this paper we report on the first example of a carbonylchromium-mediated cycloaddition of an alkyne to cycloheptatriene, which again is photochemically initiated and selectively involves the 1,6-positions of the cycloheptatriene ligand. Noteworthy, hydrogen undergoes an analogous selective 1,6-addition to cycloheptatriene in a photocatalytic process using Cr(CO)₃(η⁶-CHT) (**1**) as the catalyst.

Results and Discussion

UV-Vis irradiation of Cr(CO)₃(η⁶-1,3,5-cycloheptatriene) (**1**) in the presence of excess bis(trimethylsilyl)ethyne leads to the formation of a single 1:1 adduct (**2**) as a result of [6 + 2] cycloaddition of the alkyne to the metal-coordinated cycloheptatriene (Scheme 1). The composition and the struc-

ture of **2**, Cr(CO)₃{η^{4:2}-7,8-bis(trimethylsilyl)bicyclo[4.2.1]nona-2,4,7-triene}, are established on the basis of elemental analysis, mass, IR, and NMR spectroscopic data. Moreover, the oxidative decomposition of the complex with cerium(IV) ammonium nitrate liberates the organic ligand, 7,8-bis(trimethylsilyl)bicyclo[4.2.1]nona-2,4,7-triene (**3**), which is identified by a comparison of the ¹H- and ¹³C-NMR spectra with literature data¹⁾ and thus provides more compelling evidence of the identity of **2**.

Scheme 1



The infrared spectrum of **2** exhibits two strong bands in the CO stretching vibrational region (1968 and 1892 cm⁻¹) with relative intensities consistent with the expected *fac* structure of the Cr(CO)₃ moiety. Furthermore, the number of signals in both the ¹H- and ¹³C-NMR spectra of **2** and **3** indicate a structure with C_s symmetry.

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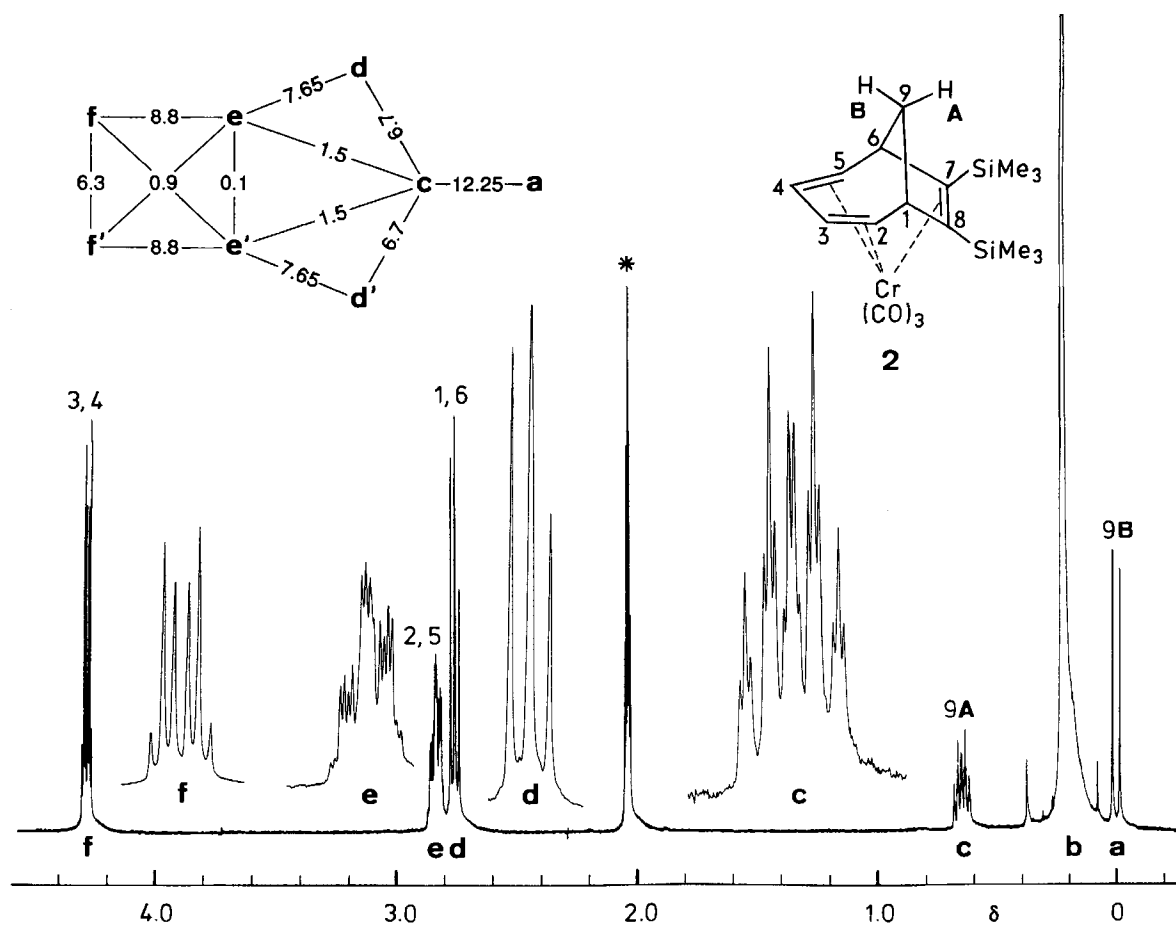


Figure 1. ¹H-NMR spectrum of **2** in [D₈]toluene at 295 K (the inset diagram shows the coupling constants in Hz; * = solvent peak)

In detail, the ¹H-NMR spectrum of **2** (Figure 1) exhibits five multiplets, with relative intensities of 1:1:2:2:2, and a singlet which is associated with the 18 protons of the two trimethylsilyl groups. The assignments and connectivities are based on selective decoupling experiments. Thus, saturation of 1-H/6-H converts the signals of 2-H/5-H and 3-H/4-H into a typical AA'XX' pattern, which is accordingly analyzed⁸). The chemical shifts of these four protons at δ = 4.28 and 2.83 are typical of a (η⁴-1,3-diene)metal moiety, thus providing further evidence of the structure of **2** shown in Scheme 1. Very different coupling patterns are observed for the two protons at the methylene bridge, 9-H_A and 9-H_B. The signal at higher field (9-H_B, δ = -0.02) appears as a doublet indicative of geminal coupling only. As can be seen from a molecular model, 9-H_B forms dihedral angles of ca. 90° with 1-H/6-H, which is in accord with the absence of vicinal coupling and thus establishes the above assignment. The 9-H_A signal (δ = 0.63) shows, in addition to the strong geminal coupling, further splittings due to the vicinal and long-range couplings listed in the inset of Figure 1. Compared with previous assignments of the respective signals in the ¹H-NMR spectra of the related 1,3-diene adduct complexes²⁻⁴), the positions of 9-H_A and 9-H_B are in the reversed order.

Variable-temperature ¹³C-NMR spectroscopy reveals the fluxional behaviour of **2**, which involves a CO site exchange

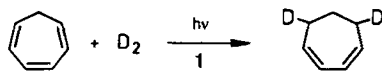
due to rotation of the organic ligand relative to the Cr(CO)₃ moiety. In addition to the 6 lines associated with the organic ligand (see Experimental), the ¹³C{¹H}-NMR spectrum at 243 K exhibits two signals in the metal carbonyl region at δ = 230.23 and 230.18 with a 2:1 intensity ratio. These latter two signals broaden upon raising the temperature and coalesce near 273 K. Line-shape analysis of the temperature-dependent spectra^{9,10}) yields the activation parameters for the CO scrambling process: ΔH[‡] = 57.5 kJ mol⁻¹ and ΔS[‡] = 18 J K⁻¹ mol⁻¹. This rotational barrier is somewhat higher than previously reported for the η⁶-cycloheptatriene complex **1**¹¹). Apparently, the homoconjugated η^{4,2}-triene ligand in **2** is more rigidly bound to the Cr(CO)₃ group than the fully conjugated cycloheptatriene in **1**. In continuation of this trend, the 1,3-diene adducts of **1** (cf. Scheme 1) with isolated mono- and diene units in the organic ligand are rigid up to ca. 370 K²).

The ¹H- and ¹³C-NMR spectra of the free organic ligand (**3**, see Experimental) are in reasonably good accord with published data¹). The coupling pattern in the ¹H-NMR spectrum (not previously analyzed in detail) is fairly similar to that in complex **2**, but naturally some of the chemical shifts differ significantly due to the absence of upfield coordination shifts which are effective in the metal complex. A comparison of ¹³C{¹H}-NMR spectra of **3** and **2** likewise reveals characteristic coordination shifts of the olefinic carbon atoms.

The isolated yield of **2** from preparative scale runs with broad-band irradiation through solidex glass ($\lambda > 280$ nm) does not exceed 60%, although monitoring the reaction by means of infrared spectroscopy shows almost complete disappearance of the starting material **1** after several hours of irradiation. In analytical scale experiments, aimed at the determination of quantum yields with monochromatic irradiation ($\lambda = 365$ nm), quantitative IR spectroscopy reveals similar deficits (20–40%) in the material balances. Apparently, some decomposition occurs with the formation of unidentified products, which renders it difficult to correctly account for internal light-filter effects¹²⁾ in the evaluation of quantum yields. Furthermore, it seems possible that some of the decomposed material is insoluble and thus may falsify the measurement of light absorption by the solution. As a result of this, we note that the quantum yields, evaluated for the disappearance of the starting material **1**, somewhat scatter between 0.060 and 0.084, whereby the latter value seems more reliable as it refers to an experiment with relatively low conversion of **1**.

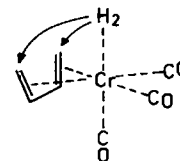
Besides the above stoichiometric reactions with bis(trimethylsilyl)ethyne, (η^6 -cycloheptatriene)Cr(CO)₃ (**1**) shows also some interesting photocatalytic properties with respect to the hydrogenation of cycloheptatriene. This process almost selectively yields 1,3-cycloheptadiene, as detected by gas chromatography. In a typical run with a catalyst-to-substrate ratio of 1:50 a turnover number of ca. 25 has been achieved. 1,4-Cycloheptadiene is not detectable in the reaction mixture by GC, but traces of cycloheptene are found. An analogous experiment with D₂ (Scheme 2) yields the di-deuterated product, C₇H₈D₂, as shown by mass spectrometry. From the NMR spectra of this product, which is isolated by preparative GC, we recognize that the hydrogenation occurs selectively in the 1,6-positions of 1,3,5-cycloheptatriene. In the ¹H-NMR spectrum the intensity of the signal at $\delta = 2.11$ for the two CH₂ groups in the 5,7-positions is reduced by ca. 50%, thus indicating that two of these four methylene protons are replaced by deuterium atoms. Accordingly, the ¹³C{¹H}-NMR spectrum of [5,7-D₂]-1,3-cycloheptadiene shows a triplet ($\delta = 31.69$, ¹J_{C-D} = 19.7 Hz) of the CHD groups in the 5,7-positions, the individual lines of which exhibit further, weak triplet splitting (1.0 Hz) due to long-range C–D coupling. Similarly weak long-range C–D couplings are observed for the CH₂ group (quintet) and the olefinic carbon atoms (triplets). Incorporation of deuterium into the other positions of 1,3-cycloheptadiene, if occurring at all, is below the NMR detection level.

Scheme 2



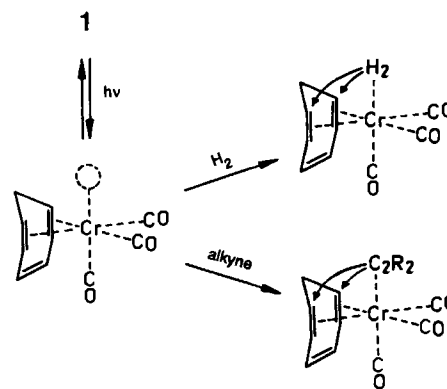
The selectivity of this process parallels that of the photocatalytic *cis*-1,4-hydrogenation of conjugated dienes^{13–15)}, which involves Cr(CO)₃(η^4 -diene) as the precursor of the actual catalyst. Photolytic CO dissociation generates *fac*-

Cr(CO)₃(η^4 -diene)¹⁶⁾ with a vacant coordination site suitable for binding H₂ and transferring it to the 1,4-positions of the diene. The analogous *fac*-Cr(CO)₃(η^4 -NBD) species^{17–19)} has been invoked as an intermediate in the formation of nortricyclene, the major product of the photocatalytic hydrogenation of norbornadiene.



By analogy, *fac*-Cr(CO)₃($\eta^{2,2}$ -1,3,5-cycloheptatriene) is an attractive candidate for the active species in the photocatalytic hydrogenation of cycloheptatriene. Thus, the proposed mechanism (Scheme 3) involves the photoinduced $\eta^6 \rightarrow \eta^{2,2}$ hapticity change of the metal-coordinated 1,3,5-cycloheptatriene, whereupon a hydrogen molecule occupies the resulting vacant coordination site and is subsequently transferred to the 1,6-positions of the cycloheptatriene ligand. Displacement of 1,3-cycloheptadiene by another substrate molecule would complete the catalytic cycle with the Cr(CO)₃ group as the repeating unit.

Scheme 3



A similar mechanism could also apply to the photoinitiated reaction of **1** with bis(trimethylsilyl)ethyne (Scheme 1). The incoming alkyne could occupy the vacant coordination site in the *fac*-Cr(CO)₃($\eta^{2,2}$ -1,3,5-cycloheptatriene) species, followed by cycloaddition of the two organic ligands within the coordination sphere of the complex (Scheme 3). This mechanism implicates competition of the intramolecular $\eta^{2,2} \rightarrow \eta^6$ reverse hapticity change with a bimolecular step, viz., the coordination of the alkyne. This could explain the relatively low quantum yield (ca. 0.08) observed for the conversion of **1** into **2** even in the presence of a large excess of bis(trimethylsilyl)ethyne.

However, we must not fail to notice that **1** is susceptible to photosubstitution of CO by other ligands²⁰⁾. Thus, an alternative mechanism cannot be ruled out, which involves initial photolytic CO detachment from the starting complex **1**, followed by coordination of the alkyne, its cycloaddition to cycloheptatriene, and re-coordination of the CO liberated

in the first step. Indeed, in a recent study²¹⁾ complex **1** was shown to undergo two primary photoreactions, release of CO and $\eta^6 \rightarrow \eta^4$ hapticity change, but only the former process was concluded to be involved in the photoinduced addition of 1,3-dienes to **1** (Scheme 1).

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Experimental

Reactions and manipulations of the organometallic compounds were performed under argon and in argon-saturated solvents. $\text{Cr}(\text{CO})_3(\eta^6\text{-}1,3,5\text{-cycloheptatriene})$ (**1**) was prepared according to the published procedure²²⁾; UV-Vis (*n*-hexane): $\lambda_{\text{max}} = 279 \text{ nm}$ ($\epsilon = 5910 \text{ l mol}^{-1} \text{ cm}^{-1}$), 346.5 (4200), 385 (sh, 2690), and 497 (br, 420). Bis(trimethylsilyl)ethyne (Fluka), hexacarbonylchromium (Merck), and deuterium gas (Promochem) were used as received. Cycloheptatriene (Fluka, techn.) was purified by distillation prior to use. — UV-Vis: Bruins Instruments Omega 10. — IR: Perkin-Elmer 881. — NMR: Bruker AC 270 and AM 400 (internal standards: $[\text{D}_6]\text{benzene}$ or $[\text{D}_8]\text{toluene}$ at $\delta = 7.15$ or 2.03 for ^1H NMR and at $\delta = 128.0$ or 20.4 for ^{13}C NMR). — MS: Hewlett-Packard MSD and Finnigan-MAT 311A.

1) $\{\eta^{4,2-7,8}\text{-Bis}(\text{trimethylsilyl})\text{bicyclo}[4.2.1]\text{nona-}2,4,7\text{-triene}\}\text{tricarboonylchromium}$ (**2**)

1a) *Preparative-Scale Procedure*: Complex **1** (0.80 g, 3.5 mmol) and bis(trimethylsilyl)ethyne (2.0 g, 12 mmol) in *n*-pentane (300 ml) were irradiated at ambient temp. for 5 h by using a water-cooled immersion lamp vessel (solidex glass, $\lambda > 280 \text{ nm}$) and a Philips HPK 125-W mercury lamp. The solution was evaporated to ca. 20 ml, filtered and cooled to dry-ice temperature, whereupon red crystals precipitated. Recrystallization from *n*-pentane (20 ml) yielded 0.84 g (60%) of **2** (red crystals, m.p. 154°C). — MS: m/z 398 $[\text{M}^+]$, 342 $[\text{M}^+ - 2 \text{ CO}]$, 314 $[\text{M}^+ - 3 \text{ CO}]$, and other, more prominent peaks resulting from fragmentation of the organic ligand. — IR (*n*-hexane): $\tilde{\nu} = 1968$ and 1892 cm^{-1} (ν_{CO} bands). — UV-Vis (*n*-hexane): $\lambda_{\text{max}} = 306 \text{ nm}$ ($\epsilon = 3520 \text{ l mol}^{-1} \text{ cm}^{-1}$), 369.5 (4810), 421 (3860). — ^1H NMR (400.1 MHz, $[\text{D}_8]\text{toluene}$, 295 K): $\delta = 4.28$ (f: 3-H/4-H), 2.83 (e: 2-H/5-H), 2.75 (d: 1-H/6-H), 0.63 (c: 9- H_A), 0.23 (b: CH_3), and -0.02 (a: 9- H_B); coupling constants are listed in Figure 1, which also shows the numbering scheme. — $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, $[\text{D}_6]\text{benzene}$, 243 K): $\delta = 230.23$ (2 CO), 230.18 (CO), 92.19 (C-3/C-4), 73.02 (C-7/C-8), 63.85 (C-2/C-5), 45.57 (C-1/C-6), 34.71 (C-9), 1.22 (CH_3); the assignments are supported by DEPT experiments.

$\text{C}_{18}\text{H}_{26}\text{CrO}_3\text{Si}_2$ (398.6) Calcd. C 54.24 H 6.58 Cr 13.05 Si 14.09
Found C 54.29 H 6.61 Cr 13.13 Si 14.15

1b) *Quantum Yields*: Irradiations of 3.0-ml aliquots of a stock solution of **1** (ca. 4 mM) and bis(trimethylsilyl)ethyne (ca. 200 mM) in *n*-hexane were carried out at $25 \pm 1^\circ\text{C}$ in quartz cuvettes ($d = 1 \text{ cm}$), using a Hanovia 1000-W Hg-Xe lamp in connection with a Schoeffel Instruments GM 252 grating monochromator and a modified version of an electronically integrating actinometer²³⁾, which was calibrated by ferri oxalate actinometry²⁴⁾; light intensities were of the order of $5 \cdot 10^{-6} \text{ Einstein min}^{-1}$ absorbed by the 3.0-ml sample. Concentrations of **1** and **2** were determined by means of quantitative IR spectroscopy (PE 881 spectrometer operating with slit program 3 and filter 4; IR cell with CaF_2 windows, $d = 493.8 \mu\text{m}$) using the following molar absorbance data of **1** ($\epsilon = 5620 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 1991 cm^{-1} , 4990 at 1930 , 4490 at 1907) and **2** ($\epsilon = 8850 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 1968 cm^{-1} , 9730 at 1892). Quantum yields

(disappearance of **1**) were evaluated with internal light filter corrections¹²⁾ (molar absorbance data at 365 nm : $\epsilon = 3540 \text{ l mol}^{-1} \text{ cm}^{-1}$ for **1**, $\epsilon = 4730$ for **2**) after 12, 22, 35, and 60% conversion of **1**: $\Phi = 0.084, 0.068, 0.060$, and 0.065 , respectively.

2) *7,8-Bis(trimethylsilyl)bicyclo[4.2.1]nona-2,4,7-triene* (**3**): Complex **2** (0.08 g) in $[\text{D}_8]\text{toluene}$ (0.5 ml) was stirred with an aqueous solution (2 ml) of cerium(IV) ammonium nitrate (0.3 g), whereupon the red colour of **2** disappeared. The organic phase containing **3** was separated and dried with anhydrous calcium chloride prior to recording the NMR spectra. — ^1H NMR (400.1 MHz, $[\text{D}_8]\text{toluene}$, 295 K): $\delta = 5.91$ (e: 2-H/5-H), 5.69 (f: 3-H/4-H), 3.15 (d: 1-H/6-H), 1.75 (c: 9- H_A), 1.45 (a: 9- H_B), 0.16 (b: CH_3); $J_{ac} = -11.4$, $J_{ad} = J_{ad'} = 0.2$, $J_{cd} = J_{cd'} = 6.8$, $J_{ce} = J_{ce'} = 1.2$, $J_{de} = J_{de'} = 7.3$, $J_{ee'} = 0.6$, $J_{ef} = J_{ef'} = 11.25$, $J_{ef''} = J_{ef'''} = 0.85$, $J_{ff} = 7.25 \text{ Hz}$; the numbering scheme follows that of **2** in Figure 1. — $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, $[\text{D}_8]\text{toluene}$, 293 K): $\delta = 146.64$ (C-7/C-8), 137.82 (C-3/C-4), 124.42 (C-2/C-5), 52.37 (C-1/C-6), 30.37 (C-9), and 1.91 (CH_3); the assignments were supported by DEPT experiments. — After recording the NMR spectra the solvent was removed in vacuum leaving behind an oily film of **3**, the mol. mass of which was determined by MS: m/z 262 $[\text{M}^+]$.

3) *Photocatalytic Hydrogenation of 1,3,5-Cycloheptatriene*: A solution of complex **1** (0.030 g, 0.13 mmol) and 1,3,5-cycloheptatriene (0.629 g, 6.84 mmol) in *n*-hexane (10 ml; containing 0.503 g of *n*-octane as the internal GC standard) was placed in a cylindrical cuvette ($l = 1 \text{ cm}$, $d = 5 \text{ cm}$), which was attached to a gas burette filled with H_2 . The solution was vigorously stirred and irradiated through a Schott (Mainz) OG 515 cut-off filter ($\lambda \geq 500 \text{ nm}$) by using an Osram XBO 1600 W Xe high-pressure lamp. After ca. 6 h the take-up of H_2 ceased (ca 3.3 mmol). GC analysis (Varian F 20; steel capillary column, 100 m, squalane, 80°C , 1.6 atm Ar, 0.1 μl , FID) of the volatile components stripped off in vacuum showed the formation of 1,3-cycloheptadiene (0.348 g, 54%) and cycloheptene (0.015 g, 2%) and the presence of unreacted 1,3,5-cycloheptatriene (0.250 g, 40%), as identified by a comparison with authentic samples. — A similar photocatalytic run, but on a larger scale and by using D_2 instead of H_2 , yielded $[\text{5,7-}\text{D}_2\text{-}1,3\text{-cycloheptadiene}]$ which was isolated (98.5% purity) by means of preparative gas chromatography (Gerstel AMPG, steel column, 6 m \times 40 mm, 20% DC 200 on Chromosorb P, 100°C , N_2 , 11.5 ml) and characterized as follows. — MS: m/z 96 $[\text{M}^+]$. — ^1H NMR (270.1 MHz, $[\text{D}_6]\text{benzene}$, 300 K): $\delta = 5.77$ (m, 4H), 2.11 (m, 2H), 1.66 (m, 2H); authentic sample of 1,3-cycloheptadiene: $\delta = 5.70$ (m, 4H), 2.16 (m, 4H), 1.68 (m, 2H). — $^{13}\text{C}\{^1\text{H}\}$ NMR (67.9 MHz, $[\text{D}_6]\text{benzene}$, 297 K): $\delta = 133.55$ (t, 1.1 Hz, C-1/C-4), 125.65 (t, 1.0 Hz, C-2/C-3), 31.69 (tt, $^1J_{\text{C,D}} = 19.2, 1.0 \text{ Hz}$, C-5/C-7), 25.67 (quint, 0.6 Hz, C-6); authentic sample of 1,3-cycloheptadiene: $\delta = 133.53, 125.62, 32.22, 25.99$; the gated-decoupled spectrum of $[\text{5,7-}\text{D}_2\text{-}1,3\text{-cycloheptadiene}]$ showed $^1J_{\text{C,H}}$ at C-1/C-4 (d, 154 Hz), C-2/C-3 (d, 154 Hz), C-5/C-7 (d, 125 Hz), and C-6 (t, 126 Hz) in addition to the complicated pattern of C—D and long-range C—H couplings.

CAS Registry Numbers

1: 12125-72-3 / **2**: 136445-22-2 / **3**: 88061-83-0 / $(\text{H}_3\text{C})_3\text{SiC}\equiv\text{CSi}(\text{CH}_3)_3$: 14630-40-1 / 1,3,5-cycloheptatriene: 544-25-2 / 1,3-cycloheptadiene: 4054-38-0 / cycloheptene: 628-92-2 / $[\text{5,7-}\text{D}_2\text{-}1,3\text{-cycloheptadiene}]$: 136445-21-1

* Dedicated to Professor *Paul Binger* on the occasion of this 60th birthday.

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