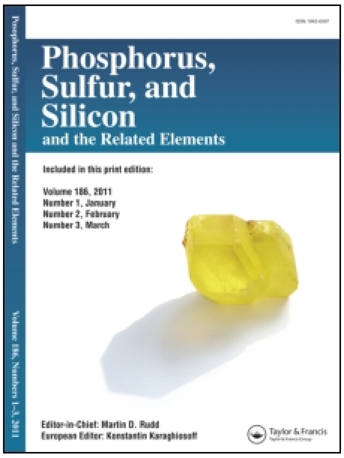

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Catalytic Hydrosilylation of Substituted Acetophenones by 1,1,3,3-Tetrametyldisiloxane with Complexes Rhodium (I) and Platinum (II)

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To cite this Article Zuev, Vjacheslav V. and de Vekki, Dimitry A.(2005) 'Catalytic Hydrosilylation of Substituted Acetophenones by 1,1,3,3-Tetrametyldisiloxane with Complexes Rhodium (I) and Platinum (II)', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 9, 2071 — 2083

To link to this Article: DOI: 10.1080/104265090902859

URL: http://dx.doi.org/10.1080/104265090902859

Phosphorus, Sulfur, and Silicon, 180:2071–2083, 2005
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/104265090902859

Catalytic Hydrosilylation of Substituted Acetophenones by 1,1,3,3-Tetrametyldisiloxane with Complexes Rhodium (I) and Platinum (II)

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The hydrosilylation of a range of para-substituted acetophenones $XC_6H_4COCH_3$ ($X = H$, Me, MeO, F, Cl, NO_2) with 1,1,3,3-tetramethyl disiloxane mediated by complexes of rhodium (I) and platinum (II) was investigated. The complexes of platinum (II) are less effective than complexes of rhodium (I), but display greater selectivity. Six 1-(1′-arylethoxy)-1,1,3,3-tetramethyl disiloxanes have been synthesized by hydrosilylation using several coupling catalysts.

Keywords Hydrosilylation; substituted acetophenones; rhodium; platinum

For development of organic chemistry, such synthetic methods are needed that combine simple protocol with a variety of structures. The hydrosilylation of various functional groups catalyzed by transition metal complexes are one of the simplest methods for the modification of organic substrates.[1] This reaction also serves as a unique and effective method for selective reduction of carbon-heteroatom bonds (including

Received August 13, 2004; accepted October 5, 2004.

Dimitry A. de Vekki gratefully acknowledges financial support for the President of the Russian Federation (grant N MK-133.2003.03), the Ministry of Education of the Russian Federation (grant N PD02-1.3-130), and the Government of Sankt Petersburg (grant N PD03-1.3-39). We also thank Dr. V. N. Spevak for providing the $[PtC_{44}H_{28}N_4]$ complex and Prof. V. A. Galishev for providing the $[Rh(Ph_2PNCO)_2(CO)Cl]$ complex.

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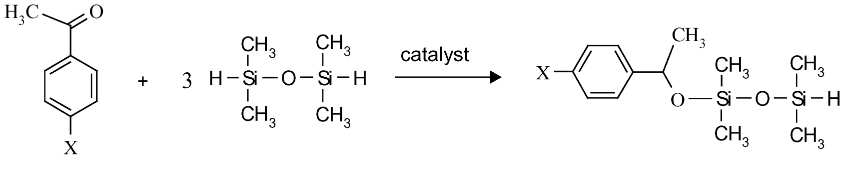
asymmetric reduction).[2,3] The limitation of this reaction is the use of hydrosilanes (for example chlorosilanes) giving air-sensitive products. To solve this problem, we have chosen 1,1,3,3-tetramethyl disiloxane as a reagent leading to stable products of hydrosilylation, which also may be used in the next steps of hydrosilylation.

The acetyl group is one of the most convenient synthon in organic chemistry because its introduction into aromatic and heteroaromatic compounds is very simple. The possibility of synthesis as a result of hydrosilylation of the acetyl group with chiral catalysts of chiral alcohols[3] was also of interest. The para-substituted acetophenones with electron-donating and electron-withdrawing substituents were chosen as substrates for hydrosilylation. They permit us to investigate the influence of electronic properties of a substituent on the rate and direction of hydrosilylation. We used as catalysts the complexes of rhodium (I) and platinum (II). They proved effective catalysts for hydrosilylation of ketones[4,5] and vinylsiloxanes.[6,7]

RESULTS AND DISCUSSION

Our reason for selecting a relatively high temperature for hydrosilylation (70°C) was caused by an attempt to obtain maximal yields in a short time. However, this high reaction temperature may lead to a decrease in optical induction when chiral catalytic complexes are used.[2]

Catalytic hydrosilylation of investigated acetophenones with excess (1:3 molar ratio) of 1,1,3,3-tetramethyl disiloxane produces only silyl ether (Scheme 1).

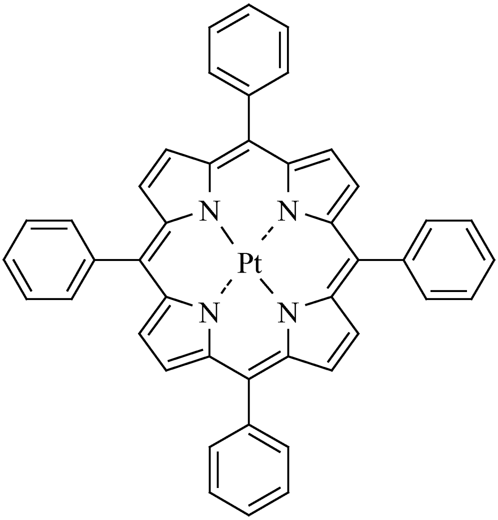


$X = H, CH_3, OCH_3, F, Cl, NO_2$

SCHEME 1

This behavior differs from that in the hydrosilylation of acetophenone with hydrosilanes when the formation of silyl ethers of enols also are observed. When dihydrosilanes are used, the products of biaddition are formed.[4] Only one byproduct was observed. It was the product of the hydrosilylation of acetophenones with 1,1,3,3,5,5-hexamethyl trisiloxane. The trisiloxane was formed at the catalytic disproportional of the starting disiloxane. This process and other side reactions in hydrosilylation with hydrosiloxanes were investigated in detail in reference.[8] The yields of these by-products are 1–2% (according to ^{1}H NMR data) and do not depend on the catalysts used.

The selection of catalytic complexes was based on their solubility in the reaction mixture because hydrosilylation takes place in homogeneous conditions. We used the Wilkinson catalyst [Rh(Ph_3P)$_3$Cl] (which gave good results in hydrosilylation of ketones[1,9]), [Rh(Ph_2PNCO)$_2$(CO)Cl], and [Rh(acac)(CO)Cl] complexes of rhodium (I), as well as 1-methylcycloocta-1,5-diene (MCOD) complexes of palladium (II) [Pd(MeCOD)Cl_2]. The platinum (II) complexes [Pt(L)(L′)Cl_2] were selected with phospine, stibine, sulfoxide, and cyclooctadiene ligands. The tetraazaphorfirine complex [$PtC_{44}H_{28}N_4$] (Scheme 2), which is plane, is of interest because its catalytic activity is due to the coordination at the p_z-orbital.



SCHEME 2

We used a solution of $Na_2[PtCl_6]$ in *i*-PrOH instead of an industrial Speier catalyst (solution of H_2PtCl_6 in *i*-PrOH), which has the same catalytic activity but is more stable.

Table I summaries the hydrosilylation of acetophenone with 1,1,3,3-tetramethyl disiloxane catalyzed by several metal complexes. The Wilkinson catalyst gave the best results. The 80% conversion was achieved after 63 h at 70°C. This corresponds to the literature data.[1] The platinum (II) complexes studied are less effective as catalysts for

TABLE I The Conversion of Parasubstituted Acetophenones $XC_6H_4COCH_3$ at Hydrosilylation with 1,1,3,3-Tetramethyl Disiloxane (70°C, $c_K = 1.42 \times 10^{-3}$ mol · dl^{-1}) Calculated from ^1H NMR Spectra of Reaction Mixtures

	Substituent X (δ_H, ppm, ^1H, $COC\underline{H}_3$)					
Catalyst	H (2.35)[a]	Me (2.32)[a]	MeO (2.51)[a]	F (2.27)[a]	Cl (2.51)[a]	NO_2 (2.63)[a]
cis-$[Pt(Ph_3Sb)_2Cl_2]$	16.7	*[b]	*	13.1	12.8	*
cis-$[Pt(Et_2SO)_2Cl_2]$	17.2	17.7	≅100	77.9	42.2	13.3
cis-$[Pt(Ph_3P)_2Cl_2]$	*	*	*	12.2	5.3	28.3[c]
(−)-cis-Pt(Me-*p*-TolSO)(Py)Cl_2]	*	19.5	≅100	27.1	34.3	*
cis-[Pt(EtCN)(dmso)Cl_2]	*	*	*	68.7	52.8	*
[Pt(MeCOD)Cl_2]	19.8	19.5	≅100	56.7	50.0	23
$[PtC_{44}H_{28}N_4]$	*	*	≅100	15.5	33.3	*
$Na_2[PtCl_6] \times 6H_2O$	41.5	41.7	58.2	*	*	*
[Rh(acac)$(CO)_2$]	*	*	*	*	≅100	≅100[c]
$[Rh(Ph_3P)_3Cl]$	79.5	80.1	*	*	*	100[c]
Reaction time, h	63	63	60	61	63	60

[a] Value of ^1H chemical shift (δ, ppm) of the $COC\underline{H}_3$ group of parasubstituted acetophenones. $XC_6H_4COCH_3$ in chloroform-d solution.

[b] (*) The hydrosilylation with this catalyst was not provided.

[c] The hydrosilylation was accompanied with the reduction (∼50%).

the hydrosilylation of acetophenone; conversions were about 20% after 63 h. The solution of $Na_2[PtCl_6]$ in *i*-PrOH gave better results (conversion 41.5%). In comparison with other hydrosilanes (($MeSiHCl_2$, $MePhSiH_2$, Ph_2SiH_2) used for hydrosilylation of acetophenone, the activity of 1,1,3,3-tetramethyl disiloxane is lower for most catalytic complexes. For example, in the hydrosilylation of acetophenone with diphenilsilane, 50% conversion was achieved after 81.6 min at 60°C[4] using cis-$[Pt(Et_2SO)_2Cl_2]$ as a catalyst. In the case of 1,1,3,3,-tetramethyl disiloxane, 17.2% conversion was achieved after 63 h at at 70°C.

The introduction in the substrate of such a weak electron-donating substituent as the methyl group changes only slightly the course of hydrosilylation (Table I). The use of the chiral platinum (II) complexes (−)-cis-[Pt(Me-*p*-TolSO)PyCl_2] was relatively successful because the conversion in this case was about only 20%. This complex contains an optically active ligand, (+)-methyl-*para*-tolylsulfoxide (Me-*p*-TolSO), and is promising for asymmetric synthesis.

The methoxy group reverses the pattern of reaction. The substituent with powerful electron-donating properties (+I and +M effects) leads to almost complete conversion when platinum (II) complexes are used

(Table I). Moreover, the activity of $Na_2[PtCl_6]$ in a *i*-PrOH solution does not greatly increases.

The presence in acetophenones of electro-withdrawing substituents with a strong –I effect and a low +M effect (F and Cl) leads to increasing conversion of hydrosilylation with platinum (II) complexes (Table I) as compared to that with 4-methylacetophenone. However, conversion is much lower than in the case of 4-methoxyacetophenone. Cis-$[Pt(Ph_3P)_2Cl_2]$ has the lowest activity in good agreement withthe activities of plane-square complexes of platinum (II) used in hydrosilylation.[10] The catalytic activity of complexes of platinum (II) in hydrosilylation of 4-chloroacetophenone decreases in the following order:

$$\begin{aligned}&cis\text{-}[Pt(Et_2SO)_2Cl_2] > cis\text{-}[Pt(EtCN)(dmso)Cl_2] > [Pt(MeCOD)Cl_2]\\&\quad\gg(-)\text{-}cis\text{-}[Pt(Me\text{-}p\text{-}TolSO)PyCl_2] > [PtC_{44}H_{28}N_4]\\&\qquad > cis\text{-}[Pt(Ph_3Sb)_2Cl_2] > cis\text{-}[Pt(Ph_3P)_2Cl_2].\end{aligned}$$

In contrast to platinum (II) complexes, the rhodium (I) complex $[Rh(acac)(CO)_2]$ allows us to achieve complete conversion of 4-chloroacetophenone (Table I).

4-nitroacetophenone as a substrate has two features. First, the nitro group is the strongest electron-withdrawing substituent. Second, it may be reduced to the amino group with hydrosilanes becoming an electron-donating substituent. In this connection, the most active complexes of rhodium (I) were used, and for comparison cis-$[Pt(Et_2SO)_2Cl_2]$, $[Pt(MeCOD)Cl_2]$, $[Pd(MeCOD)Cl_2]$, and mixed rhodium-platinum complex $[Rh(CO)_2Cl_2]\cdot[Pt(Ph_2PCH{=}CH_2)_2]$ were also applied (Table I). The complexes of rhodium (I) achieved the maximal conversion of the substrate, but their action was accompanied by the reduction of the nitro group (about 50%). One exception is $[Rh(Ph_2PNCO)_2(CO)Cl]$. Its action was not accompanied by reduction, but the conversion of 4-nitroacetophenone was less than 59% (for 60 h at 70°C). $[Pd(MeCOD)Cl_2]$ was less active in comparison with the complexes of rhodium (I) (conversion about 95%), but more selective (~65%). The hydrosilylation of 4-nitroacetovenone was not accompanied by the reduction with cis-$[Pt(Et_2SO)_2Cl_2]$ and $[Pt(MeCOD)Cl_2]$, but the conversion was low (Table I). In the case of cis-$[Pt(Ph_3P)_2Cl_2]$, the fraction of reduction was about 45%.

Thus, the hydrosilylation of para-substituted acetophenones with 1,1,3,3-tetramethyl disiloxane depends on the substituent nature and on the catalyst, and may be used for preparative synthesis of silyl ethers of various structures.

Six new 1-(1′-arylethoxy)-1,1,3,3-tetramethyl disiloxanes were synthesized (see the Experimental section). In the hydrosilylation of 4-methyl- and 4-methoxyacetophenones, a chiral (−)-cis-[Pt(Me-*p*-TolSO)$_2$Cl$_2$] was used as a catalyst, and optically active silyl ethers with specific optical rotation, $[\alpha]_D^{18} = +0.8^\circ$ and $+1.05^\circ$ for methyl and methoxy derivatives, respectively, were synthesized. The degree of optically induction was not determined.

For comparison of catalytic activity of complexes, hydrosilylation was examined at a short time interval because at low conversions their values may be used as kinetic parameters. Among rhodium (I) complexes, [Rh(Ph$_2$PNCO)$_2$(CO)Cl] was chosen because only in this case the hydrosilylation of 4-nitroacetophenone was not accompanied by the reduction of a nitro group. Among platinum (II) complexes, [Pt(MeCOD)Cl$_2$] and cis-[Pt(Et$_2$SO)$_2$Cl$_2$] was chosen (Table II).

It is not possible to describe the conversion of para-substituted acetophenones at hydrosilylation with 1,1,3,3-tetramethyl disiloxane using the Hammett relationship with σ parameters because both high and low conversion was observed for acetophenones both with electron-donating and with electron-withdrawing substituents (Table II). It results from the indirect influence of a substituent on the reaction center (aceto group). The effect of the substituent causes redistribution of electron density on the reaction center and this redistribution may be estimated from the ^{1}H NMR chemical shift of the COCH$_3$ group (Table II). A linear dependence was observed between the ^{1}H NMR chemical shift of the COCH$_3$ group in substituted para-acetophenones and their conversion in hydrosilylation with 1,1,3,3-tetramethyl disiloxane catalyzed with [Rh(Ph$_2$PNCO)$_2$(CO)Cl] (Figure 1). This correlation may be rationalized in terms of mechanism[3] in which the reaction could proceed

TABLE II The Conversion of Parasubstituted Acetophenones XC$_6$H$_4$COCH$_3$ at Hydrosilylation with 1,1,3,3-Tetramethyl Disiloxane (3 h, 70°C, $c_K = 1.42 \times 10^{-3}$ mol · dl^{-1})

X	Catalyst			^{13}C chemical shift of C=O (δ, ppm,)
	[Rh(Ph$_2$PNCO)$_2$(CO)Cl]	cis-[Pt(Et$_2$SO)$_2$Cl$_2$]	[Pt(MeCOD)Cl$_2$]	
HO	67	*	*	*
MeO	57	94.7	≅ 100	196.46
Me	40	48.5	35.2	196.55
H	57.5	8.2	28.9	197.09
F	34.5	24.7	21.1	195.35
Cl	61	27.9	28.2	196.39
NO$_2$	97	45.9	65.6	196.10

*The hydrosilylation with this catalyst was not provided.

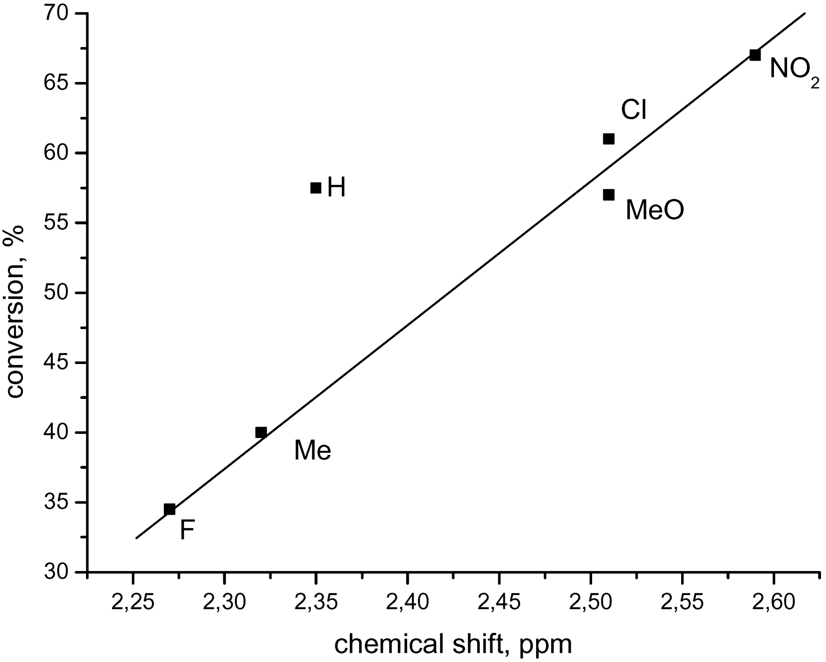


FIGURE 1 The conversion of para-acetophenones $XC_6H_4COCH_3$ (X = H, Me, MeO, F, Cl, NO_2) in the hydrosilylation with 1,1,3,3-tetramethyl disiloxane via a ^1H chemical shift (δ, ppm) of the $COCH_3$ group (3 h, 70°C, $[Rh(Ph_2PNCO)_2(CO)Cl]$, $c_K = 1.42 \times 10^{-3}$ mol · dl^{-1}).

via the rapid reversible oxidative addition of hydrosilane to the metal followed by π-coordination of the keto group and then by the insertion of the π-bond moiety into the Rh—Si bond. Although details of this mechanism are still controversial, it may be assumed that the rate of the formation and the stability of the intermediate is controlled by the distribution of electron density in the aceto group. This assumption is supported by the observed linear dependence between the ^1H NMR chemical shift of the $COCH_3$ group in substituted para-acetophenones and their conversion in hydrosilylation with 1,1,3,3-tetramethyl disiloxane catalyzed with $[Rh(Ph_2PNCO)_2(CO)Cl]$ because the chemical shift depends on electron density distribution and shielding effects, which influence intermediate stability.

The situation for hydrosilylation of para-substituted acetophenones with platinum (II) complexes is different. In reaction with cis-$[Pt(Et_2SO)_2Cl_2]$ complexes as a catalyst, the introduction of any substituent into the aromatic ring leads to increasing conversion (Table II).

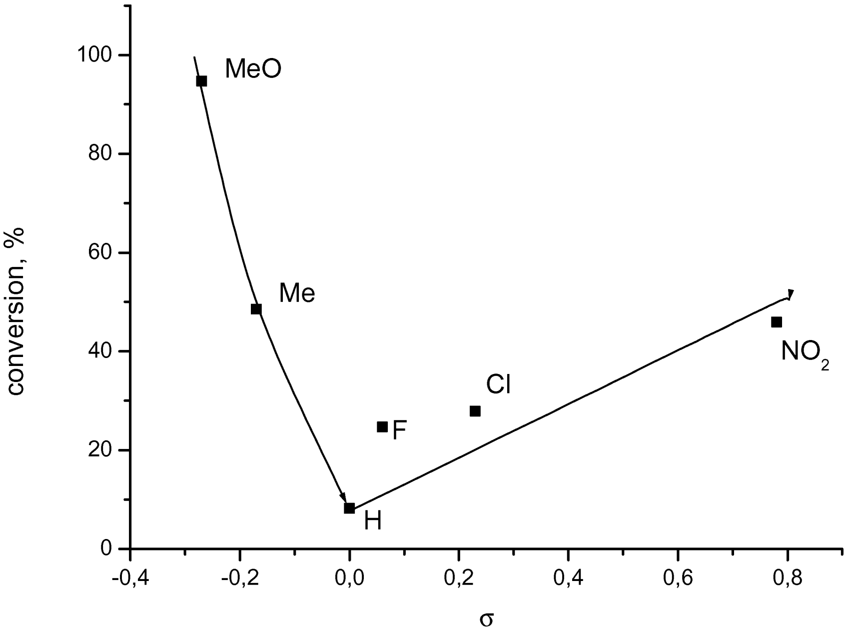


FIGURE 2 The conversion of para-acetophenones $XC_6H_4COCH_3$ (X = H, Me, MeO, F, Cl, NO_2) in the hydrosilylation with 1,1,3,3-tetramethyl disiloxane via the σ Hammett parameter of substituent X (3 h, 70°C, cis-$[Pt(Et_2SO)_2Cl_2]$, $c_K = 1.42 \times 10^{-3}\ \mathrm{mol \cdot dl^{-1}}$).

The U-like dependence of the conversion via the σ Hammett parameter of the substituent was observed (Figure 2). The same dependence has been detected earlier for the hydrosilylation of para-substituted styrenes with different hydrosilanes in the presence of $[Pt(Un)(\mu\text{-}Cl_2)]_2$ complexes as the catalyst, where Un a is substituted para-styrene.[11] The U-like dependence of the conversion was connected with the stability of $[Pt(Un)(\mu\text{-}Cl_2)]_2$ complexes, which have antibat dependence via the σ Hammett parameter of the substituent.[12] The stability of complexes changes in the following order: H > Cl > CH_3 > NO_2 > OCH_3. It is clear that for acetophenones, their ability for coordination with the metal complex and the stability of the resulting intermediate correlate with the distribution of electron density on the reaction center. This distribution is connected with the ^{13}C chemical shift of the $COCH_3$ group. As can be seen from Figure 3, the dependence of the ^{13}C chemical shift of the CO group of substituted acetophenones via σ Hammett parameter of the substituent is the same as the dependence of conversion. This supports the proposed mechanism of hydrosilylation.

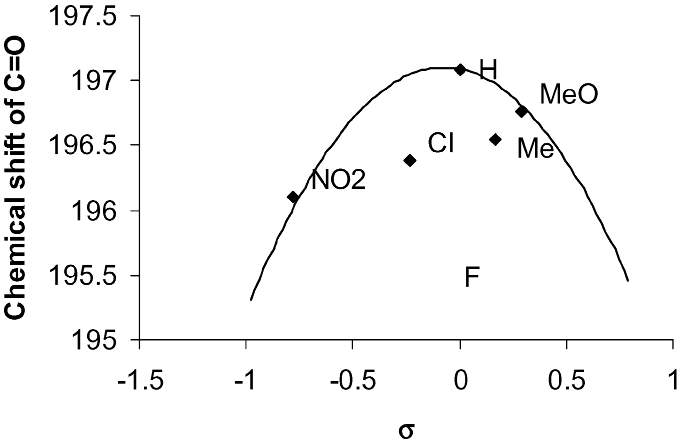


FIGURE 3 The ^{13}C chemical shift (δ, ppm) of the C=O group of para-acetophenones $XC_6H_4COCH_3$ (X = H, Me, MeO, F, Cl, NO_2) via the σ Hammett parameter of substituent X.

The hydrosilylation with [Pt(MeCOD)Cl_2] changes only slightly the conversion of substituted acetophenones (Table II). The main tendency in hydrosilylation remains valid.

Therefore, the complete pattern of catalytic action of each metal complex needs careful investigation of its geometry and ligand environment and depends on the substrate and the reagent.

CONCLUSION

A set of metal complexes of Rh and Pt as well as one of Pd was examined for their ability to catalyze the thermal hydrosilylation of para-substituted acetophenones with electron-donating and electron-withdrawing substituents by 1,1,3,3-tetramethyl disiloxane. The most effective complexes were the rhodium complexes. A linear dependence was observed between the conversion the of substituted acetophenones and the σ Hammett parameter of the substituent. In general, platinum complexes exhibited a much lower catalytic activity in the hydrosilylation of substituted acetophenones, although their selectivity was higher. The U-like dependence of conversion via the σ Hammett parameter of the substituent was observed.

In this study, the number of metal complexes examined as catalysts for acetophenones hydrosilylation was limited, and the reaction conditions were generally not optimized. However, the results demonstrate that the acetophenones conversion is sensitive to changes in the metal catalyst as well as in the substituent in the acetophenone aromatic ring. This lays the foundation of the work of both searching for better catalytic systems and optimizing reaction conditions towards desired maximal conversion for much shorter time at a lower temperature.

EXPERIMENTAL

^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker DRX300 spectrometer at 300.13 and 75.468 MHz, respectively. Chemical shifts are reported in ppm relative to $CHCl_3$ (δ 7.26 for ^{1}H) and $CDCl_3$ (δ 76.9 for ^{13}C).^{1}H-NMR data are reported as follows: (a) chemical shift in ppm (δ), (b) multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad), (c) relative intensity, (d) coupling constant (Hz), and (e) interpretation; ^{13}C-NMR data are reported as follows: (a) chemical shift in ppm (δ) and (b) interpretation. IR spectra were obtained on a Bruker IFS-88 infrared spectrometer (liquid on a KBr disk). Specific optical rotations $[\alpha]_D$ were measured with a Pepol 60(UNICAM) polarimeter for 1% wt solutions in ethanol. The refraction index was obtained on an IFS-22 (USSR) Abbe type refractometer.

Acetophenone (Reachim,USSR), 4-chloro-, 4-fluoro-,4-nitroacetophenones (Acros,Russia), 4-methylacetophenone (Fluka), 4-methoxyacetophenone and 1,1,3,3-methyl disiloxane (Aldrich) were distilled before use. The metal complexes (−)-cis-$[Pt(Me\text{-}p\text{-}TolSO)_2Cl_2]$,[13] (−)-*cis*-$[Pt(Me\text{-}p\text{-}TolSO)PyCl_2]$,[14] *cis*-$[Pt(EtCN)(dmso)Cl_2]$,[15] [Rh(acac)(CO)Cl],[16] $[Rh(Ph_3P)Cl_3]$, $[Pd(MeCOD)Cl_2]$, $[Pt(MeCOD)Cl_2]$, *cis*-$[Pt(Et_2SO)_2Cl_2]$,*cis*-$[Pt(Ph_3P)_2Cl_2]$, and $Na_2[PtCl_6] \times 6H_2O$ and *cis*-$[Pt(Ph_3Sb)_2Cl_2]$[17] were synthesized following the literature methods.

2-Phenyl-3,5-dioxa-4,4′,6,6′-tetramethyl-4,6-disilahexane

A mixture of 1 g acetophenone (8.3 mmol), 4.4 mL of 1,1,3,3-tetramethyldisiloxane (25 mmol), and 2 mL of 1.42×10^{-3} mol/L solution of cis-$[Pt(EtSO)_2Cl_2]$ complex in CH_2Cl_2 was heated in sealed tube for 70 h at 70°C. After that, from the reaction mixture was distilled 1,1,3,3-tetramethyldisiloxane and CH_2Cl_2. Residue was distillated in vacuum. Yield 2.0 g (95%) as transparent colorless liquid, b.p. 58°C (2 mmHg), $n_D^{18} = 1.4524$, $d_4^{20} = 0.9675$. IR (neat): 3020, 2960, 2932, 2880 (CH), 2120(Si—H) 1520, 1258, 1060. ^{1}H-NMR ($CDCl_3$), δ: 0.13 s (CH_3-Si—O, 6H); 0.22 s, 0.24 s (CH_3-Si—H, 6H); 1.56 d (CH_3, 3H, J = 6.9 Hz); 4.82–4.84 m (Si—H, 1H); 5.09 k (CH, 1H, J = 6.9 Hz); 7.33–7.46 m (orto- and para-arom. CH, 4H); 7.25–7.31 m (para arom. CH,1H). ^{13}C-NMR ($CDCl_3$), δ: −0.94, −0.78 (CH_3-Si—O); 0.41(CH_3-Si—H); 26.66 (CH_3); 70.16 (CH); 146.03(ipso-C); 125.13(orto); 127.94(meta); 126.68(para).

Anal. calc. for $C_{11}H_{22}O_2Si_2$: C, 54.49; H, 9.15; Si, 23.17%. Found: C, 54.01; H, 8.97; Si, 24.02%.

2-(4-Methyl-phenyl)-3,5-dioxa-4,4′,6,6′-tetramethyl-4,6-disilahexane

Was synthesized by a similar way with (−)-cis-[Pt(Me-p-TolSO)$_2$Cl$_2$] as a catalyst. Yield 95% as transparent colorless liquid. b.p. 72°C (3 mmHg); $n_D^{18} = 1.4568$, $d_4^{20} = 0.9618$. $[\alpha]_D^{17} = +0.8^\circ$ in 1% wt solution in ethanol. IR (neat): 3020, 2960, 2932, 2880 (CH), 2122(Si—H) 1520, 1258, 1060. ^{1}H-NMR (CDCl$_3$), δ: 0.25 s (CH$_3$-Si—O, 6H); 0.31 s, 0.33 s (CH$_3$-Si—H, 6H); 1.67 d (—H—C$\underline{H}_3$, 3H, J = 6.9 Hz); 2.51 s (—H$_3$, 3H);4.93–4.98 br (Si—H, 1H); 5.19 k (CH, 1H, J = 6.9 Hz); 7.45 d (orto arom. CH, 2H, J = 8.5 Hz); 7.30 d (meta arom. CH, 2H, J = 8.5 Hz). ^{13}C-NMR (CDCl$_3$), δ: −0.93, −0.75 (CH$_3$—Si—O); 0.45(CH$_3$-Si—H); 20.82(—H$_3$); 26.65 (—H—$\underline{C}$H$_3$); 70.03 (CH); 143.11 (ipso); 128.60 (ortho); 125.10 (meta); 135.99 (para). Anal. calc. for $C_{12}H_{25}O_2Si_2$: C, 55.97; H, 9.77; Si, 21.81%. Found: C, 55.47; H, 9.75; Si, 22.15%.

2-(4-Methoxy-phenyl)-3,5-dioxa-4,4′,6,6′-tetramethyl-4,6-disilahexane

Was synthesized by a similar way with (−)-cis-[Pt(Me-p-TolSO)$_2$Cl$_2$] as a catalyst. Yield 95% as transparent colorless liquid, b.p. 92°C (4 mmHg); $n_D^{18} = 1.4611$, $d_4^{20} = 0.9688$. $[\alpha]_D^{17} = +1.05^\circ$ in 1% wt solution in ethanol. IR (neat): 3020, 2960, 2932, 2870 (CH), 2120(Si—H) 1520, 1258, 1060. ^{1}H-NMR (CDCl$_3$), δ: 0.19 s (CH$_3$-Si—O, 6H); 0.31 s, 0.27 s (CH$_3$-Si—H, 6H); 1.60 d (—H—C$\underline{H}_3$, 3H, J = 6.9 Hz); 3.84 s (—H$_3$, 3H); 4.87–4.94 br (Si—H, 1H); 5.11 k (CH, 1H, J = 6.9 Hz); 7.40 d (ortho arom. CH, 2H, J = 8.5 Hz); 6.97 d (meta arom. CH, 2H, J = 8.5 Hz). ^{13}C-NMR (CDCl$_3$), δ: −1.05, −0.87 (CH$_3$-Si—O); 0.29 (CH$_3$-Si—H); 54.50 (—H$_3$); 26.52 (—H—$\underline{C}$H$_3$); 69.68 (CH); 138.07 (ipso); 126.28 (orto); 113.40(meta); 158.38(para). Anal. calc. for $C_{12}H_{25}O_3Si_2$: C, 52.37; H, 9.25; Si, 21.10%. Found: C, 52.70; H, 9.21; Si, 20.54%.

2-(4-Fluoro-phenyl)-3,5-dioxa-4,4′,6,6′-tetramethyl-4,6-disilahexane

Was synthesized by a similar way with [Rh(Ph$_2$PNCO)(CO)Cl] as a catalyst. Yield 96% as transparent colorless liquid, b.p. 82°C (3 mmHg); $n_D^{18} = 1.4452$, $d_4^{20} = 0.9712$. IR (neat): 3020, 2960, 2932, 2880 (CH), 2121(Si—H) 1520, 1258,1060. ^{1}H-NMR (CDCl$_3$), δ: 0.07, 0.13 s (CH$_3$-Si—O, 6H); 0.22 s, 0.23 s (CH$_3$-Si—H, 6H); 1.47 d (—H—C$\underline{H}_3$, 3H, J = 6.9 Hz); 4.72 hp (Si—H, 1H, J = 3 Hz); 5.04 k (CH, 1H, J = 6.9 Hz); 7.33 k (ortho CH,2H, J = 3.1 Hz); 7.02 t (meta CH, 2H, J = 8.5 Hz). ^{13}C-NMR ($CDCl_3$), δ: −0.75, −0.89 (CH_3-Si—O); 0.46 (CH_3-Si—H); 26.70 (—H—$\underline{C}H_3$); 69.59 (CH); 141.95(ipso); 126.79 d (ortho, J = 7.9 Hz); 114.76 d(meta, J = 20.7 Hz); 161.75 d (para, J = 168.3 Hz). Anal. calc. for $C_{11}H_{21}O_2Si_2F$: C, 50.67; H, 8.21; Si, 21.70%. Found: C, 50.72; H, 8.13; Si, 21.57%.

2-(4-Chloro-phenyl)-3,5-dioxa-4,4′,6,6′-tetramethyl-4,6-disilahexane

Was synthesized by similar a way with [Rh(Ph_2PNCO)(CO)Cl] as a catalyst. Yield 96% as transparent colorless liquid, b.p. 96°C (4mmHg); $n_D^{18} = 1.4571$, $d_4^{20} = 0.9832$. IR (neat): 3020, 2960, 2932, 2870, (CH), 2123(Si—H) 1520, 1260, 1060. ^{1}H-NMR ($CDCl_3$), δ: 0.11, 0.18 s (CH_3-Si—O, 6H); 0.20 ,0.21 (CH_3-Si—H, 6H); 1.49 d ($C\underline{H}_3$, 3H, J = 6.9 Hz); 4.77 hp (Si—H, 1H, J = 3 Hz); 5.03 k (CH, 1H, J = 6.9 Hz); 7.33 s (ortho and meta arom. CH,4H). ^{13}C-NMR ($CDCl_3$), δ: −0.18, −0.33 (CH_3-Si—O); 1.03 (CH_3-Si—H); 27.19 (CH-$\underline{C}H_3$); 70.10 (CH); 145.30(ipso); 127.17 (ortho); 128.70 (meta); 132.94 (para). Anal. calc. for $C_{11}H_{21}O_2Si_2Cl$: C, 47.25; H, 7.41; Si, 21.07; Cl 12.77%. Found: C, 47.71; H, 7.65; Si, 20.28; Cl, 12.80%.

2-(4-Nitro-phenyl)-3,5-dioxa-4,4′,6,6′-tetramethyl-4,6-disilahexane

Was synthesized by a similar way with [Rh(Ph_2PNCO)(CO)Cl] as a catalyst. Yield 76% as transparent colorless liquid, b.p. 96°C (4 mmHg); $n_D^{18} = 1.4511$, $d_4^{20} = 0.9612$. IR (neat): 3017, 2971, 2932, 2880 (CH), 2127(Si—H) 1520, 1265, 1060. ^{1}H-NMR ($CDCl_3$), δ: 0.07, 0.08 s (CH_3-Si—O, 6H); 0.18 , 0.19s (CH_3-Si—H, 6H); 1.46 d (CH-$C\underline{H}_3$, 3H, J = 6.9 Hz); 4.65 hp (Si—H, 1H, J = 3 Hz); 5.07 k (CH, 1H, J = 6.9 Hz); 7.50 d (ortho arom. CH, 2H); 8.19 d (meta arom. CH, 2H, J = 8.5 Hz). ^{13}C-NMR ($CDCl_3$), δ: −1.27, −0.97 (CH_3-Si—O); 10.27 (CH_3-Si—H); 26.51 (CH-$\underline{C}H_3$); 69.36 (CH); 146.90 (ipso); 125.96 (ortho); 123.45 (meta); 153.62 (para). Anal. calc. for $C_{11}H_{21}O_4NSi_2$: C, 45.45; H, 7.44; Si, 20.27; N, 4.56%. Found: C, 45.96; H, 7.36; Si, 19.54; N, 4.87%.

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