

Photocatalytic hydrosilylation of conjugated dienes with triethylsilane in the presence of $\text{Cr}(\text{CO})_5\text{L}$ ($\text{L} = \text{CO}, \text{P}(\text{CH}_3)_3, \text{P}(\text{OCH}_3)_3$)

Saim Özkar^{*}, Vagif M. Akhmedov¹, Ceyhan Kayran

Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey

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Abstract

The effect of donor ligands on the chromium carbonyl photocatalysed hydrosilylation of 1,3-butadiene, 2-methyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, *trans*-1,3-pentadiene with triethylsilane was studied. Photocatalytic hydrosilylation of dienes conducted in the presence of $\text{Cr}(\text{CO})_5\text{L}$ ($\text{L} = \text{P}(\text{CH}_3)_3$ or $\text{P}(\text{OCH}_3)_3$) yields the *cis*-1,4-adducts, 1-triethylsilyl-2-butene derivatives, as the main products; these have been isolated by distillation or preparative GC and fully characterised by NMR spectroscopy. As with the photocatalytic hydrosilylation of dienes in the presence of $\text{Cr}(\text{CO})_6$, we propose a mechanism which involves the initial conversion of $\text{Cr}(\text{CO})_5\text{L}$ into *fac*- $\text{Cr}(\text{CO})_3\text{L}(\eta^4\text{-1,3-diene})$ followed by a further photolytic CO substitution by triethylsilane, forming a $\text{Cr}(\text{CO})_2(\text{H})(\text{SiEt}_3)\text{L}(\eta^4\text{-1,3-diene})$ intermediate. The addition of hydride to diene occurs reversibly to form an $\eta^3\text{-enyl}$ ligand 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. $\text{Cr}(\text{CO})_5\text{L}$ complexes form active species which are much more stable than the one generated from $\text{Cr}(\text{CO})_6$ in the absence of any donor ligands. Thus, introduction of an equimolar amount of donor ligand (trimethylphosphine or trimethylphosphite) increases the life of the catalyst. This leads to the achievement of larger turn-over numbers (80 or 70) compared with the value of 30 for just $\text{Cr}(\text{CO})_6$. $\text{Cr}(\text{CO})_5\text{L}$ ($\text{L} = \text{P}(\text{C}_6\text{H}_5)_3, \text{P}(\text{C}_6\text{H}_{11})_3$ or $\text{C}_5\text{H}_4\text{N}$) proved inactive in the attempted photocatalytic hydrosilylation of dienes.

Keywords: Carbonyl; Chromium; Diene; Hydrosilylation; Photocatalysis; Phosphine

1. Introduction

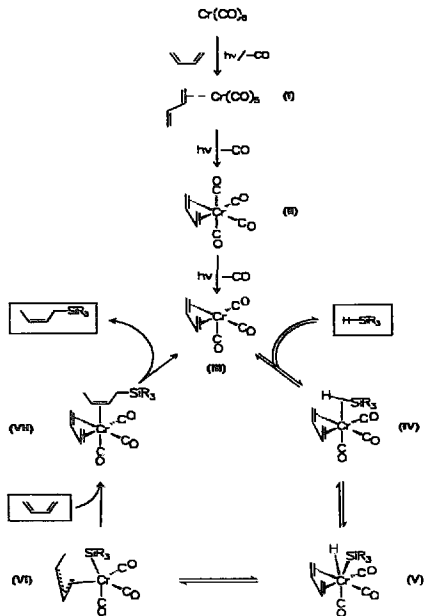
The development of the synthesis of organosilicon compounds using a variety of transition metal complexes has been one of the most remarkable advances in chemistry in the recent decades [1]. Hydrosilylation of various conjugated dienes catalysed by transition metal complexes provides convenient routes to unsaturated organosilicon compounds and also serves as a unique and effective method for the selective formation of carbon–silicon bonds. A typical example is the photocatalytic hydrosilylation of conjugated diolefins with some alkylsilanes using Group 6 metal carbonyl complexes as catalysts [2,3]. The reactions yielded exclusively the *cis*-1,4-adducts. Recently, we reported the results of an extensive study on the mechanistic details of the chromium-carbonyl photocatalysed hydrosilyla-

tion of 1,3-dienes with triethylsilane [4]. The proposed mechanism (Scheme 1) involves the initial conversion of $\text{Cr}(\text{CO})_6$ into $\text{Cr}(\text{CO})_4(\eta^4\text{-1,3-diene})$ followed by a further photolytic CO substitution by trialkylsilane forming a $\text{Cr}(\text{CO})_3(\text{H})(\text{SiR}_3)(\eta^4\text{-1,3-diene})$ intermediate. Experiments with $\text{Et}_3\text{Si-D}$ showed a reversible addition of the hydride to diene to form an $\eta^3\text{-enyl}$ ligand 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 (Scheme 1) [4].

It is well known that the catalytic activity and selectivity of transition metal complexes very often depend on the nature of other ligands present in the coordination sphere of the metal ion in the course of the catalytic reaction [5]. Therefore, the presence of a donor ligand, such as trialkylphosphine, in the reaction medium is expected to affect many steps in the mechanism proposed for the photocatalytic hydrosilylation of conjugated dienes. For instance, its trivial involvement in the first CO-substitution in hexacarbonylchromium(0) would

^{*} Corresponding author. E-mail: sozkar@roruqaal.cc.metu.edu.tr.

¹ On leave of absence from Baku State University, Azerbaijan.



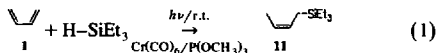
Scheme 1.

lead to the formation of pentacarbonyltrialkylphosphinechromium(0) which might react further with substrates to form an active catalyst. Such an active species might have catalytic activity and selectivity different from those produced from hexacarbonylchromium(0) in the photocatalytic hydrosilylation of dienes. This has motivated us to investigate the effect of donor ligands on the photocatalytic addition of Si-H to the conjugated dienes. 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), and 2-methyl-1,3-butadiene (4) with triethylsilane using either a 1:1 mixture of $\text{Cr}(\text{CO})_6$ and L, or $\text{Cr}(\text{CO})_5\text{L}$ (L = $\text{P}(\text{CH}_3)_3$, $\text{P}(\text{OCH}_3)_3$, $\text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{C}_6\text{H}_{11})_3$, $\text{C}_5\text{H}_5\text{N}$) as catalysts.

2. Results and discussion

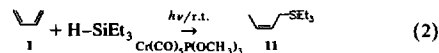
The reaction of 1,3-butadiene (1) with triethylsilane in the presence of hexacarbonylchromium(0) and trimethylphosphite (1:1 ratio) under continuous irradiation

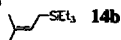
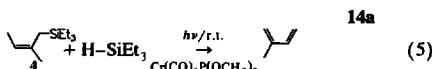
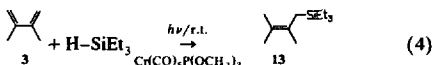
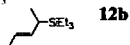
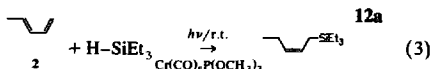
yields exclusively the *cis*-1,4-adduct, *cis*-1-triethylsilyl-2-butene (11), the same product as obtained from the photocatalytic hydrosilylation using just hexacarbonylchromium(0) [2] (Eq. (1)).



IR spectroscopic monitoring of the reaction reveals that, in addition to the gradual disappearance of the Si-H stretching band at 2102 cm^{-1} and CO-stretching band of $\text{Cr}(\text{CO})_6$ at 1980 cm^{-1} , four bands first grow in at 2073 s, 1985 vw, 1963 s, and 1949 vs cm^{-1} , which are readily assigned to the well known $\text{Cr}(\text{CO})_5\text{P}(\text{OCH}_3)_3$ complex [6]. These bands then start to lose intensity with concomitant development of three new CO-stretching bands at 1989, 1917, and 1900 cm^{-1} upon continuing irradiation. The latter bands are assigned to *fac*- $\text{Cr}(\text{CO})_5\text{P}(\text{OCH}_3)_3(\eta^4\text{-1,3-butadiene})$, which has been isolated from the photolytic reaction of $\text{Cr}(\text{CO})_5\text{P}(\text{OCH}_3)_3$ and 1,3-butadiene in *n*-hexane at -20°C [7]. Once this complex is generated upon irradiation in the solution, the IR spectrum remains practically unaltered in the CO-stretching region throughout the photocatalytic hydrosilylation. These observations imply that the photocatalytic reactions can also be started by using either $\text{Cr}(\text{CO})_5\text{P}(\text{OCH}_3)_3$ or *fac*- $\text{Cr}(\text{CO})_5\text{P}(\text{OCH}_3)_3(\eta^4\text{-1,3-butadiene})$ as catalytic precursor. Indeed, continuous irradiation of 1,3-butadiene and triethylsilane in the presence of either $\text{Cr}(\text{CO})_5\text{P}(\text{OCH}_3)_3$ or *fac*- $\text{Cr}(\text{CO})_5\text{P}(\text{OCH}_3)_3(\eta^4\text{-1,3-butadiene})$ gives the same 1,4-hydrosilylation product, *cis*-1-triethylsilyl-2-butene (11). The photolytic conversion of $\text{Cr}(\text{CO})_5\text{P}(\text{OCH}_3)_3$ into *fac*- $\text{Cr}(\text{CO})_5\text{P}(\text{OCH}_3)_3(\eta^4\text{-1,3-butadiene})$ requires additional time before the catalytic cycle starts. After this conversion there is no difference between the two experiments started with either $\text{Cr}(\text{CO})_5\text{P}(\text{OCH}_3)_3$ or *fac*- $\text{Cr}(\text{CO})_5\text{P}(\text{OCH}_3)_3(\eta^4\text{-1,3-butadiene})$ with respect to the rates and products of the hydrosilylation. However, the use of $\text{Cr}(\text{CO})_5\text{P}(\text{OCH}_3)_3$ is preferred in order to avoid laborious isolation of *fac*- $\text{Cr}(\text{CO})_5\text{P}(\text{OCH}_3)_3(\eta^4\text{-1,3-butadiene})$.

Continuous irradiation of various acyclic 1,3-dienes, triethylsilane, and $\text{Cr}(\text{CO})_5\text{P}(\text{OCH}_3)_3$ (in molar ratio 20:20:1) in *n*-hexane solution results in nearly quantitative hydrosilylation of the diene, as monitored by GC. The products of these photocatalytic hydrosilylations are found to be the same as those obtained from the reactions using just hexacarbonylchromium(0), as detected by means of GC-MS and fully characterized by ^1H and ^{13}C NMR spectroscopy [4].



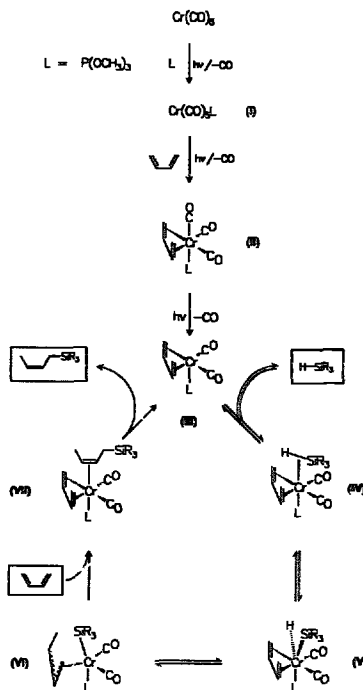


The reactions in Eqs. (2) and (4) give only one hydrosilylation product, while two hydrosilylation products are formed by the reactions in Eqs. (3) and (5). Continuous irradiation of *trans*-1,3-pentadiene (2), triethylsilane, and pentacarbonyltrimethylphosphitechromium(0) (in molar ratio 20:20:1) in hexane solution results in the formation of two hydrosilylation products, *cis*-1-(triethylsilyl)-2-pentene (12a) and *trans*-4-(triethylsilyl)-2-pentene (12b) in ca. 25:1 ratio, as detected by means of GC-MS. 12a is a *cis*-1,4-hydrosilylation product while 12b has been shown to result from a 1,2-hydrosilylation with attachment of the triethylsilyl group to C-2 of the diene [4]. Two 1,4-addition products, *cis*-1-(triethylsilyl)-2-methyl-2-butene (14a) and *cis*-1-(triethylsilyl)-3-methyl-2-butene (14b), are formed from the photocatalytic reaction of 2-methyl-1,3-butadiene (4) with triethylsilane in the presence of pentacarbonyltriethylphosphitechromium(0), Eq. (5), in ca. 3:1 ratio, as detected by means of GC-MS.

In all cases, monitoring of the reaction by using IR spectroscopy shows the initial conversion of $\text{Cr}(\text{CO})_2(\text{P}(\text{OCH}_3)_3)_2$ (I) into the respective *fac*- $\text{Cr}(\text{CO})_2(\text{P}(\text{OCH}_3)_3)_2(\eta^4\text{-1,3-diene})$ (II). The photochemical formation of complexes of this type from pentacarbonyl(trialkylphosphine)chromium(0) and diene is known [7–9] and their role as the precursor to the active catalyst in the photocatalytic hydrogenation of norbornadiene [10] has been tested. As expected, the hydrosilylation of 1,3-butadiene under continuous irradiation in the presence of *fac*- $\text{Cr}(\text{CO})_2(\text{P}(\text{OCH}_3)_3)_2(\eta^4\text{-1,3-butadiene})$ as catalyst instead of $\text{Cr}(\text{CO})_2(\text{P}(\text{OCH}_3)_3)_2$ gives the same results. Based on the X-ray structural analysis of an analogous tungsten complex [11], *fac*- $\text{Cr}(\text{CO})_2(\text{P}(\text{OCH}_3)_3)_2(\eta^4\text{-1,3-butadiene})$ (II) is assumed to have the trimethylphosphite ligand on a facial position close to the C-2 and C-3 carbon atoms of the diene ligand. As with the mechanism outlined in Scheme 1, photolytic detachment of CO from *fac*- $\text{Cr}(\text{CO})_2(\text{P}(\text{OCH}_3)_3)_2(\eta^4\text{-1,3-butadiene})$ should provide entrance to the catalytic cycle by creating the vacant coordination site on the transition metal centre required

for binding the silane prior to its transfer onto the diene ligand (Scheme 2).

Since all the dienes give the same 1,4-hydrosilylated products as in the reactions using just hexacarbonylchromium(0) it may be assumed that the vacant coordination site of the $\text{Cr}(\text{CO})_2(\text{P}(\text{OCH}_3)_3)_2(\eta^4\text{-1,3-butadiene})$ fragment (III) is in an axial position, suited for the 1,4-addition of $\text{R}_3\text{Si-H}$ to the diene. However, no evidence exists for the relative position of the trimethylphosphite ligand in III. We have shown that insertion of the metal into the Si-H bond in a non-classical $\eta^2\text{-(H-SiR}_3\text{)}$ complex leads to the formation of a complex containing hydrido and trialkylsilyl ligands [4]. In the present case, this type of reaction would lead to the formation of $\text{Cr}(\text{CO})_2(\eta^2\text{-1,3-diene})(\text{hydrido})(\text{trialkylsilyl})\text{P}(\text{OCH}_3)_3$ (V). If so, the 1,4-addition of $\text{R}_3\text{Si-H}$ to the diene should occur in stepwise fashion, in contrast to the transfer of H_2 to the diene, which by means of PHIP experiments has been shown to proceed rapidly via an $\eta^2\text{-H}_2$ bound intermediate [12]. The subsequent transfer of R_3Si to the organic



Scheme 2.

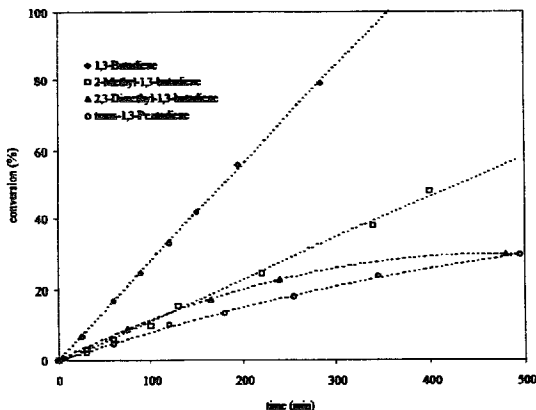


Fig. 1. Conversion of triethylsilane vs. time plots for dienes.

substrate, take-up of a new diene substrate molecule, release of the trialkylsilyl-butene product, and coordination of R_3Si-H would then complete the catalytic cycle.

A plot of the conversion of triethylsilane vs. time (Fig. 1) reflects the reactivity of the diene in the photocatalytic hydrosilylation in the presence of pentacarbonyltrimethylphosphitechromium(0) (I) under the same conditions (molar ratio of triethylsilane:diene:complex I is 20:20:1, 10 mM substrate in 200 ml *n*-hexane at room temperature in the same apparatus). 1,3-Butadiene is found to undergo the fastest photocatalytic hydrosilylation among the dienes investigated. A methyl sub-

stituent in the diene slows down the photocatalytic reaction. This might be attributed to the steric hindrance between the methyl group(s) of the diene and trimethylphosphite ligand in the catalytically active species. Such a substituent effect on the rate of photocatalytic hydrosilylation was not obvious in the case of hexacarbonylchromium(0), though slight differences were noticed on passing from butadiene to the methyl-substituted derivatives.

In order to study the effect of various donor ligands, photocatalytic hydrosilylation of 1,3-butadiene was performed by using $Cr(CO)_6$, $(CO)_5CrP(OCH_3)_3$,

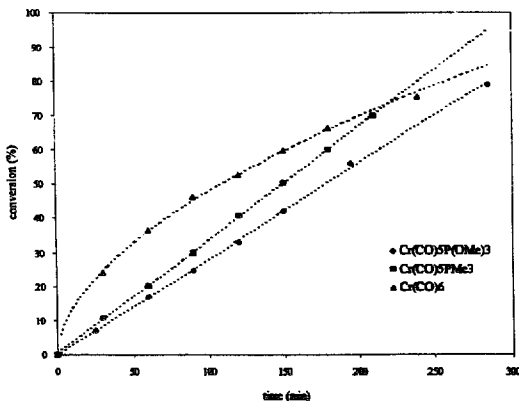
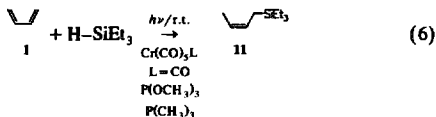


Fig. 2. Conversion of triethylsilane vs. time plots for 1,3-butadiene in the presence of three different catalysts.

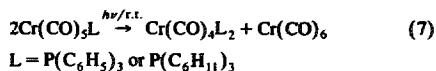
$(\text{CO})_5\text{CrP}(\text{CH}_3)_3$, $(\text{CO})_5\text{CrP}(\text{C}_6\text{H}_5)_3$, $(\text{CO})_5\text{CrP}(\text{C}_6\text{H}_{11})_3$, and $(\text{CO})_5\text{Cr}(\text{pyridine})$ as catalyst under the same conditions (molar ratio of triethylsilane:diene:complex is 20:20:1, 10 mM substrate in 200 ml *n*-hexane at room temperature in the same apparatus). The results of these experiments show that only the first three complexes catalyse the hydrosilylation of 1,3-butadiene under continuous irradiation, yielding the same 1,4-hydrosilylated product, *cis*-1-triethylsilyl-2-butene, **11** (Eq. (6)).



IR spectroscopic monitoring of the photocatalytic reactions enables one to compare the rate of conversion of triethylsilane for the three catalysts (Fig. 2). In the case of $\text{Cr}(\text{CO})_6$ the conversion of triethylsilane is quite fast at the beginning of the reaction. However, the rate of conversion decreases as the reaction proceeds. This might be due to the gradual decrease in the amount of the catalyst. Indeed, the IR spectroscopic monitoring of the reaction shows further that the total area under the CO stretching bands of $\text{Cr}(\text{CO})_6$ and $\text{Cr}(\text{CO})_5(\eta^4\text{-1,3-diene})$ decreases under continuous irradiation. In the case of $(\text{CO})_5\text{CrP}(\text{OCH}_3)_3$ or $(\text{CO})_5\text{CrP}(\text{CH}_3)_3$, the rate of conversion of triethylsilane is practically constant throughout the photocatalytic hydrosilylation. IR spectroscopic monitoring of the reaction indicates that there is no momentous change in the total concentration of the catalysts, $(\text{CO})_5\text{CrL}$ and $\text{Cr}(\text{CO})_5(\eta^4\text{-1,3-diene})\text{L}$. The turn-over numbers are estimated to be greater than 80 and 70, for $(\text{CO})_5\text{CrP}(\text{OCH}_3)_3$ and $(\text{CO})_5\text{CrP}(\text{CH}_3)_3$ respectively, from measurement of the amounts of catalyst consumed; this is achieved by monitoring the intensity decrease in the IR absorption band for the CO stretching when the silane is completely used up. These values are notably larger than the turn-over number of 30 found when just hexacarbonylchromium(0) is used in the same photocatalytic reaction [2]. This observation implies that the introduction of trimethylphosphine or trimethylphosphite in 1:1 ratio into the medium stabilizes the active catalyst towards any oxidation or decomposition (thermal or photochemical) which would lead to its death.

In contrast to $(\text{CO})_5\text{CrP}(\text{OCH}_3)_3$ or $(\text{CO})_5\text{CrP}(\text{CH}_3)_3$, the analogous complexes $(\text{CO})_5\text{CrP}(\text{C}_6\text{H}_5)_3$, $(\text{CO})_5\text{CrP}(\text{C}_6\text{H}_{11})_3$, and $(\text{CO})_5\text{Cr}(\text{pyridine})$ were found not to be catalytically active in the photolytic hydrosilylation of 1,3-diene. Both pentacarbonyltriphenylphosphinechromium(0) and pentacarbonyltris(cyclohexyl)phosphinechromium(0) undergo disproportion-

ation under the reaction conditions upon continuous irradiation.



Hexacarbonylchromium(0) formed from this disproportionation reaction acts as catalyst in the 1,4-hydrosilylation of 1,3-butadiene, whereby the rate of reaction is slow due to the reduced amount of hexacarbonylchromium(0).

$(\text{CO})_5\text{Cr}(\text{pyridine})$ is rapidly converted to a mixture of many carbonyl complexes upon irradiation of the solution, as observed in the CO-stretching region of the IR spectrum. Among all the carbonyl complexes photo-generated from $(\text{CO})_5\text{Cr}(\text{pyridine})$ in the solution, only tetracarbonyl($\eta^2\text{-1,3-butadiene}$)chromium(0) could be identified. Owing to the presence of the latter carbonyl complex in a trace amount in the solution, a small portion of triethylsilane (3%, monitored by IR spectroscopy) is converted into the *cis*-1-triethylsilyl-2-butene, **11**.

3. Conclusion

The results of this investigation show that the hydrosilylation of the conjugated dienes with triethylsilane occurs almost exclusively as a 1,4-addition in the presence of hexacarbonylchromium(0), pentacarbonyltrimethylphosphinechromium(0), or pentacarbonyltrimethylphosphitechromium(0). Moreover, there is convincing evidence that the mechanism involves initial conversion of $\text{Cr}(\text{CO})_5\text{L}$ into *fac*- $\text{Cr}(\text{CO})_3\text{L}(\eta^4\text{-1,3-diene})$ followed by a further photolytic CO substitution by triethylsilane forming a $\text{Cr}(\text{CO})_2(\text{H})(\text{SiEt}_3)\text{L}(\eta^4\text{-1,3-diene})$ intermediate. The addition of hydride to diene occurs reversibly to form an $\eta^3\text{-enyl}$ ligand 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. $\text{Cr}(\text{CO})_5\text{L}$ complexes form active species which are much more stable than that generated from $\text{Cr}(\text{CO})_6$ in the absence of any donor ligands. Thus, the introduction of an equimolar amount of the donor ligand (trimethylphosphine or trimethylphosphite) makes the life of catalyst longer, leading to larger turn-over numbers.

4. Experimental section

All of the reactions and manipulations involving the metal carbonyl catalysts were carried out either in vacuum or under dry inert atmosphere (N_2 or Ar). Solvents were distilled after refluxing over metallic sodium or phosphorus pentoxide under nitrogen for several days.

Triethylsilane (Merck), hexacarbonylchromium(0) (Aldrich), were available commercially and used without further purification. The dienes (except 1,3-butadiene²) were commercially available (Aldrich) and distilled before use. Photochemical reactions were carried out in an immersion-well apparatus [13] (solidex glass, $\lambda > 280$ nm) by using a Hanau TQ 150 high pressure mercury lamp, which was cooled by circulating water or precooled methanol. Pentacarbonyltrimethylphosphinechromium(0) [14], pentacarbonyltrimethylphosphitechromium(0) [14], and *fac*-tricarbonyltrimethylphosphite(η^4 -1,3-butadiene)chromium(0) [7] were prepared according the literature procedures.

NMR spectra were recorded on a Bruker DPX 400 spectrometer (400.132 MHz for ¹H, 100.613 MHz for ¹³C, and 161.996 MHz for ³¹P) using TMS as internal reference for ¹H and ¹³C, and H₃PO₄ in a capillary as external reference for ³¹P. Perkin–Elmer 16 PC FTIR and 1430 IR spectrophotometers were used to follow the disappearance of the $\nu_{\text{Si-H}}$ absorption band at 2102 cm⁻¹ and spectral changes in the CO-stretching region 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. GC-MS spectra were obtained by using a Perkin–Elmer R22 GC apparatus (OV-1, 30 in column, 60–280 °C, H₂ carrier gas) combined with a Finnigan MAT CH 7A mass spectrometer (EI).

All of the hydrosilylation products isolated were shown to have the same spectroscopic data as those reported previously [4]. In the case of 1,3-butadiene, the turn-over number was determined for the *fac*-Cr(CO)₃P(OCH₃)₃(η^4 -1,3-butadiene) and *fac*-Cr(CO)₃P(CH₃)₃(η^4 -1,3-butadiene) by determining the loss in the catalyst concentration when the triethylsilane had been completely consumed (i.e. when the Si–H band disappeared in the IR spectrum). Both complexes have IR absorption bands for the CO stretching vibration at 1989, 1917, and 1900 cm⁻¹, and 1981, 1909, and 1885 cm⁻¹ respectively. The changes in concentrations

for the *fac*-Cr(CO)₃P(OCH₃)₃(η^4 -1,3-butadiene) or *fac*-Cr(CO)₃P(CH₃)₃(η^4 -1,3-butadiene) were determined by measuring the intensity loss of the highest frequency bands at 1989 ($\epsilon = 3690$ l mol⁻¹ cm⁻¹) or 1981 cm⁻¹ ($\epsilon = 4820$ l mol⁻¹ cm⁻¹) respectively.

Acknowledgements

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