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Photocatalytic Hydrosilylation of Conjugated Dienes with Triethylsilane in the Presence of $Cr(CO)_6$

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Chromium carbonyl photocatalyzed hydrosilylation of 1,3-butadiene, *trans*-1,3-pentadiene, 2,3-dimethyl-1,3-butadiene, 2-methyl-1,3-butadiene, *trans*-2-methyl-1,3-pentadiene, and 1,3-cyclohexadiene with triethylsilane yields the *cis*-1,4-adducts, 1-(triethylsilyl)-2-butene derivatives, as the main products which have been isolated by distillation or preparative GC and fully characterized by NMR spectroscopy. The proposed mechanism involves the initial conversion of $Cr(CO)_6$ into $Cr(CO)_4(\eta^4\text{-1,3-diene})$ followed by a further photolytic CO substitution by triethylsilane forming a $Cr(CO)_3(H)(SiEt_3)(\eta^4\text{-1,3-diene})$ intermediate. Experiments with $D{-}SiEt_3$ lead to the conclusion that reversible addition of the hydride to the diene with formation of an η^3-enyl intermediate occurs prior to the irreversible silyl transfer to the organic moiety. The 1,4-hydrosilylation adduct is then replaced by new substrates to complete the catalytic cycle.

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Introduction

The hydrosilylation of unsaturated organic substrates is widely used for the production of organosilicon compounds.[1−3] $Alkyl{-}SiR_3$ products are obtained from the reaction of $H{-}SiR_3$ with an alkene in the presence of various transition metal catalysts. The mechanism proposed by Harrod and Chalk[4] involves the formation of a $[M](\eta^2\text{-alkene})(SiR_3)(H)$ type species which then undergoes insertion of the alkene into the M−H bond, followed by reductive elimination of the $alkyl{-}SiR_3$ product. An alternative route via a $(2\text{-}R_3Si{-}alkyl)[M](H)$ intermediate, generated by insertion of the alkene into the M−Si bond, and subsequent C−H reductive elimination seems also likely.[5] Moreover, β-hydrogen abstraction from the silylated alkyl group rationalizes the concurrent formation of $alkenyl{-}SiR_3$ products observed at higher alkene:$H{-}SiR_3$ substrate ratios,[5] whereby the excess alkene serves as the hydrogen acceptor. Meanwhile, alkene insertion into a M−Si bond is recognized as a fairly common process which plays a key role in catalytic hydrosilylation processes employing, for example, the $Co(CO)_3$[6] or Rh(Cp)(Et)[7] groups as the repeating unit in the catalytic cycle.

The importance of hydrosilylation has stimulated us to look closely into one of the hydrosilylation methods, the photocatalytic hydrosilylation of diolefins, using group 6 metal carbonyl complexes. In a preliminary communication[8] we described a specific investigation into the photocatalytic 1,4-hydrosilylation of 1,3-butadiene (**1**) with triethylsilane using hexacarbonylchromium(0) and hexacarbonylmolybdenum(0) as catalysts. The reaction yielded exclusively the *cis*-1,4-adduct, *cis*-1-(triethylsilyl)-2-butene (**11**), in accordance with previous results[9] obtained in the reactions of various acyclic conjugated dienes with trimethylsilane, triethoxysilane, and diphenylsilane. However, details for the isolation and characterization of the adducts had not been given there, and triethylsilane was only briefly mentioned in the reaction with *trans*-1,3-pentadiene.

In this paper we report in full detail on the photocatalytic 1,4-hydrosilylation of 1,3-butadiene (**1**), *trans*-1,3-pentadiene (**2**), 2,3-dimethyl-1,3-butadiene (**3**), 2-methyl-1,3-butadiene (**4**), *trans*-2-methyl-1,3-pentadiene (**5**), and 1,3-cyclohexadiene (**6**) with triethylsilane. The photocatalytic 1,4-addition of $H{-}SiEt_3$ to **6** is the first example of the group 6 metal carbonyl photocatalyzed hydrosilylation of a conjugated cyclic diene. Emphasis is placed on both the preparative and mechanistic aspects.

Results and Discussion

Preparative Results and Characterization of Products. The reaction of 1,3-butadiene (**1**) with triethylsilane in the presence of hexacarbonylchromium(0) or hexacarbonylmolybdenum(0) under continuous irradiation yields exclusively the *cis*-1,4-adduct, *cis*-1-(triethylsilyl)-2-butene (**11**), eq 1.

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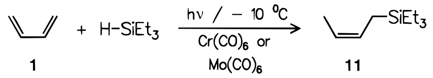
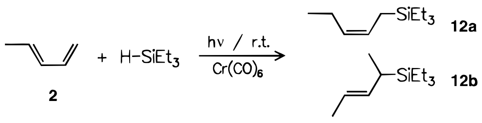


(1)

In our preliminary report[8] the assignment of the *cis*-geometry for **11** was based on the NMR spectral data of the isolated product. The value of 10.6 Hz, observed for the coupling between the olefinic protons, is compelling evidence for the *cis*-geometry of **11**. Values in the range 10.4−12.0 Hz have been reported for the trimethylsilyl analogue of **11**, while *trans*-geometries result in higher values (15−18 Hz) for the *trans-vicinal* olefinic coupling.[10,11] This geometry is also confirmed by the ^{13}C-NMR chemical shifts of C-1 (13.20 ppm) and C-4 (12.80 ppm) of the compound **11**. These values would be at too high a field for two carbon atoms *trans* to each other. It is known that *cis*-carbon atoms shield each other via a γ shielding effect exerted by the protons of a carbon at a γ position to the one being considered.[12] Allylic carbons of *cis*-butene resonate at 10.0 ppm, while those of *trans*-butene appear at 17.3 ppm, shifted about 7 ppm downfield with respect to those of the *cis*-isomer.

Continuous irradiation of *trans*-1,3-pentadiene (**2**), triethylsilane, and hexacarbonylchromium(0) (in a molar ratio of 50:50:1) in *n*-hexane solution results in nearly quantitative hydrosilylation of the diene, as monitored by GC. Two isomeric hydrosilylation products, **12a**,**b**, eq 2, are formed in ca. 25:1 ratio as detected by means of GC−MS. A third isomer in trace amount was detected by GC−MS in a large scale run (0.15 mol), from which pure samples of the isomers **12a**,**b** were isolated by means of preparative GC.



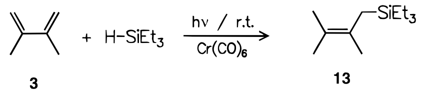
(2)

These two hydrosilylation products are fully characterized by ^{1}H- and ^{13}C-NMR spectroscopy. This way, the main product **12a** is identified as *cis*-1-(triethylsilyl)-2-pentene, which results from *cis*-1,4-hydrosilylation with attachment of the triethylsilyl group to C-1 of the diene. The coupling between the two olefinic protons (^{3}J = 10.3 Hz) is indicative of the *cis*-geometry of **12a**. The minor product **12b** is similarly characterized as *trans*-4-(triethylsilyl)-2-pentene, based on the larger coupling between the two olefinic protons (^{3}J = 15.2 Hz). This latter finding contrasts with the previously reported[9] *cis*-structure of the analogous product obtained with trimethylsilane.

The ^{13}C-NMR data of **12a**,**b** are consistent with the above assignments. The allylic carbon atoms of **12a** resonate at δ = 13.49 (C-1) and 20.77 ppm (C-4), which compares well with the respective data of **11**, allowing for a ca. 7 ppm downfield shift of C-4 due to the attached methyl group. However, the chemical shifts of the allylic carbon atoms of **12b** (C-1, 18.27 ppm; C-4, 23.57 ppm) reflect the *trans*-geometry at the olefinic unit.

The minor isomer **12b** may be considered either as the result of 1,2-hydrosilylation, with attachment of the triethylsilyl group to C-2 of the diene or as a *trans*-1,4-hydrosilylation product, with attachment of the triethylsilyl moiety to C-4 of the diene. Unequivocal decision in favor of the 1,2-hydrosilylation comes from the reaction of *trans*-1,3-pentadiene (**2**) with triethylsilane-d_1 which yields the D-labeled products **12a#** and **12b#** (see eq 9). The ^{13}C{^{1}H}-NMR spectrum of **12b#** shows that only the methyl group (C-5) next to the SiEt$_3$ substituent carries the D-label.

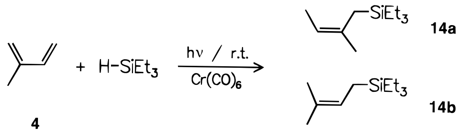
The reaction of 2,3-dimethyl-1,3-butadiene (**3**) with triethylsilane in the presence of the carbonylchromium catalyst under continuous irradiation yields one product, 1-(triethylsilyl)-2,3-dimethyl-2-butene (**13**), resulting from 1,4-hydrosilylation, eq 3. Monitoring of the reaction by GC shows nearly quantitative conversion of the starting materials into the product. However, due to some loss of material in the workup procedure the yield of the isolated product after purification by distillation amounts to ca. 40%.



(3)

The product **13** is unambiguously identified by NMR spectroscopy. The ^{1}H-NMR spectrum of **13** shows a singlet at δ = 1.58 ppm for the allylic methylene protons and three other singlets at δ = 1.626, 1.634, and 1.644 ppm for the allylic methyl groups. The absence of any ^{1}H-NMR signals in the olefinic region eliminates alternative structures which would result from 1,2-addition of triethylsilane. Accordingly, the ^{13}C{^{1}H}-NMR spectrum exhibits four signals at δ = 20.65, 20.90, 21.29, and 21.40 ppm for the allylic carbons and two signals at δ = 120.84 and 125.68 ppm for the olefinic carbons.

Two 1,4-addition products, *cis*-1-(triethylsilyl)-2-methyl-2-butene (**14a**) and 1-(triethylsilyl)-3-methyl-2-butene (**14b**), are formed from the photocatalytic reaction of isoprene (**4**) with triethylsilane in the presence of hexacarbonylchromium(0), eq 4, in 76% and 22% yields, respectively, as determined by GC. Pure samples of both products are separated by distillation which, however, goes along with some loss of material.



(4)

Both isomers are unequivocally identified by NMR spectroscopy. The observation of only one ^{1}H-NMR signal for the olefinic protons in both **14a** and **14b** at δ = 5.06 and 5.16 ppm, respectively, is indicative of 1,4-addition in both cases. The strong coupling of the olefinic proton with one of the two methyl groups ($^{3}J_{3,4}$ = 6.8 Hz) not only identifies **14a** as the product in which the triethylsilyl moiety is attached to C-1 of **4** but also allows an unequivocal assignment of the two methyl groups in this product. In the case of **14b**, it is the silylated CH$_2$ group which shows the corresponding coupling ($^{3}J_{1,2}$ = 8.4 Hz) with the olefinic proton. The assignment of the *cis*-structure of **14a** is based on the observation that C-4 resonates at δ = 14.15 ppm, not far from C-1 (δ = 17.87 ppm), which compares well with the respective data of C-1 (δ = 13.82 ppm) and C-4 (δ =

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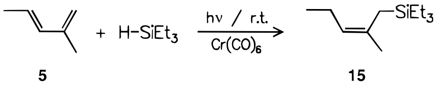
17.70 ppm) in **14b**. The fact that C-5 resonates at $\delta = 26.47$ ppm in **14a** and $\delta = 25.92$ ppm in **14b**, i.e., at a lower field than C-4, can be attributed to the absence of the γ shielding effect, which is present between the C-1 and C-4 in both isomers.

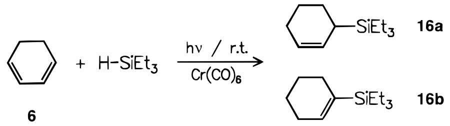
The photocatalytic reaction of *trans*-2-methyl-1,3-pentadiene (**5**) with triethylsilane, eq 5, yields only one product, *cis*-1-(triethylsilyl)-2-methyl-2-pentene (**15**), which is isolated by distillation and identified NMR spectroscopy.



(5)

The ^{1}H-NMR spectrum of **15** gives also only one signal in the olefinic region which eliminates any possibility of a 1,2-addition. The coupling pattern of H-5 and H-4 is indicative of an ethyl moiety, which in turn implies that in the 1,4-hydrosilylation the triethylsilyl unit is attached to the terminal carbon C-1 of the diene. In the ^{13}C-NMR spectrum of **15**, one observes the signals of the methyl groups C-5 and C-6 at $\delta = 14.59$ and 26.41 ppm, respectively. The large difference between their chemical shifts is ascribed to the deshielding effect exerted by the olefinic carbon C-2 on C-6. The *cis*-geometry of **15** is assigned by the similar chemical shift of C-4 ($\delta = 22.04$ ppm) compared with that in **12a** ($\delta = 20.77$ ppm).

The photocatalytic reaction of 1,3-cyclohexadiene with an equimolar amount of triethylsilane, eq 6, yields



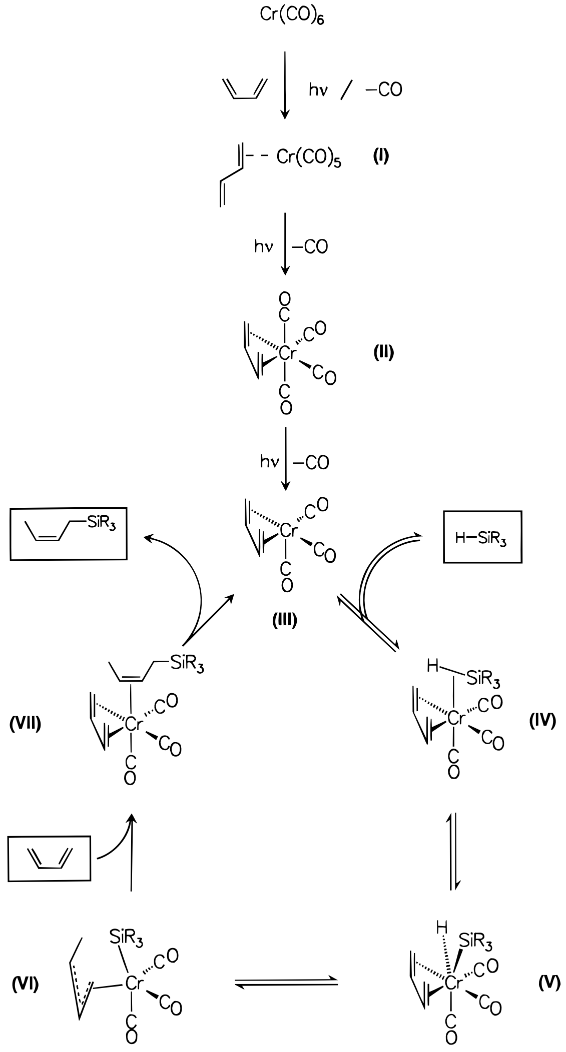
(6)

3-(triethylsilyl)-1-cyclohexene (**16a**) as the main product, anticipated to be formed from 1,4-hydrosilylation. Unexpectedly, however, a second isomer, 1-(triethylsilyl)-1-cyclohexene (**16b**), is found, the formation of which can only be rationalized in terms of a double-bond migration subsequent to the initial hydrosilylation.

Both the ^{1}H- and ^{13}C-NMR spectra are consistent with the assigned structure of **16a**. An INADEQUATE spectrum clearly establishes the sequence $=CHCH_2CH_2CH_2CH(SiEt_3)CH=$, thus ruling out an alternative structure, 4-(triethylsilyl)-1-cyclohexene, which cannot be excluded on the basis of the ^{1}H- and ^{13}C-NMR data alone. The structure of **16b** is evident from the observation of only one olefinic proton signal (H-2) in the ^{1}H-NMR spectrum and only one proton-coupled olefinic carbon atom (C-2) in the ^{13}C-NMR spectrum.

Mechanistic Aspects. In all cases IR spectroscopic monitoring of the reaction shows the initial conversion of $Cr(CO)_6$ into the respective $Cr(CO)_4(\eta^4$-1,3-diene) (**II**), presumably via a $Cr(CO)_5(\eta^2$-1,3-diene) intermediate (**I**), Scheme 1. The photochemical formation of complexes of the type **I** and **II** from group 6 hexacarbonylmetal(0) and dienes is known,[13-15] and the role of **II** or $Cr(CO)_4$($\eta^{2:2}$-norbornadiene) as the precursor to the active

Scheme 1



catalyst in the photocatalytic hydrogenation of conjugated dienes[16] or norbornadiene[17] is well established. Expectedly, the hydrosilylation of 1,3-butadiene under continuous irradiation in the presence of $Cr(CO)_4(\eta^4$-1,3-butadiene) as catalyst instead of hexacarbonylchromium(0) gives the same result.

As outlined in Scheme 1, photolytic detachment of CO from **II** should provide the entry to the catalytic cycle by creating the vacant coordination site on the transition metal center required for binding the silane prior to its transfer onto the diene ligand. The $Cr(CO)_3(\eta^4$-1,3-diene) fragments of type **III**, photogenerated in low-temperature matrices, were shown to possess a *fac*-$Cr(CO)_3$ skeleton.[18] This implies that the vacant

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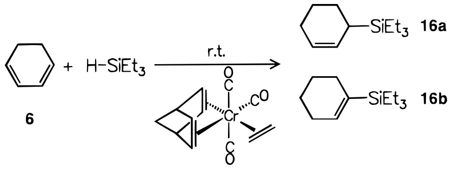
coordination site is in an axial position, sterically well suited for mediating the 1,4-addition of H−SiR$_3$ to the diene.

The analogous hydrogenation of a diene is likely to involve the concerted transfer of H$_2$ via a nonclassical η^2-H$_2$ complex,[19] in accordance with the results of PHIP experiments.[20] By contrast, the hydrosilylation proceeds in a stepwise fashion, as will be demonstrated below. Reversible transfer of the hydrogen atom occurs prior to the irreversible attachment of the silyl group to the diene substrate. With this information in mind it seems reasonable to postulate, analogous to the Chalk−Harrod mechanism,[4] a reversible hydride transfer involving the two intermediates of the type Cr(CO)$_3$(η^4-1,3-diene)(H)(SiR$_3$) (**V**) and Cr(CO)$_3$(η^3-enyl)(SiR$_3$) (**VI**). However, regarding the initial coordination of the silane to the vacant coordination site at the metal, formation of a nonclassical η^2-(H−SiR$_3$) complex of type Cr(CO)$_3$(η^4-1,3-diene)(η^2-H-SiR$_3$) (**IV**), prior to the oxidative addition, may be envisaged.[21,22] The binding of H−SiEt$_3$ to the Cr(CO)$_5$ fragment, for example, has been investigated by means of photoacoustic calorimetry.[23] The results indeed suggest that the silane undergoes incomplete oxidative addition to the metal with formation of a three-center two-electron bond. This notion is in accord with the trends observed in the kinetics of silane displacement by CO from a series of Cr(CO)$_5$(silane) species, generated by flash photolysis of Cr(CO)$_6$.[24]

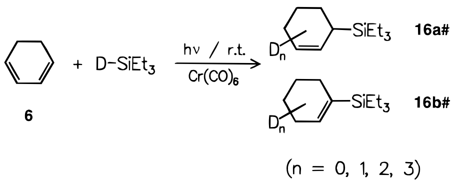
The previously reported iron compounds of the type Fe(CO)$_3$(η^3-*anti*-butenyl)(trialkylsilyl)[11] may be considered precedent to the formation of the Cr(CO)$_3$(η^3-enyl)(SiR$_3$) species of type **VI**. The subsequently occurring transfer of SiR$_3$ to the η^3-enyl ligand and takeup of a new diene substrate molecule (→**VII**), release of the (trialkylsilyl)butene product (→**III**), and coordination of another H−SiR$_3$ molecule (→**IV**) would then complete the catalytic cycle.

The catalytic process as such does not require the action of light, once the active species containing the repeating Cr(CO)$_3$ unit has been generated. This is evident from experiments without irradiation in which Cr(CO)$_3$(η^4-norbornadiene)(η^2-ethene), photogenerated from Cr(CO)$_4$(η^4-norbornadiene) in ethene-saturated solution at −50 °C,[25] serves as a source of the active catalyst. The ethene complex was previously employed to simulate the generation of the active catalyst in the photocatalytic hydrogenation[25] and hydrosilylation[26] of norbornadiene, whereby the weakly bound ethene plays the role of a stand-in ligand which is readily lost at ambient temperature. This way, hundreds of hydrosilylation turnovers have been achieved in the dark by warming this complex to ambient temperature in the presence of a sufficiently large excess of norbornadiene and triethylsilane.[26] In the present study, an analogous experiment has been carried out with a conjugated diene, 1,3-cyclohexadiene (**6**), which reacts with triethylsilane in the presence of a catalytic amount of Cr(CO)$_3$(η^4-norbornadiene)(η^2-ethene) to yield the two (triethylsilyl)cyclohexene isomers **16a**,**b**, eq 7. A small amount of (triethylsilyl)norbornene is also formed, thus indicating that the norbornadiene is removed, at least in part, by hydrosilylation from the Cr(CO)$_3$ unit, which then is available for the catalytic hydrosilylation of 1,3-cyclohexadiene. It is noteworthy that the ratio of the two products **16a**,**b** (ca. 6:1) is similar to that obtained in the photoinduced catalysis, eq 6. This finding indicates that the same catalytic cycle is operative in either case, thus confirming the proposed role of the Cr(CO)$_3$ group as a thermally repeating unit in the photocatalytic process.



(7)

Evidence for the stepwise mechanism of the hydrosilylation with reversible hydride transfer, proposed in Scheme 1, comes from experiments using deuterium-labeled silane, D−SiEt$_3$, instead of H−SiEt$_3$. The reaction of 1,3-cyclohexadiene (**6**) with D−SiEt$_3$ was initially designed to confirm the 1,4-addition of the trialkylsilane to the conjugated diene. However, quite unexpectedly, IR spectroscopy reveals that extensive D/H exchange between the two substrates takes place. Concurrent with the disappearance of the Si−D stretching band at 1534 cm^{-1}, a new feature grows in at the position of the Si−H stretching vibration at 2102 cm^{-1}, which then both diminish (and finally vanish) upon completion of the photocatalytic process. This observation prompted us to monitor, by means of GC−MS, the deuterium contents of the substrates and of the products during the course of the catalytic reactions, eq 8.



(8)

The results of such an experiment, performed with a Cr(CO)$_6$/1,3-cyclohexadiene/D−SiEt$_3$ molar ratio of 1:50:50, are listed in Table 1. First of all we note that, in accordance with the IR spectroscopic observations, the deuterium content of triethylsilane gradually decreases from 100% to 0% while the conversion approaches 75%. However, no deuterium incorporation is found for the free 1,3-cyclohexadiene at any stage of the reaction, whereas the two silylated products, denoted at **16a#** and

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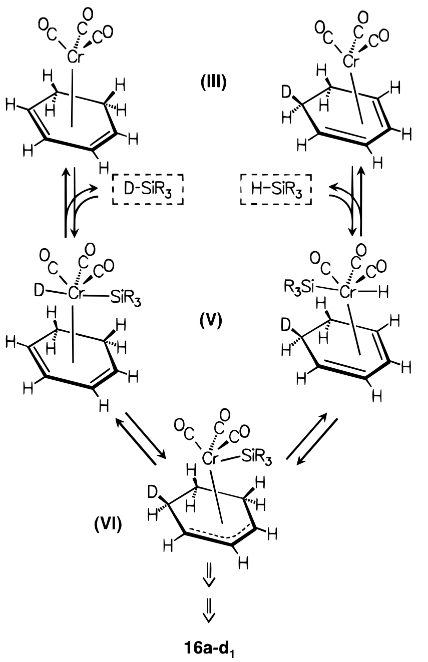
Table 1. Photocatalytic Reaction of 1,3-Cyclohexadiene (6, 75 mmol) with Triethylsilane-d_1 (75 mmol) in the Presence of $Cr(CO)_6$ (1.5 mmol): Conversion,[a] Yields of 16a# and 16b#,[a] and Abundance of the Isotopomers[b]

conversion (%)	triethylsilane		16a#					16b#				
	d_0 (%)	d_1 (%)	yield (%)	d_0 (%)	d_1 (%)	d_2 (%)	d_3 (%)	yield (%)	d_0 (%)	d_1 (%)	d_2 (%)	d_3 (%)
0	0	100	0					0				
8.8	10	90	8.2	3	21	36	40	0.5	5	23	34	38
21.7	25	75	20.2	5	27	34	34	1.5	4	29	33	34
47.8	50	50	36.1	12	31	32	25	3.2	11	29	34	26
59.6	75	25	51.3	17	32	30	21	5.1	16	29	32	23
64.4	80	20	54.8	22	30	29	19	5.6	18	32	28	22
75.5	100	0	67.6	27	32	26	15	7.7	22	31	27	20

[a] Based on the initial amount of substrates. [b] Free 1,3-cyclohexadiene remains undeuterated throughout.

Scheme 2



16b#, carry up to three D-labels from the very beginning. Noticeably, the triply deuterated products predominate at the initial stage of the catalytic reaction but decrease with the diminishing deuterium content of the D/H−$SiEt_3$ substrate. This leads to the conclusion that the coordinated 1,3-cyclohexadiene, prior to the hydrosilylation, rapidly incorporates up to two D-labels delivered from D−$SiEt_3$ with simultaneous release of H−$SiEt_3$. This way, the deuterium content of the resulting hydrosilylation products, ranging from d_0 through d_3, is rationalized in terms of the addition of D/H−$SiEt_3$ to the coordinated d_0-, d_1-, and d_2-1,3-cyclohexadiene. These findings confirm the concept of the stepwise course of events in the hydrosilylation process, the hydrogen atom being transferred prior to the silyl group. Furthermore, the liberation of H−$SiEt_3$ implies that both the coordination of the triethylsilane and the hydride transfer occurring subsequently with formation of the hydrido−triethylsilyl intermediate **V** are reversible processes.

Regarding the mechanism of the D/H exchange between the triethylsilane and the coordinated diene, we propose a sequence of steps outlined in Scheme 2. In competition with the silyl transfer (which leads to monodeuterated (triethylsilyl)cyclohexene **16a**−d_1), the $Cr(CO)_3(\eta^3$-cyclohexenyl)(trialkylsilyl) species of type **VI** may undergo abstraction of the *endo*-D or *endo*-H from either of the two β-positions with re-formation of a Cr-$(CO)_3(\eta^4$-1,3-cyclohexadiene)(hydrido)(trialkylsilyl) complex of the type **V**. In the latter case, i.e., *endo*-H abstraction, reductive elimination of the silane yields H−$SiEt_3$, which may be released into the bulk solution, while the remaining η^4-1,3-cyclohexadiene ligand in the species of type **III** carries the D-label. The repetition of the above sequence of steps with a new D−$SiEt_3$ substrate molecule from the bulk solution either leads to the doubly deuterated (triethylsilyl)cyclohexene product **16a**-d_2 or incorporates a second D-label into the coordinated diene in species **III**. The latter process, followed by further H−$SiEt_3$/D−$SiEt_3$ exchange, finally gives rise to the formation of the triply deuterated (triethylsilyl)cyclohexene product **16a**−d_3. Clearly, it is only those *two* methylene protons of the diene ligand in the *endo*-position to the metal which are susceptible to H/D-exchange, as long as the metal resides on the same side of the diene. In fact, once coordinated, the diene remains bound to the transition metal until the catalytic cycle is complete, since no D-labeled free 1,3-cyclohexadiene is observed. Hence it is readily conceivable that the coordinated diene takes up no more than two D-labels and, consequently, the ultimate hydrosilylation product contains a maximum number of three deuterium atoms.

The $^{13}C\{^1H\}$-NMR spectrum of **16a#** provides information on the location of the deuterium atoms. In addition to the parent lines associated with the undeuterated compound (**16a**) one observes a number of signals with different chemical shifts, induced by the deuterium substitution in the various positions. Some of these additional signals in the aliphatic region show triplet patterns with $^1J_{C-D}$ values of ca. 19−20 Hz, while the olefinic carbon atoms retain their singlet nature. Hence it follows that the olefinic carbon atoms are not deuterated, as anticipated from the proposed mechanism. The possible isotopomers of **16a** with deuterium substitution at the three methylene carbon atoms, but only in *endo*-positions relative to the $SiEt_3$ group, are listed in Scheme 3, although not all of them are distinguishable in the NMR spectrum.

The minor isomer **16b** cannot be directly formed by either 1,4- or 1,2-addition of H−$SiEt_3$ to 1,3-cyclohexadiene. The position of the silyl group at an olefinic carbon atom requires a C=C double-bond migration subsequent to the initial hydrosilylation, presumably via $Cr(CO)_3(\eta^3$-1-(triethylsilyl)cyclohexenyl)(H) intermediate of type **VIII** (Scheme 4). However, as an obvious prerequisite for this process to occur, the metal has to move from one face of the six-membered ring to the other, since initially the β-hydrogen at the silyl-substituted carbon is in *exo*-position and cannot be abstracted by the metal. In accord with the proposed

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Scheme 3

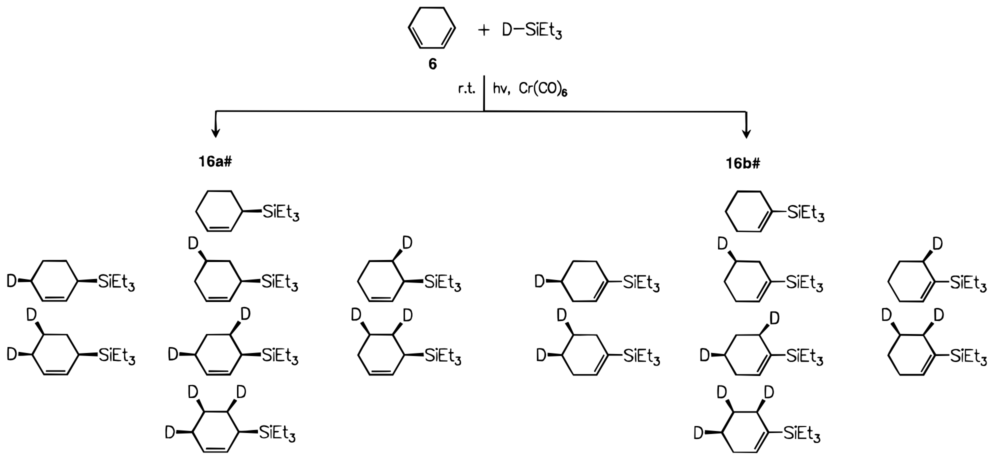
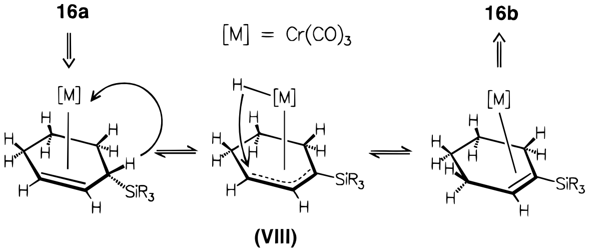


Table 2. Photocatalytic Reaction of 1,3-Cyclohexadiene (6, 15 mmol) with Triethylsilane-d_1 (75 mmol) in the Presence of $Cr(CO)_6$ (1.5 mmol): Conversion of 1,3-Cyclohexadiene (6),[a] Yields of 16a# and 16b#,[b] and Abundance of the Isotopomers[c]

conversion (%)	triethylsilane		16a#					16b#				
	d_0 (%)	d_1 (%)	yield (%)	d_0 (%)	d_1 (%)	d_2 (%)	d_3 (%)	yield (%)	d_0 (%)	d_1 (%)	d_2 (%)	d_3 (%)
0	0	100	0					0				
7.3	7	93	3.0	0	12	25	63	0.8	0	9	23	68
14.9	7	93	9.6	0	12	25	63	2.8	0	10	24	66
23.6	9	91	16.9	0	12	25	63	5.2	0	10	25	65
35.4	11	89	26.4	0	12	27	61	8.6	0	10	26	64
59.0	16	84	40.1	1	12	28	59	14.8	0	12	27	61
78.9	23	77	54.0	1	12	29	58	23.3	1	12	29	58
91.3	26	74	57.0	1	12	31	56	24.9	2	12	30	56
97.9	29	71	67.4	1	12	31	56	28.1	2	13	31	54

[a] 60 mmol of triethylsilane-d_0/d_1 remains unreacted. [b] Based on the initial amount of 1,3-cyclohexadiene. [c] 1,3-Cyclohexadiene (free substrate) remains essentially undeuterated up to 35% conversion but incorporates deuterium toward the completion of the reaction (80% d_0), at which stage the products contain trace amounts of d_4 isotopomers (not listed in this table).

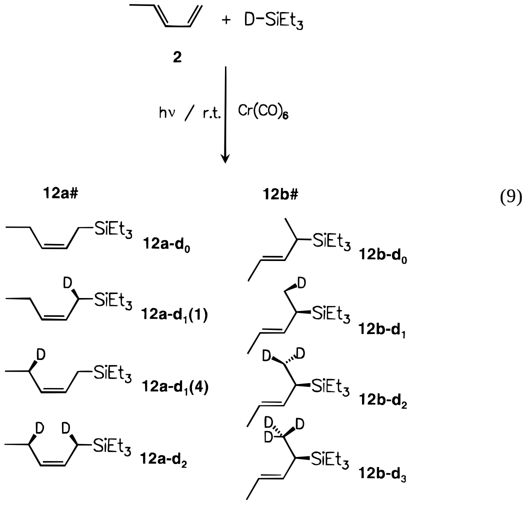
Scheme 4



plain 1,3-hydrogen shift, the deuterium content of the product is found to be unaffected by this process, i.e., the D-labeling pattern of **16b#** follows essentially that of **16a#** (Table 1). Noticeably, the **16a#**/**16b#** product ratio changes slightly in favor of **16b#** as the reaction proceeds to completion. This is in accord with the notion of the 1,3-hydrogen shift as a secondary process and has also been observed for the **16a**/**16b** product ratio in the hydrosilylation of 1,3-cyclohexadiene (**6**) with H–SiEt$_3$.

With a large excess of D–SiEt$_3$ over 1,3-cyclohexadiene (ratio 5:1, Table 2) the silane naturally shows much less D/H exchange compared to the above run with a 1:1 substrate ratio, while the abundances of the isotopomers in both **16a#** and **16b#** are changed significantly in favor of the highly deuterated ones. It is worth noting that the portion of the minor product **16b#** becomes significantly larger, varying from initially ca. 0.2 to ultimately ca. 0.3. Furthermore, some incorporation of deuterium in the free 1,3-cyclohexadiene is found in this experiment, particularly at higher conversion, though not less than 80% remains undeuterated throughout. It seems likely that the large excess of the silane present in the solution favors the displacement of the η^4-1,3-cyclohexadiene from the metal.

A substantial H/D exchange between the diene and the silane is also observed in the photocatalytic reaction of *trans*-1,3-pentadiene (**2**) with D–SiEt$_3$ which yields the D-labeled products **12a#** and **12b#**, eq 9. The



(9)

product ratio is similar to that of **12a**,**b** obtained with H–SiEt$_3$, eq 2, **12a#** being the major product. Both IR spectroscopy and MS analysis of samples drawn during the course of the catalysis reveal the intermediate release of H–SiEt$_3$, thus indicating that also in this case

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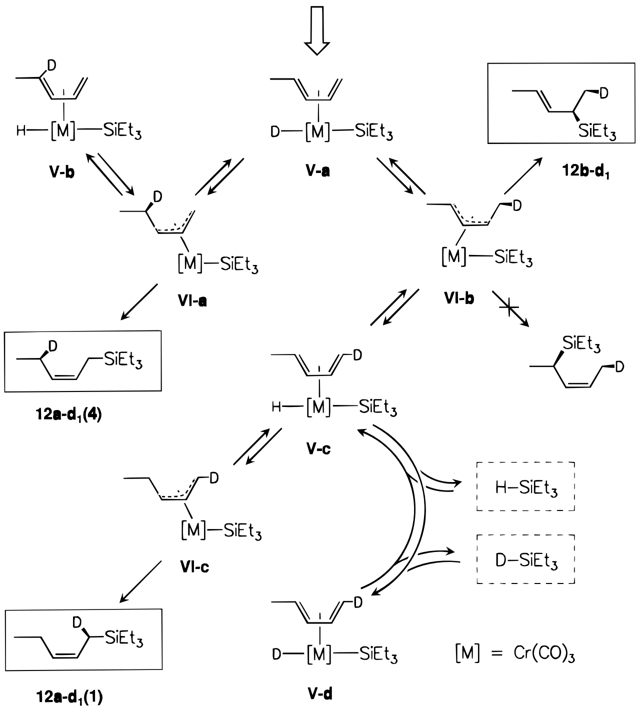
Scheme 5



the binding of the silane to the metal and the hydride transfer to the diene are reversible processes.

The isolated product **12a#** is a $d_0/d_1/d_2/d_3$ mixture of isotopomers (29/51/16/4%) as determined by MS analysis. The D-label is distributed over two positions, C-1 and C-4, which in the ^{13}C{^{1}H}-NMR spectrum each give rise to a triplet ($^1J = 18$ and 19 Hz, respectively) and a singlet, indicative of CHD and CH$_2$ groups in either position. Deuteration at C-4 would be expected from the 1,4-addition of D-SiEt$_3$, and this isotopomer [**12a**-d_1(4)] is in fact predominant, as can be seen from the integrated signals in the ^{1}H-NMR spectrum. The formation of the other positional isotopomer [**12a**-d_1(1)] can be rationalized in terms of the initial deuteride transfer to C-1 of the diene (→**VI-b**), followed by 1,4-hydrogen shift (→**V-c** → **VI-c**) and attachment of SiEt$_3$ to C-1, as illustrated in Scheme 5.

As a side reaction, **V-c** may undergo an H−SiEt$_3$/D−SiEt$_3$ exchange to form **V-d** which then, by analogy with the conversion **V-a** → **12a**-d_1(4), yields the doubly deuterated product **12a**-d_2. The silane H−SiEt$_3$ released in this process is now available for a D−SiEt$_3$/H−SiEt$_3$ exchange of **V-a** to generate the nondeuterated intermediate of type **V** which ultimately gives rise to the formation of **12a**-d_0. The failure of **VI-b** to undergo SiEt$_3$ transfer to C-4 with formation of a *cis*-4-(triethylsilyl)-2-pentene product may be due to steric hindrance by the adjacent methyl group.

The ^{13}C{^{1}H}-NMR spectrum of **12b#** reveals that the incorporated D-label is localized exclusively at C-5, the methyl group next to the SiEt$_3$ substituent. The group of signals associated with C-5 consists of a singlet, a triplet ($^1J_{CD} = 19.3$ Hz), and a quintet ($^1J_{CD} = 19.3$ Hz) corresponding to the presence of CH$_3$, CH$_2$D, and CHD$_2$ in this position. This finding is consistent with the MS analysis which shows that the isolated **12b#** sample is composed of **12b**-d_0 (19%), **12b**-d_1 (44%), **12b**-d_2 (23%), and **12b**-d_3 (14%), although the septet expected for C-5 in the latter isotopomer is barely visible in the ^{13}C{^{1}H}-NMR spectrum of **12b#**. However, the presence of all four isotopomers is evident from the appearence of four singlets associated with the adjacent, silylated carbon atom C-4. These singlets are separated by ca. 0.09 ppm, due to the cumulative isotope effect of the increasing number of deuterium atoms at C-5 on going from **12b**-d_0 through **12b**-d_3. The position of the D-labels at C-5 in the deuterated components of **12b#** indicates that this minor product results from a 1,2-hydrosilylation of *trans*-1,3-pentadiene. Thus, the formation of the monodeuterated product **12b**-d_1 logically involves the initial deuteride transfer to C-1 of the diene (**V-a** → **VI-b**), followed by the attachment of the SiEt$_3$ moiety to C-2 (Scheme 5). The analogous sequence of steps starting with **V-d**, generated via **V-c** by H−SiEt$_3$/D−SiEt$_3$ exchange, yields the bisdeuterated product **12b**-d_2, etc.

It is interesting to note that the observed regioselectivity in the 1,4-hydrosilylation of the unsymmetrical dienes correlates reasonably well with the coefficients in the LUMO of the dienes. Methyl substitution at C-1 or C-2 in the 1,3-butadiene chain makes the coefficient at C-4 larger than that at C-1.[27] Given that the mechanism involves the hydride transfer in the first step (Scheme 1), this nucleophile is expected to attack preferentially C-4. This in turn would direct the silyl group to C-1, in accordance with *cis*-1-(triethylsilyl)-2-pentene (**12a**) and *cis*-1-(triethylsilyl)-2-methyl-2-butene (**14a**) being the major products obtained from *trans*-1,3-pentadiene (**2**) and 2-methyl-1,3-butadiene (**4**), respectively. Carrying two methyl groups at the respective positions, *trans*-2-methyl-1,3-pentadiene (**5**) shows the cumulative effect of the two substituents in a sense that *cis*-1-(triethylsilyl)-2-methyl-2-pentene (**15**) is the sole product. We are aware that this is an oversimplified picture as it considers the free diene, not the coordinated one, and does not account for any steric effect which might be likewise relevant. Moreover, we must not fail to note that the ultimate product does not necessarily reflect the direction of the initial hydride transfer, as can be realized from the detailed investigation into the hydrosilylation of *trans*-1,3-pentadiene. From the **12a**/**12b** product ratio obtained in the reaction with H−SiEt$_3$, eq 2, one might conclude that the initial hydride transfer to C-4 predominates by a factor in the order of 25. However, the reaction with D−SiEt$_3$, eq 9, reveals the occurrence of *a* 1,4-hydrogen shift subsequent to the initial deuteride transfer to C-1 (see Scheme 5). This process remains unobserved in the hydrosilylation with H−SiEt$_3$ and thus feigns an almost exclusive hydride attack at C-4. Nevertheless, the initial deuteride transfer to C-4 is favored by a factor of ca. 1.5, as can be estimated from the NMR spectra of the D-labeled product **12a#**.

It is noteworthy that the hydrosilylation of 1,4-cyclohexadiene (**7**) with H−SiEt$_3$, eq 10, gives the same products as 1,3-cyclohexadiene, **16a**,**b**, though with a slightly different ratio in favor of the main product **16a** and with incomplete conversion of the starting materials. Apparently, the overall reaction involves the

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[27] The extended Hückel program in the program package "HyperChem Version 3.0" (Autodesk Inc., 1992) was used to calculate the MO coefficients in the LUMO of the conjugated diene π systems. 1,3-Butadiene (**1**): C-1 (−0.651 37), C-2 (0.458 04), C-3 (0.458 04), C-4 (−0.651 37). 1,3-Pentadiene (**2**): C-1 (−0.644 47), C-2 (0.478 71), C-3 (0.412 30), C-4 (−0.663 91). 2-Methyl-1,3-butadiene (**4**): C-1 (−0.622 25), C-2 (0.449 77), C-3 (0.448 90), C-4 (−0.665 82). 2-Methyl-1,3-pentadiene (**5**): C-1 (−0.614 31), C-2 (0.469 31), C-3 (0.434 32), C-4 (−0.679 21).

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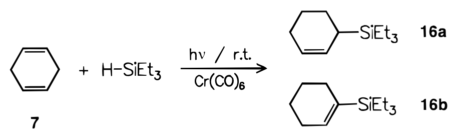
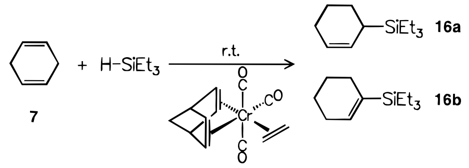


(10)

isomerization of 1,4-cyclohexadiene to 1,3-cyclohexadiene prior to the hydrosilylation on the transition metal center. However, neither could the free 1,3-cyclohexadiene be detected by GC nor was $Cr(CO)_4(\eta^4$-1,3-cyclohexadiene) observed by means of IR spectroscopy at any stage of the conversion. The IR spectra recorded during the catalytic run show nothing but a CO stretching vibrational pattern [2073 (vw), 1952 (vs), 1944 (m) cm^{-1}] indicative of a $Cr(CO)_5$ unit which most probably carries the η^2-coordinated 1,4-cyclohexadiene. Hence it seems that the isomerized diene does not accumulate but immediately undergoes hydrosilylation.

Although the mechanism of this process is not yet elucidated in detail, the $Cr(CO)_3$ moiety is likely to act as the repeating unit in the catalytic cycle, as proved by performing the hydrosilylation of **7** in the dark using $Cr(CO)_3(\eta^4$-norbornadiene)$(\eta^2$-ethene) as the precursor of the active catalyst, eq 11.



(11)

Conclusion

The results of this investigation confirm that the hydrosilylation of conjugated dienes occurs predominantly, if not exclusively, as a 1,4-addition. Moreover, there is conclusive evidence that this process proceeds in a stepwise fashion, involving a hydride transfer prior to the silation. In accordance with this mechanistic picture, the hydride transfer occurs preferentially at that terminal carbon atom which makes the largest contribution to the LUMO of the diene. Experiments with D-labeled silane revealed that the hydride transfer, but not the silation, is reversible.

Various other dienes (*trans*,*trans*-2,4-hexadiene, *trans*,*trans*-1,4-diphenyl-1,3-butadiene, 2,3-methoxy-1,3-butadiene, 1-carbethoxy-1,3-butadiene, 1,4-(dicarbethoxy)-1,3-butadiene, 1,3-cycloheptadiene, 1,3-cyclooctadiene, and 1,5-cyclooctadiene) proved unreactive in the attempted photocatalytic hydrosilylation, although most of them upon irradiation in the presence of $Cr(CO)_6$ form the respective $Cr(CO)_4(\eta^4$-diene) complex. The photochemistry of the latter compounds is currently under investigation in order to find an explanation of their failure in the photocatalysis. Apart from this, exploratory investigations with carbonyl−molybdenum and −tungsten catalysts are underway. Compared to chromium, both metals apparently are less reactive with respect to the photocatalytic hydrosilylation of dienes, although some promising results are achieved with $Mo(CO)_6$ by varying the reaction conditions.

Experimental Section

All reactions and manipulations involving the metal carbonyl catalysts were carried out either in vacuum or under dry inert atmosphere (N_2 or Ar). Photochemical reactions were carried out in an immersion-well apparatus[28] (solidex glass, $\lambda > 280$ nm) by using a Hanau TQ 150 or a Philips HPK 125-W high-pressure mercury lamp, which was cooled by circulating water or precooled methanol.

Solvents were distilled after refluxing over metallic sodium or phosphorus pentoxide under nitrogen for several days. Triethylsilane, triphenylsilane (Merck), hexacarbonylchromium(0), hexacarbonylmolybdenum(0), and hexacarbonyltungsten(0) (Aldrich) were commercially available and used without further purification. Triethylsilane-d_1 ($D-SiEt_3$) was prepared from Et_3Si-Cl and $LiAlD_4$ in diethyl ether (by analogy to the reported[29] reduction of chlorosilanes with $LiAlH_4$) and purified by distillation (boiling point 69 °C at 200 Torr; $H-SiEt_3$ content less than 3%, as determined by MS). The dienes (except 1,3-butadiene)[30] were commercially available (Fluka) and distilled before used. Tetracarbonyl$(\eta^4$-1,3-butadiene)chromium(0)[13] and tricarbonyl$(\eta^4$-norbornadiene)$(\eta^2$-ethene)chromium(0)[25] were prepared according to the literature procedures.

NMR spectra were recorded on a Bruker AC-80 spectrometer (80.131 MHz for ^1H, 20.149 MHz for ^{13}C), and a Bruker AM 400 spectrometer (400.1 MHz for ^1H, 100.6 MHz for ^{13}C) using TMS as internal reference. Assignments of the NMR signals are based on the C−H-correlated 2D NMR spectra and appropriate decoupling experiments. Perkin-Elmer 1600 FTIR and 1430 IR spectrophotometers were used to follow the changes in the ν_{Si-H}, ν_{Si-D}, and ν_{CO} spectral regions in monitoring the reactions. Routine gas chromatographic analyses were performed on a Perkin-Elmer F33 chromatograph using a flame ionization detector and a 6 ft OV-1 column or on a Varian 3700 instrument. GC−MS spectra were obtained by using a Perkin-Elmer R22 GC apparatus (OV-1, 30 in. column, 60−280 °C, H_2 carrier gas) combined with a Finnigan MAT CH 7A mass spectrometer (EI); no attempts were made to separate D-labeled isotopomers. A Gerstel AMPG-60 apparatus was used for preparative GC.

Photocatalytic Reactions of Dienes with Triethylsilane and Related Thermal Reactions. 1,3-Butadiene. $Cr(CO)_6$ (0.16 g, 0.71 mmol) and triethylsilane (1.4 mL, 9.0 mmol) were stirred and irradiated in a saturated solution of 1,3-butadiene (**1**) in *n*-hexane (60 mL) at −10 °C for 14 h. The solution was then filtered, the solvent evaporated, and the residue distilled (80 °C/15 Torr) to yield 0.67 g (44% yield) of a colorless liquid, *cis*-1-(triethylsilyl)-2-butene (**11**). ^{13}C-NMR (CD_2Cl_2): $\delta = 3.73$ (C-5, t, $J_{CH} = 117.4$ Hz), 7.60 (C-6, q, $J_{CH} = 125.6$ Hz), 12.80 (C-4, q, $J_{CH} = 125.1$ Hz), 13.20 (C-1, t, $J_{CH} = 119.1$ Hz), 120.93 (C-3, d, $J_{CH} = 154.8$ Hz), 126.41 (C-2, d, $J_{CH} = 153.2$ Hz) ppm. ^1H-NMR (CD_2Cl_2): $\delta = 0.56$ (H-5), 0.96 (H-6), 1.52 (H-1), 1.59 (H-4), 5.32 (H-3), 5.45 (H-2) ppm; $^3J_{5,6} = 7.9$, $^3J_{1,2} = 8.5$, $^3J_{2,3} = 10.7$, $^3J_{3,4} = 6.6$, $^4J_{1,3} = 1.4$, $^4J_{2,4} = 1.5$ Hz.

***trans*-1,3-Pentadiene (2). Method a.** *trans*-1,3-Pentadiene (**2**) (15 mL, 0.15 mol), $Cr(CO)_6$ (0.66 g, 3.0 mmol) and triethylsilane (24 mL, 0.15 mol) were stirred and irradiated in *n*-hexane (500 mL) at room temperature for ca. 24 h at which time the triethylsilane was largely consumed. Evaporation of the solvent followed by bulb-to-bulb distillation of the residue (room temperature, 10^{-2} Torr) yielded an almost colorless liquid (15.6 g, 56% yield) of three (triethylsilyl)pentene isomers (identified by GC−MS, $M^+ = m/e$ 184; 3.4%, 0.7%, and 95.5%) as the crude product. Separation by means of preparative GC (column 6 m, 20 mm diameter, 20% SE-30 on Volasphere A4, 150 °C; carrier gas N_2, 620 mL min^{-1}) afforded *cis*-1-(triethylsilyl)-2-pentene (**12a**, 9.9 g, 99.9% purity), *trans*-4-(triethylsilyl)-2-pentene (**12b**, 0.1 g, 94.5% pu-

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[30] The authors wish to thank Dr. T. Savasci of PETKIM Refinery, Kocaeli, Turkey, for the supply of 1,3-butadiene.

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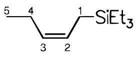
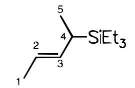
rity), and small amount of an intermediate fraction containing 14% of a third isomer in addition to 12% of **12a** and 74% of **12b**.



12a



12b

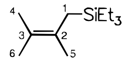
12a. ^{13}C-NMR (CD_2Cl_2): $\delta = 3.68$ (C-6, t, $J_{CH} = 117.9$ Hz), 7.61 (C-7, q, $J_{CH} = 125.8$ Hz), 13.49 (C-1, t, $J_{CH} = 118.5$ Hz), 14.52 (C-5, q, $J_{CH} = 125.7$ Hz), 20.77 (C-4, t, $J_{CH} = 125.5$ Hz), 125.26 (C-2, d, $J_{CH} = 153.2$ Hz), 129.58 ppm (C-3, d, $J_{CH} = 154.0$ Hz). ^{1}H-NMR (CD_2Cl_2): $\delta = 0.55$ (H-6), 0.95 (H-7), 0.96 (H-5), 1.51 (H-1), 2.04 (H-4), 5.23 (H-3), 5.38 (H-2) ppm; $^3J_{6,7} = 8.0$, $^3J_{1,2} = 8.6$, $^3J_{2,3} = 10.4$, $^3J_{3,4} = 7.0$, $^3J_{4,5} = 7.5$, $^4J_{1,3} = 1.3$, $^4J_{2,4} = 1.6$ Hz.

12b. ^{13}C-NMR (CD_2Cl_2): $\delta = 2.47$ (C-6, t, $J_{CH} = 118.6$ Hz), 7.75 (C-7, q, $J_{CH} = 125.6$ Hz), 14.42 (C-5, q, $J_{CH} = 126.0$ Hz), 18.27 (C-1, q, $J_{CH} = 126.0$ Hz), 23.57 (C-4, d, $J_{CH} = 118.2$ Hz), 120.53 (C-2, d, $J_{CH} = 153.3$ Hz), 134.85 ppm (C-3, d, $J_{CH} = 146.2$ Hz). ^{1}H-NMR (CD_2Cl_2): $\delta = 0.55$ (H-6), 0.95 (H-7), 1.06 (H-5), 1.64 (H-1), 1.68 (H-4), 5.24 (H-2), 5.48 (H-3) ppm; $^3J_{6,7} = 8.1$, $^3J_{1,2} = 6.3$, $^3J_{2,3} = 15.2$, $^3J_{3,4} = 7.9$, $^3J_{4,5} = 7.3$, $^4J_{1,3} = 1.5$, $^4J_{2,4} = 1.3$ Hz.

Method b. In a small-scale experiment, a solution of *trans*-1,3-pentadiene (**2**) (1.5 mL, 15 mmol), $Cr(CO)_6$ (66 mg, 0.3 mmol), triethylsilane (2.4 mL, 15 mmol), and *n*-octane (1.4085 g, internal standard for GC) in *n*-hexane (50 mL) was stirred and irradiated at room temperature for 140 min. Monitoring the course of the reaction by GC (capillary column 44 m, OV-1, temp prog 50−250 °C/6 °C min^{-1}; FID; carrier gas H_2, 0.8 bar; samples 0.2 μL) showed the gradual disappearance of **2** (GC factor $F = 1.028$) and triethylsilane ($F = 1.377$) with the concurrent formation of the (triethylsilyl)pentene isomers ($F = 1.334$) **12a**,**b** (86% and 3% ultimate yields, respectively).

Method c. *trans*-1,3-Pentadiene (**2**) (15 mL, 0.15 mol), $Cr(CO)_6$ (0.51 g, 2.3 mmol), and triethylsilane-d_1 (19 mL, 0.12 mol) were stirred and irradiated in *n*-hexane (200 mL) at room temperature. Monitoring the course of the reaction by IR spectroscopy showed the gradual disappearance of the ν_{Si-D} stretching band at 1532 cm^{-1} with the concomitant appearance of a ν_{Si-H} stretching band at 2102 cm^{-1}. After 29 h both the $D-SiEt_3$ and $H-SiEt_3$ were largely consumed. Samples drawn during the course of the catalysis were analyzed by GC−MS, which confirmed the gradual incorporation of H into the triethylsilane, whereby the d_0/d_1 ratio approaches a value of ca. 40/60. Moreover, incorporation of D into the free 1,3-pentadiene was detected (ca. 20% d_1), and the two products, denoted as **12a#** and **12b#**, were found to be $d_0/d_1/d_2/d_3$ mixtures (ca. 20% d_0, 55% d_1, 20% d_2, and 5% d_3). Evaporation of the solvent followed by bulb-to-bulb distillation of the residue (room temperature, 10^{-2} Torr) yielded an almost colorless liquid (15.4 g, 70% yield) as the crude product. Separation by means of preparative GC (column 8 m, 20 mm diameter, 20% SE-30 on Volasphere A4, 130 °C; carrier gas N_2, 600 mL min^{-1}) afforded pure samples of **12a#** (7.54 g; >99% purity, by GC; 29% d_0, 51% d_1, 16% d_2, and 4% d_3, by MS) and **12b#** (0.18 g; >95% purity, by GC; 19% d_0, 44% d_1, 23% d_2, and 14% d_3, by MS). ^{13}C{^{1}H}-NMR spectrum of **12a#** (CD_2Cl_2): $\delta =$ *4.40* (C-6, s); *8.24* (C-7, s); *14.11* (C-1, s), 13.77 (C-1, t, $^1J_{CD} = 18.3$ Hz); *15.16* (C-5, s), 15.05 (C-5, s); *21.47* (C-4, s), 21.13 (C-4 t, $^1J_{CD} = 19.2$ Hz); *125.65* (C-2, s); *130.24* (C-3, s), 130.20 (C-3, s) ppm. ^{13}C{^{1}H}-NMR spectrum of **12b#** (CD_2Cl_2): $\delta =$ *2.51* (C-6, s); *7.79* (C-7, s); *14.46* (C-5, s), 14.17 (C-5, t, $^1J_{CD} = 19.3$ Hz), 13.89 (C-5, q, $^1J_{CD} = 19.2$ Hz); *18.30* (C-1, s); *23.62* (C-4, s), 23.53 (C-4, s), 23.44 (C-4, s), 23.34 (C-4, s); 120.57 (C-2, s); 134.89 (C-3, s); the chemical shift data printed in italics refer to the undeuterated compound and/or to those carbon atoms in the deuterated compound which are not affected by the D-label.

2,3-Dimethyl-1,3-butadiene (3). Method a. 2,3-Dimethyl-1,3-butadiene (**3**) (17 mL, 0.15 mol), $Cr(CO)_6$ (0.66 g, 3.0 mmol) and triethylsilane (24 mL, 0.15 mol) were stirred and irradiated in *n*-hexane (500 mL) at room temperature for 24 h at which time the consumption of triethylsilane was complete. Evaporation of the solvent followed by bulb-to-bulb distillation (room temperature, 10^{-2} Torr) of the residue yielded 16.1 g of a colorless liquid as crude product. GC analysis showed one main component, which was separated by distillation using a concentric tube column (reflux ratio 200:1) to yield 10.9 g (37% yield) of a colorless liquid, 1-(triethylsilyl)-2,3-dimethyl-2-butene (**13**; >99% purity, by GC), bp 54.5−55.8 °C (1.0 Torr).

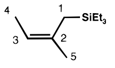


13

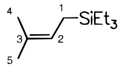
^{13}C-NMR (CD_2Cl_2): $\delta = 4.70$ (C-7, t, $J_{CH} = 117.2$ Hz), 7.72 (C-8, q, $J_{CH} = 125.4$ Hz), 20.90 (C-1, t, $J_{CH} = 117.7$ Hz), 20.65, 21.29 and 21.40 (three methyl carbons, C-4, C-5, and C-6, q, $J_{CH} = 125$ Hz), 120.84 (C-3, s), 125.68 ppm (C-2, s). ^{1}H-NMR (CD_2Cl_2): $\delta = 0.58$ (H-7), 0.98 (H-8), 1.58 (H-1), 1.626, 1.634, and 1.644 ppm (three methyl groups, H-4, H-5, and H-6); $^3J_{7,8} = 8.1$ Hz.

Method b. In a small-scale experiment, a solution of 2,3-dimethyl-1,3-butadiene (**3**) (1.7 mL, 15 mmol), $Cr(CO)_6$ (66 mg, 0.3 mmol), triethylsilane (2.4 mL, 15 mmol), and *n*-octane (1.4276 g, internal standard for GC) in *n*-hexane (50 mL) was stirred and irradiated at room temperature for 100 min. Monitoring the course of the reaction by GC (capillary column 44 m, OV-1, temp prog 50−250 °C/8 °C min^{-1}; FID; carrier gas H_2, 0.8 bar; samples 0.2 μL) showed the gradual disappearance of **3** (GC factor $F = 1.006$) and triethylsilane ($F = 1.377$) with the concurrent formation of **13** ($F = 1.390$) in quantitative yield.

2-Methyl-1,3-butadiene (4). Method a. 2-Methyl-1,3-butadiene (**4**) (15 mL, 0.15 mol), $Cr(CO)_6$ (0.66 g, 3.0 mmol), and triethylsilane (24 mL, 0.15 mol) were stirred and irradiated in *n*-hexane (500 mL) at room temperature for 6 h. Evaporation of the solvent followed by bulb-to-bulb distillation of the residue (room temperature, 10^{-2} Torr) yielded 16.0 g of a colorless liquid as crude product. Distillation using a concentric tube column (reflux ratio 100:1) afforded 3.1 g (11% yield) of 1-(triethylsilyl)-3-methyl-2-butene (**14b**) (bp 41.1−42.0 °C/1.0 Torr; 98% purity, by GC) and 8.6 g (31% yield) of *cis*-1-triethyl-2-methyl-2-butene (**14a**) (bp 44.4−45.8 °C/1.0 Torr; 99% purity, by GC), along with an intermediate fraction (0.8 g, 3% yield) containing **14a**,**b** in 1:2 ratio (by GC).



14a



14b

14a. ^{13}C-NMR (CD_2Cl_2): $\delta = 4.51$ (C-6, t, $J_{CH} = 117.9$ Hz), 7.60 (C-7, q, $J_{CH} = 125.6$ Hz), 14.15 (C-4, q, $J_{CH} = 124.6$ Hz), 17.87 (C-1, t, $J_{CH} = 116.5$ Hz), 26.47 (C-5, q, $J_{CH} = 124.4$ Hz), 116.20 (C-3, d, $J_{CH} = 151.4$ Hz), 134.85 ppm (C-2, s). ^{1}H-NMR (CD_2Cl_2): $\delta = 0.58$ (H-6), 0.98 (H-7), 1.52 (H-4), 1.54 (H-1), 1.69 (H-5), 5.07 (H-3) ppm; $^3J_{6,7} = 8.1$, $^3J_{3,4} = 6.8$, $^4J_{3,5} = 1.2$, $^4J_{1,5} = 1.4$ Hz.

14b. ^{13}C-NMR (CD_2Cl_2): $\delta = 3.75$ (C-6, t, $J_{CH} = 117.4$ Hz), 7.60 (C-7, q, $J_{CH} = 125.7$ Hz), 13.82 (C-1, t, $J_{CH} = 118.7$ Hz), 17.70 (C-4, q, $J_{CH} = 125.7$ Hz), 25.92 (C-5, q, $J_{CH} = 125.8$ Hz), 120.61 (C-2, d, $J_{CH} = 149.5$ Hz), 128.61 ppm (C-3, s). ^{1}H-NMR (CD_2Cl_2): $\delta = 0.54$ (H-6), 0.95 (H-7), 1.43 (H-1), 1.59 (H-4), 1.69 (H-5), 5.16 (H-2) ppm; $^3J_{6,7} = 8.0$, $^3J_{1,2} = 8.4$ Hz.

Method b. In a small-scale experiment, a solution of 2-methyl-1,3-butadiene (**4**) (1.5 mL, 15 mmol), $Cr(CO)_6$ (66 mg, 0.3 mmol), triethylsilane (2.4 mL, 15 mmol), and *n*-octane (1.4169 g, internal standard for GC) in *n*-hexane (50 mL) was stirred and irradiated at room temperature for 90 min. Monitoring the course of the reaction by GC (capillary column 44 m, OV-1, temp prog 50−250 °C/8 °C min^{-1}; FID; carrier

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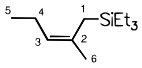
gas H_2, 0.8 bar; samples 0.2 μL) showed the gradual disappearance of **4** (GC factor $F = 0.985$) and triethylsilane ($F = 1.377$) with the concurrent formation of the (triethylsilyl)methylbutene isomers ($F = 1.34$) **14a** (76% ultimate yield) and **14b** (22% ultimate yield).

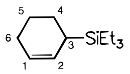
***trans*-2-Methyl-1,3-pentadiene (5).** 2-Methyl-1,3-pentadiene (**5**) (1.5 mL, 13 mmol), $Cr(CO)_6$ (0.16 g, 0.71 mmol), and triethylsilane (1.9 mL, 12 mmol) were stirred and irradiated in *n*-hexane (80 mL) at room temperature for 2 h. Evaporation of the solvent followed by bulb-to-bulb distillation of the residue (80 °C/20 Torr) afforded 0.42 g of a colorless liquid (14% yield) as a crude product. GC−MS analysis showed one main product for a hydrosilylation adduct ($M^+ = m/e$ 198), which was isolated by preparative GC (Shimadzu GC 14A, modified for micropreparative operation, double column 2 + 3 m, 2 mm diameter, 20% SE-30 on Volasphere A4, 150 °C; carrier gas N_2, 28 mL min^{-1}) yielding *cis*-1-(triethylsilyl)-2-methyl-2-pentene (**15**; 97.7% purity, by GC).



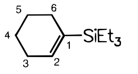
15

^{13}C-NMR (CD_2Cl_2): $\delta = 4.39$ (C-7, t, $J_{CH} = 117.4$ Hz), 7.54 (C-8, q, $J_{CH} = 125.8$ Hz), 14.59 (C-5, q, $J_{CH} = 124.6$ Hz), 18.09 (C-1, t, $J_{CH} = 119.5$ Hz), 22.04 (C-4, t, $J_{CH} = 124.8$ Hz), 26.41 (C-6, q, $J_{CH} = 122.0$ Hz), 124.65 (C-3, d, $J_{CH} = 152.0$ Hz), 132.74 ppm (C-2, s). ^{1}H-NMR (CD_2Cl_2): $\delta = 0.56$ (H-7), 0.93 (H-5), 0.96 (H-8), 1.51 (H-1), 1.67 (H-6), 1.95 (H-4), 4.95 (H-3) ppm; $^3J_{7,8} = 8.1$, $^3J_{3,4} = 6.8$, $^4J_{3,6} = 1.2$, $^4J_{1,6} = 1.4$ Hz.

1,3-Cyclohexadiene (6). Method a. 1,3-Cyclohexadiene (**6**) (14.3 mL, 0.15 mol), triethylsilane (24 mL, 0.15 mol), and $Cr(CO)_6$ (0.66 g, 3.0 mmol) were stirred and irradiated in *n*-hexane (500 mL) for 6 h at room temperature. Evaporation of the solvent followed by bulb-to-bulb distillation of the residue (room temperature, 10^{-2} Torr) yielded 17.3 g of a colorless liquid as crude product. Distillation using a concentric tube column (reflux ratio 60:1) afforded 1.0 g (3% yield) of 1-(triethylsilyl)-1-cyclohexene (**16b**) (bp 50.6 °C/1.0 Torr; 99.5% purity, by GC) and 9.1 g (31% yield) of 3-(triethylsilyl)-1-cyclohexene (**16a**) (bp 55.2−55.5 °C/1.0 Torr, purity 99.5%), along with an intermediate fraction (2.1 g, 7% yield) containing **16a**,**b** in 2:1 ratio (by GC).



16a



16b

16a. ^{13}C-NMR (CD_2Cl_2): $\delta = 2.96$ (C-7, t, $J_{CH} = 117.3$ Hz), 7.97 (C-8, q, $J_{CH} = 125.8$ Hz), 23.64 (C-3, d, $J_{CH} = 118.1$ Hz), 23.66 (C-5, t, $J_{CH} = 124.9$ Hz), 24.64 (C-4, t, $J_{CH} = 126$ Hz), 25.76 (C-6, t, $J_{CH} = 123$ Hz), 125.49 (C-1, d, $J_{CH} = 155.9$ Hz), 128.92 ppm (C-2, d, $J_{CH} = 154.1$ Hz); $^1J_{1,2} = 69.4$, $^1J_{2,3} = 36.8$, $^1J_{3,4} = 31.2$, $^1J_{4,5} = 32.5$, $^1J_{5,6} = 33.7$, $^1J_{1,6} = 40.2$ Hz (determined by 1D-INADEQUATE spectrum on a Bruker AMX 300 instrument).[31] ^{1}H-NMR (CD_2Cl_2): $\delta = 0.61$ (H-7), 1.00 (H-8), 1.61 (H-3), 1.75 (H-5), 1.82 (H-4), 2.07 (H-6), 5.68 (H-1), 5.72 (H-2) ppm; $^3J_{7,8} = 8.1$, $^3J_{1,2} = 10$ Hz.

16b. ^{13}C-NMR (CD_2Cl_2): $\delta = 2.99$ (C-7, t, $J_{CH} = 117.2$ Hz), 7.73 (C-8, q, $J_{CH} = 125.5$ Hz), 23.18 (C-4, t, $J_{CH} = 127.5$ Hz), 23.64 (C-5, t, $J_{CH} = 127.0$ Hz), 27.41 (C-6, t, $J_{CH} = 123.8$ Hz), 27.93 (C-3, t, $J_{CH} = 125.0$ Hz), 135.97 (C-1, s), 137.59 ppm (C-2, d, $J_{CH} = 154.3$ Hz). ^{1}H-NMR (CD_2Cl_2): $\delta = 0.60$ (H-7), 0.94 (H-8), 1.62 (H-4, H5), 2.03 (H-6), 2.07 (H-3), 6.00 (H-2) ppm; $^3J_{7,8} = 8.1$ Hz.

Method b. In a small-scale experiment, a solution of 1,3-cyclohexadiene (**6**) (1.4 mL, 15 mmol), $Cr(CO)_6$ (66 mg, 0.3 mmol), triethylsilane (2.4 mL, 15 mmol), and *n*-octane (0.9278 g, internal standard for GC) in *n*-hexane (50 mL) was stirred and irradiated at room temperature for 5 h, at which time the starting materials were largely consumed. Monitoring the course of the reaction by GC (capillary column 44 m, OV-1, temp prog 50−250 °C/8 °C min^{-1}; FID; carrier gas H_2, 0.8 bar; samples 0.2 μL) showed the gradual disappearance of **6** (GC factor $F = 0.993$) and triethylsilane ($F = 1.377$) with the concomitant formation of the (triethylsilyl)cyclohexene isomers ($F = 1.366$) **16a**,**b** (80% and 11% ultimate yields, respectively).

Method c. A solution of 1,3-cyclohexadiene (**6**) (7.2 mL, 75 mmol), triethylsilane-d_1 (12 mL, 75 mmol), $Cr(CO)_6$ (0.33 g, 1.5 mmol), and *n*-octane (4.2817 g, internal standard for GC) in *n*-hexane (300 mL) was stirred and irradiated at room temperature for 65 min. Monitoring the course of the reaction by IR spectroscopy showed the gradual disappearance of the ν_{Si-D} stretching band at 1532 cm^{-1} with the concomitant appearance of a ν_{Si-H} stretching band at 2102 cm^{-1}. After 65 min triethylsilane-d_1 was no longer detectable, while GC (capillary column 44 m, OV-1, temp prog 50−250 °C/8 °C min^{-1}; FID; carrier gas H_2, 0.8 bar; samples 0.2 μL) showed that ca. 75% of **6** and triethylsilane were consumed with nearly quantitative product formation. In addition, samples were analyzed by GC−MS which confirmed the gradual conversion of $D-SiEt_3$ into $H-SiEt_3$ and showed that 1,3-cyclohexadiene remains undeuterated throughout, while the products 3-(triethylsilyl)-1-cyclohexene and 1-(triethylsilyl)-1-cyclohexene, denoted as **16a#** and **16b#**, carry up to three D-labels. The results of the GC and GC−MS analyses of the samples drawn during the course of the catalysis are listed in Table 1. Evaporation of the solvent followed by bulb-to-bulb distillation of the residue yielded 13.8 g of a colorless liquid as crude product. Distillation using a concentric tube column (vide supra) afforded 3.3 g of **16a#** (bp 54.4 °C/0.5 Torr; 99.5% purity, by GC) together with two lower boiling fractions (2.35 and 1.13 g) containing 40% and 3.5% (by GC) of **16b#**, respectively, in addition to **16a#**. ^{13}C{^{1}H}-NMR spectrum of **16a#** (CD_2Cl_2): δ = *2.82* (C-7, s); *7.84* (C-8, s); *23.51*/23.40 (C-3/C-5, s), 23.28 (C-3/C-5, s), 23.12 (C-5, t, $^1J_{CD} = 20$ Hz), 23.01 (C-5, t, $^1J_{CD} = 20$ Hz), 22.89 (C-5, t, $^1J_{CD} = 20$ Hz); *24.48* (C-4, s), 24.47 (C-4, s), 24.37 (C-4, s), 24.36 (C-4, s), 24.08 (C-4, t, $^1J_{CD} = 19$ Hz), 24.06 (C-4, t, $^1J_{CD} = 19$ Hz), 23.96 (C-4, t, $^1J_{CD} = 19$ Hz), 23.95 (C-4, t, $^1J_{CD} = 19$ Hz); *25.71* (C-6, s), 25.59 (C-6, s), 25.51 (C-6, s), 25.49 (C-6, s), 25.21 (C-6, t, $^1J_{CD} = 19$ Hz), 25.18 (C-6, t, $^1J_{CD} = 19$ Hz), 25.10 (C-6, t, $^1J_{CD} = 19$ Hz), 25.08 (C-6, t, $^1J_{CD} = 19$ Hz); *125.28* (C-1, s), 125.35 (C-1, s); *128.86* (C-2, s), 128.93 (C-2, s) ppm; the chemical shift data printed in italics refer to the undeuterated compound, as cross-checked by adding **16a** to a sample of **16a#**.

Method d. A solution of 1,3-cyclohexadiene (**6**) (1.4 mL, 15 mmol), triethylsilane-d_1 (12 mL, 75 mmol), $Cr(CO)_6$ (0.33 g, 1.5 mmol), and *n*-octane (1.9997 g, internal standard for GC) in *n*-hexane (300 mL) was stirred and irradiated at room temperature for 60 min. At this time the total amount of **6** and 15 mmol of the triethylsilane were consumed with nearly quantitative formation of **16a#** and **16b#** in an ultimate ratio of ca. 2:1, as monitored by GC (capillary column 44 m, OV-1, temp prog 50−250 °C/8 °C min^{-1}; FID; carrier gas H_2, 0.8 bar; samples 0.2 μL). IR monitoring showed the gradual conversion of the starting $D-SiEt_3$ into a ca. 3:1 mixture of $D-SiEt_3$ and $H-SiEt_3$. This latter result was confirmed by GC−MS analysis, which also showed that the products **16a#** and **16b#** carry up to three D-labels. The results of the GC and GC−MS analyses of the samples drawn during the course of the catalysis are listed in Table 2. Evaporation of the solvent followed by bulb-to-bulb distillation of the residue yielded 2.1 g of a colorless liquid as crude product. Separation by means of preparative GC (column 6 m, 20 mm diameter, 20% SF-96 on Volasphere A4, 150 °C; carrier gas N_2, 630 mL min^{-1}) afforded **16a#** (0.60 g; 89.2% purity, by GC) and **16b#** (0.41 g; 95% purity, by GC).

Method e. A cold solution (−30 °C) of 1,3-cyclohexadiene (**6**) (3.7 mL, 40 mmol), triethylsilane (6.4 mL, 40 mmol), Cr-

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[31] The authors wish to thank Dipl.-Ing. H. Bandmann (Universität Essen-GHS, Institut für Organische Chemie) for recording the 1D-INADEQUATE spectra.

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$(CO)_3$(η^4-norbornadiene)(η^2-ethene) (ca. 1.8 mmol, *in situ* generated),[25] and *n*-octane (2.0223 g, internal standard for GC) in *n*-hexane (200 mL) was warmed to room temperature and stirred for 100 min, at which time the triethylsilane was no longer detectable in the IR spectrum. GC and GC−MS analyses of the samples drawn during the catalytic run showed the gradual consumption of the starting material with concomitant formation of (triethylsilyl)norbornene (identified by GC−MS, $M^+ = m/e$ 208; 97 mg, 0.47 mmol), **16a** (72% ultimate yield) and **16b** (12% ultimate yield).

1,4-Cyclohexadiene (7). Method a. 1,4-Cyclohexadiene (**7**) (14.0 mL, 0.15 mol), triethylsilane (24 mL, 0.15 mol), and $Cr(CO)_6$ (0.66 g, 3.0 mmol) were stirred and irradiated in *n*-hexane (500 mL) for 48 h at room temperature, at which time the consumption of triethylsilane (60%) ceased. Evaporation of the solvent followed by bulb-to-bulb distillation of the residue (room temperature, 10^{-2} Torr) yielded 10.2 g of a colorless liquid as crude product. Distillation using a concentric tube column (reflux ratio 60:1) afforded 0.6 g (2% yield) of 1-(triethylsilyl)-1-cyclohexene (**16b**; 90% purity, by GC) and 4.9 g (17% yield) of 3-(triethylsilyl)-1-cyclohexene (**16a**; 99.5% purity, by GC), along with an intermediate fraction (1.3 g, 4%) containing **16a**,**b** in 4:1 ratio (by GC).

Method b. In a small-scale experiment, a solution of 1,4-cyclohexadiene (**7**) (1.4 mL, 15 mmol), $Cr(CO)_6$ (66 mg, 0.3 mmol), triethylsilane (2.4 mL, 15 mmol), and *n*-octane (1.0051 g, internal standard for GC) in *n*-hexane (50 mL) was stirred and irradiated at room temperature for 5 h, at which time the consumption of triethylsilane (62%) ceased. Monitoring the course of the reaction by GC (capillary column 44 m, OV-1, temp prog 50−250 °C/8 °C min^{-1}; FID; carrier gas H_2, 0.8 bar; samples 0.2 μL) showed the gradual disappearance of **6** (GC factor $F = 0.985$) and triethylsilane ($F = 1.377$) with the concomitant formation of the (triethylsilyl)cyclohexene isomers ($F = 1.366$) **16a**,**b** (90% and 6% ultimate yields, respectively, based on the consumed starting materials).

Method c. A cold solution (−30 °C) of 1,4-cyclohexadiene (**7**) (3.7 mL, 40 mmol), triethylsilane (6.4 mL, 40 mmol), Cr$(CO)_3$(η^4-norbornadiene)(η^2-ethene) (ca. 1.8 mmol, *in situ* generated),[25] and *n*-octane (1.9968 g, internal standard for GC) in *n*-hexane (200 mL) was warmed to room temperature and stirred for 140 min, at which time the triethylsilane was no longer detectable in the IR spectra. GC of the samples drawn during the catalytic run showed the gradual consumption of the starting materials with concomitant formation of (triethylsilyl)norbornene (identified by GC−MS, $M^+ = m/e$ 208; 184 mg, 0.88 mmol), **16a** (65% ultimate yield), and **16b** (20% ultimate yield).

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