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HYDROSILYLATION OF α,β-UNSATURATED ALDEHYDES AND KETONES BY *trans*-DI-μ-HYDRIDO-BIS(SILYL)BIS-(TRIALKYLPHOSPHINE)DIPLATINUM COMPLEXES *

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Summary

The diplatinum complexes $[\{Pt(\mu\text{-}H)(SiR_3)(PR'_3)\}_2]$ readily catalyse the hydrosilylation of the α,β-unsaturated aldehydes and ketones RCH : CHCHO (R = H, Me, or Ph), PhCH : C(Me)CHO, PhCH : CHC(Me)O, Me_2C : CHC(Me)O, $\overline{CH_2(CH_2)_2CH}$: CHC : O, and $(PhCH : CH)_2CO$. The silanes studied were $MePh_2SiH$, Et_3SiH and $EtMe_2SiH$. In all cases, 1,4-addition products were obtained in high yield usually as equi-molar mixtures of two isomers, except for cyclohex-2-enone which is constrained to afford a single product. Tetraphenylcyclopentadienone and diphenylmethylsilane gave the 1,2-adduct $Ph_4C_4CHOSiMePh_2$.

The ^1H and ^{13}C NMR spectra of the various products are reported and assigned.

Introduction

We have previously demonstrated that the diplatinum complexes $[\{(Pt(\mu\text{-}H)(SiR_3)(PR'_3)\}_2]$ [1] are remarkably efficient homogeneous catalysts for the hydrosilylation of olefins and alkynes [2]. In general reactions occur exothermally, at room temperature or below, with catalyst : reactant ratios of 10^{-4}—10^{-6} : 1. Hydrosilylation of C=O groups is also of synthetic interest but has received much less attention [3—5]. Since silicon—oxygen bonds are easily hydrolyzed, hydrosilylation of C=O groups can lead to hydrogenation, hence 1,4-addition of organosilanes to α,β-unsaturated aldehydes and ketones may be used as a method for the selective reduction of their carbon—carbon double bonds [6]. Herein we describe use of the diplatinum compounds $[\{(Pt(\mu\text{-}H)(SiR_3)(PR'_3)\}_2]$ as catalysts for Si—H addition to C=O.

* Dedicated to Professor Helmut Behrens on the occasion of his 65th birthday on May 30th, 1980.

Results and discussion

No hydrosilylation reactions were observed below 100°C when the compounds Me_2CO, $MePhCO$, Ph_2CO, Et_2CO, $Me(CH_2Cl)CO$, $MeCHO$, Pr^iCHO or cyclohexanone were treated with $MePh_2SiH$ in a 1 : 1.2 mol ratio in the presence of catalytic amounts of $[\{Pt(\mu\text{-}H)(SiMe_2Ph)[P(C_6H_{11})_3]\}_2]$. After several days at 100°C products observed by GLC were those corresponding to decomposition of diphenylmethylsilane, as verified by studies carried out in the absence of the aldehydes or ketones.

In contrast, reactions of $MePh_2SiH$ with PhCH : CHCHO, PhCH : C(Me)-CHO, PhCH : CHC(Me)O, CH_2 : CHCHO, MeCH : CHCHO, Me_2C : CHC(Me)O and cyclohex-2-enone occurred readily between 60 and 100°C in the presence of the catalyst to afford in high yield the 1,4-addition products I—VII (Table 1) purified by fractional distillation. With tetraphenylcyclopentadienone, 1,2-addition occurred to give the yellow crystalline compound VIII. α,β-Unsaturated carboxylic acids and esters were not readily hydrosilylated with the catalyst system.

Compounds I—VIII were characterised by analysis and mass spectrometry, and by examination of their ^1H and ^{13}C NMR spectra (Table 2). Both GLC studies and the NMR spectra revealed that I—VI were formed as mixtures of two isomers in approximately equal amounts, but the slight disparities of each allowed correlation of the ^1H spectrum of each isomer with its corresponding ^{13}C spectrum via relative peak intensities. Moreover, for those compounds containing a CH^a : CH^b group it was possible to distinguish between the two isomers on the basis of the observed $J(H^aH^b)$ values in their ^1H NMR spectra since it is well known that $J(HH_{trans}) > J(HH_{cis})$ [7], and for compounds I, IV and V these couplings are 12 and 6 Hz, respectively. For III and VI assignments of the spectra was not possible since coupling between H^b and the CMe group was not observed. However, for II both ^1H spectra showed H^a—CMe coupling and the larger is assigned to the isomer with the *trans* CH^a : CMe arrangement.

Compounds VII and VIII were formed as single isomers. The 1,2-addition observed with tetraphenylcyclopentadienone is probably the result of the steric effects of the phenyl groups.

Hydrosilylation of cinnamaldehyde and dibenzylideneacetone with triethylsilane in the presence of $[\{(Pt(\mu\text{-}H)(SiMe_2Ph)[P(C_6H_{11})_3]\}_2]$, afforded compounds IX and X, respectively. In the case of X it was not possible to correlate the ^1H and hence the ^{13}C NMR spectra with the stereochemistry at the CH^b : $C(OSiEt_3)$ double bond of the two isomers produced. For IX, however, $J(H^aH^b)$ values allowed an assignment to be made. Reaction of $EtMe_2SiH$ with cinnamaldehyde in the presence of the catalyst gave the two isomers of XI, characterised in the usual manner (Tables 1 and 2).

Assignment of the peaks in the ^{13}C NMR spectra of the compounds was based partly on partial decoupling experiments and partly on chemical shift arguments. Thus Me groups attached to silicon are characterised by their negative shifts, while the CH_2Si group resonates (4.5—6.5 ppm) upfield from CH_2Me (17.3—20.7 ppm). For I, partial decoupling produced doublets for the pairs of resonances at 140.8 and 111.2, and at 138.5 and 110.2 ppm, respectively, hence confirming that these signals emanated from the CH : CH groups. On the

(Continued on p. 45)

TABLE 1

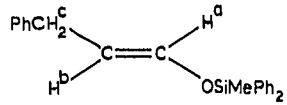
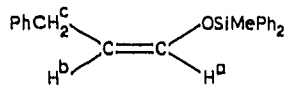
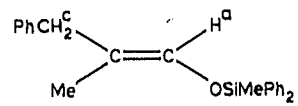
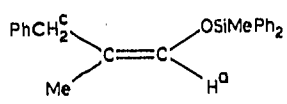
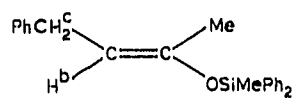
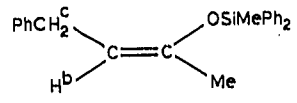
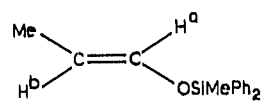
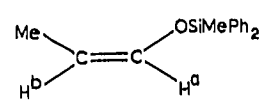
PHYSICAL AND ANALYTICAL DATA FOR THE HYDROSILYLATION PRODUCTS

Compound [a]		B.p. (°C/mmHg)	ν_{max} (C=C) (cm^{-1})	Analysis (calcd.(%))		Mol. wt. [b]
				C	H	
(I)	$PhCH_2CH{:}C(H)OSiMePh_2$	150/0.08	1660	80.0 (80.0)	6.7 (6.7)	330
(II)	$PhCH_2C(Me){:}C(H)OSiMePh_2$	142/0.07	1670	79.9 (80.2)	7.3 (7.0)	344
(III)	$PhCH_2CH{:}C(Me)OSiMePh_2$	144/0.02	1670	79.4 (80.2)	7.2 (7.0)	344
(IV)	$MeCH{:}C(H)OSiMePh_2$	80/0.01	1665	76.5 (76.6)	7.6 (7.7)	254
(V)	$EtCH{:}C(H)OSiMePh_2$	113–119/0.175	1660	76.7 (76.1)	7.5 (7.4)	268
(VI)	$Pr^iCH{:}C(Me)OSiMePh_2$	85/0.015	1675	77.1 (77.0)	8.3 (8.4)	296
(VII)	$\overline{CH_2(CH_2)_3CH{:}C}OSiMePh_2$ [c]	118–124/0.025	1670	78.1 (77.6)	7.4 (7.5)	294
(VIII)	$(Ph)\overline{C{:}(Ph)C{\cdot}(Ph)C{:}(Ph)C{\cdot}C}(H)OSiMePh_2$ [c]	143 [d]	—	85.4 (85.1)	6.0 (5.7)	—
(IX)	$PhCH_2CH{:}C(H)OSiEt_3$	72/0.05	1655	72.5 (72.6)	9.7 (9.8)	248
(X)	$PhCH_2CH{:}C(OSiEt_3)CH{:}CHPh$	156–158/0.08	1630	79.8 (78.9)	8.9 (8.6)	—
(XI)	$PhCH_2CH{:}C(H)OSiEtMe_2$	76–82/0.03	1655	70.0 (71.7)	9.2 (9.5)	276

[a] Compounds formed as isomeric mixtures (see Text), unless otherwise stated. [b] Determined by mass spectrometry, figures given refer to molecular ion. [c] Single isomer formed. [d] Melting point.

TABLE 2

^1H AND ^{13}C NMR DATA FOR THE HYDROSILYLATION PRODUCTS

Compound	Isomer	^1H (τ) [a]	^{13}C (δ) [a,b]
(I)		2.74 (m, 15 H, Ph), 3.68 [d of t, 1 H, H^a, $J(H^aH^b)$ 12, $J(H^aH^c)$ 1], 4.80 [d of t, 1 H, H^b, $J(H^bH^a)$ 12, $J(H^bH^c)$ 7.5], 6.87 [d, br, 2 H, H^c, $J(H^cH^b)$ 7.5], 9.36 (s, 3 H, MeSi).	141.1 [CH_2C(Ph)], 140.8 (:CH^a), 137.1–125.8 (Ph), 111.2 (:CH^b), 33.4 (CH_2), –3.0 (MeSi).
		2.74 (m, 15 H, Ph), 3.71 [d of t, 1 H, H^a, $J(H^aH^b)$ 6, $J(H^aH^c)$ 1.5], 5.31 [d of t, 1 H, H^b, $J(H^bH^a)$ 6, $J(H^bH^c)$ 7.5], 6.51 [d of d, 2 H, H^c, $J(H^cH^a)$ 1.5, $J(H^cH^b)$ 7.5], 9.35 [s, 3 H, MeSi].	141.5 [CH_2C(Ph)], 138.5 (:CH^a), 137.1–125.8 (Ph), 110.2 (:CH^b), 30.1 (CH_2), –3.0 (MeSi).
(II)		2.6 (m, 15 H, Ph), 3.66 (m, br, 1 H, H^a), 6.83 (s, 2 H, H^c), 8.42 [d, 3 H, Me, J(MeH^a) 2], 9.29 (s, 3 H, MeSi).	140.1 [CH_2C(Ph)], 135.1 (:CH^a), 134.7–125.6 (Ph), 117.7 [:C(Me)], 40.0 (CH_2), 12.8 (Me), –2.9 (MeSi).
		2.6 (m, 15 H, Ph), 3.73 (m, br, 1 H, H^a), 6.45 (s, 2 H, H^c), 8.56 [d, 3 H, Me, J(MeH^a) 1.5], 9.29 (s, 3 H, MeSi).	140.4 [CH_2C(Ph)], 135.0 (:CH^a), 134.7–125.6 (Ph), 116.9 [:C(Me)], 35.2 (CH_2), 16.8 (Me), –2.9 (MeSi).
(III) [b]		2.6 (m, 15 H, Ph), 5.04 [t, 1 H, Hb, J(HbH^c) 8], 6.77 [d, 2 H, H^c, J(H^cHb) 8], 8.25 (s, 3 H, Me), 9.29 (s, 3 H, MeSi).	148.9 [C(Me)], 141.9 [CH_2C(Ph)], 136.0–125.5 (Ph), 107.2 (:CH^b), 33.1 (CH_2), 17.8 (Me), –2.9 (MeSi).
		2.6 (m, 15 H, Ph), 5.30 [t, 1 H, H^b, $J(H^bH^c)$ 8], 6.55 [d, 2 H, H^c, $J(H^cH^b)$ 8], 8.17 (s, 3 H, Me), 9.29 (s, 3 H, MeSi).	147.0 [:C(Me)], 141.3 [CH_2C(Ph)], 136.0–125.5 (Ph), 107.8 (:CH^b), 31.6 (CH_2), 22.8 (Me), –1.7 (MeSi).
(IV)		2.42 (m, 10 H, Ph), 3.66 [d of q, 1 H, H^a, $J(H^aH^b)$ 12, J(H^{a}Me) 1.5], 4.84 [d of q, 1 H, H^b, $J(H^bH^a)$ 12, J(H^{b}Me) 7], 8.52 [d of d, 3 H, Me, J(MeH^a) 1.5, J(MeH^b) 7], 9.31 (s, 3 H, MeSi).	139.9 (:CH^a), 135.1–127.9 (Ph), 106.8 (:CH^b), 12.2 (Me), –3.0 (MeSi).
		2.42 (m, 10 H, Ph), 3.75 [d of q, 1 H, H^a, $J(H^aH^b)$ 5.5, J(H^{a}Me) 2], 5.46 [d of q, 1 H, H^b, $J(H^bH^a)$ 5.5, J(H^{b}Me) 7], 8.32 [d of d, 3 H, Me, J(MeH^a) 2, J(MeH^b) 7], 9.31 (s, 3 H, MeSi).	138.6 (:CH^a), 135.1–127.9 (Ph), 105.8 (:CH^b), 9.2 (Me), –3.0 (MeSi).

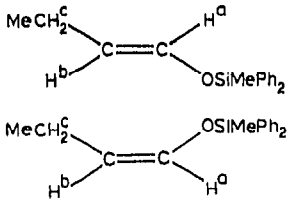
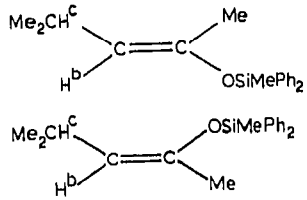
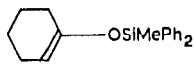
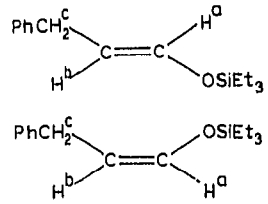
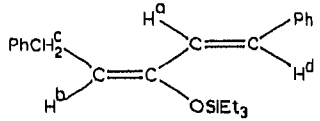
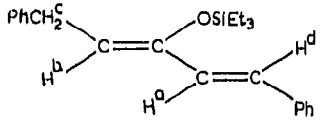
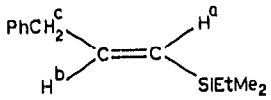
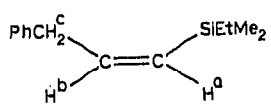
(V)		2.5 (m, 10 H, Ph), 3.76 [d of t, 1 H, H^a, $J(H^aH^b)$ 12, $J(H^aH^c)$ 1], 4.92 [d of t, 1 H, H^b, $J(H^bH^a)$ 12, $J(H^bH^c)$ 7], 6.14 [d of q, br, 2 H, H^c, $J(H^cH^b)$ 7, $J(H^cMe)$ 7], 9.10 [t, 3 H, Me, $J(MeH^c)$ 7], 9.35 (s, 3 H, MeSi).	138.9 (:CH^a), 135.1—127.8 (Ph), 114.5 (:CH^b), 20.7 (CH_2), 15.0 (Me), —3.0 (MeSi).
		2.5 (m, 10 H, Ph), 3.85 [d of t, 1 H, H^a, $J(H^aH^b)$ 5.5, $J(H^aH^c)$ 1.5], 5.51 [d of t, 1 H, H^b, $J(H^bH^a)$ 5.5, $J(H^bH^c)$ 7], 7.81 [d of q, br, 2 H, H^c, $J(H^cH^b)$ 7, $J(H^cMe)$ 7], 9.03 [t, 3 H, Me, $J(MeH^c)$ 7], 9.35 (s, 3 H MeSi).	137.3 (:CH^a), 135.1—127.8 (Ph), 113.6 (:CH^b), 17.3 (CH_2), 14.3 (Me), —3.0 (MeSi).
(VI) [b]		2.44 (m, 10 H, Ph), 5.42 [d, 1 H, H^b, $J(H^bH^c)$ 9.5], 7.73 [d of spt, 1 H, H^c, $J(H^cH^b)$ 9.5, $J(H^cMe)$ 7], 8.26 (s, 3 H, Me), 9.14 [d, 6 H, Me_2, $J(MeH^c)$ 7], 9.28 (s, 3 H, MeSi).	145.7 (:*C*Me), 136.3—127.7 (Ph), 117.3 (:CH^b), 27.0 ($CHMe_2$), 23.6 ($CH\mathit{Me}_2$), 22.3 (Me), —2.4 (MeSi).
		2.44 (m, 10 H, Ph), 5.67 [d, 1 H, H^b, $J(H^bH^c)$ 9.5], 7.23 [d of spt, 1 H, H^c, $J(H^cH^b)$ 9.5, $J(H^cMe)$ 7], 8.30 (s, 3 H, Me), 9.10 [d, 6 H, Me_2, $J(MeH^c)$ 7], 9.28 (s, 3 H, MeSi).	144.4 (:*C*Me), 136.3—127.7 (Ph), 117.0 (:CH^b), 24.9 ($CHMe_2$), 23.2 ($CH\mathit{Me}_2$), 22.8 (Me), —1.8 (MeSi).
(VII)		2.5 (m, 10 H, Ph), 5.19 (m, 1 H, CH), 8.03 (m, 4 H, CH_2), 8.45 (m, 4 H, CH_2), 9.35 (s, 3 H, MeSi).	150.2 (*C*OSi), 136.2—127.7 (Ph), 104.9 (CH), 29.9, 23.7, 23.1, 22.2 (CH_2), —2.5 (MeSi).
(VIII)	Ph_4C_4 C(H)OSiMePh$_2$	2.86 (m, 30 H, Ph), 5.07 (s, 1 H, CH), 9.92 (s, 3 H, MeSi).	151.1, 145.4 (*C*Ph), 140.2—126.5 (Ph), 56.5 (*C*HOSi), —2.4 (MeSi).
(IX)		2.72 (m, 5 H, Ph), 3.60 [d of t, 1 H, H^a, $J(H^aH^b)$ 12, $J(H^aH^c)$ 1], 4.80 [d of t, 1 H, H^b, $J(H^bH^a)$ 12, $J(H^bH^c)$ 7.5], 6.74 [d, br, 2 H, H^c, $J(H^cH^b)$ 7.5], 9.01 (m, 9 H, Me), 9.34 (m, 6 H, CH_2Si).	141.4 [$CH_2\mathit{C}$(Ph)], 141.2 (:CH^a), 131.1—125.6 (Ph), 110.1 (:CH^b), 33.7 (CH_2), 6.6 (Me), 4.5 (CH_2Si).
		2.72 (m, 5 H, Ph), 3.62 [d of t, 1 H, H^a, $J(H^aH^b)$ 6, $J(H^aH^c)$ 1.5], 5.30 [d of t, 1 H, H^b, $J(H^bH^a)$ 6, $J(H^bH^c)$ 7.5], 6.50 [d of d, 2 H, H^c, $J(H^cH^a)$ 1.5, $J(H^cH^b)$ 7.5], 9.01 (m, 9 H, Me), 9.34 (m, 6 H, CH_2Si).	142.0 [$CH_2\mathit{C}$(Ph)], 138.9 (:CH^a), 131.1—125.6 (Ph), 109.2 (:CH^b), 30.0 (CH_2), 6.6 (Me), 4.5 (CH_2Si).

TABLE 2 (continued)

Compound	Isomer	^{1}H (τ) [a]	^{13}C (δ) [a,b]
(X) [b]		2.69 (m, 10 H, Ph), 2.93 (s, 2 H, H^a + H^d), 4.84 [t, 1 H, H^b, $J(H^bH^c)$ 8], 6.38 [d, 2 H, H^c, $J(H^cH^b)$ 8], 8.94 (m, 9 H, Me), 9.19 (m, 6 H, CH_2Si).	149.4 [:C($OSiEt_3$)], 141.0 [CH_2C(Ph)], 137.0—121.0 (Ph + CH:CHPh), 114.7 (:CH^b), 32.4 (CH_2), 6.9 (Me), 5.6 (CH_2Si).
		2.69 (m, 10 H, Ph), 3.20 [d(AB), 1 H, H^a or H^d, $J(H^aH^d)$ 15.5], 3.34 [d(AB), 1 H, H^a or H^d, $J(H^aH^d)$ 15.5], 4.86 [t, 1 H, H^b, $J(H^bH^c)$ 7.5], 6.40 [d, 2 H, H^c, $J(H^cH^b)$ 7.5], 8.94 (m, 9 H, Me), 9.19 (m, 6 H, CH_2Si).	148.9 [:C($OSiEt_3$)], 141.0 [CH_2C(Ph)], 137.0—121.0 (Ph + CH:CHPh), 111.2 (:CH^b), 32.7 (CH_2), 6.9 (Me), 5.1 (CH_2Si).
(XI)		2.70 (m, 5 H, Ph), 3.62 [d of t, 1 H, H^a, $J(H^aH^b)$ 12, $J(H^aH^c)$ 1], 4.81 [d of t, 1 H, H^b, $J(H^bH^a)$ 12, $J(H^bH^c)$ 7.5], 6.73 [d, br, 2 H, H^c, $J(H^cH^b)$ 7.5], 9.01 (m, 3 H, Me), 9.35 (m, 2 H, CH_2Si), 9.38 (s, 6 H, MeSi).	141.4 [CH_2C(Ph)], 140.9 (:CH^a), 128.2—125.6 (Ph), 110.4 (:CH^b), 33.7 (CH_2), 8.1 (Me), 6.5 (CH_2Si), —2.6 (MeSi).
		2.00 (m, 5 H, Ph), 3.62 [d,of t, 1 H, H^a, $J(H^aH^b)$ 6, $J(H^aH^c)$ 1.5], 5.26 [d of t, 1 H, H^b, $J(H^bH^a)$ 6, $J(H^bH^c)$ 7], 6.51 [d of d, 2 H, H^c, $J(H^cH^a)$ 1.5, $J(H^cH^b)$ 7], 9.01 (m, 3 H, Me), 9.35 (m, 2 H, CH_2Si), 9.83 (s, 6 H, MeSi).	141.9 [CH_2C(Ph)], 138.5 (:CH^a), 128.2—125.6 (Ph), 109.7 (:CH^b), 30.0 (CH_2), 8.1 (Me), 6.5 (CH_2Si), —2.6 (MeSi).

[a] Measured in $CDCl_3$. † Hydrogen-1 decoupled, chemical shifts (δ) in ppm to high frequency of $SiMe_4$. [b] Assignment of data to particular isomers may be reversed (see text).

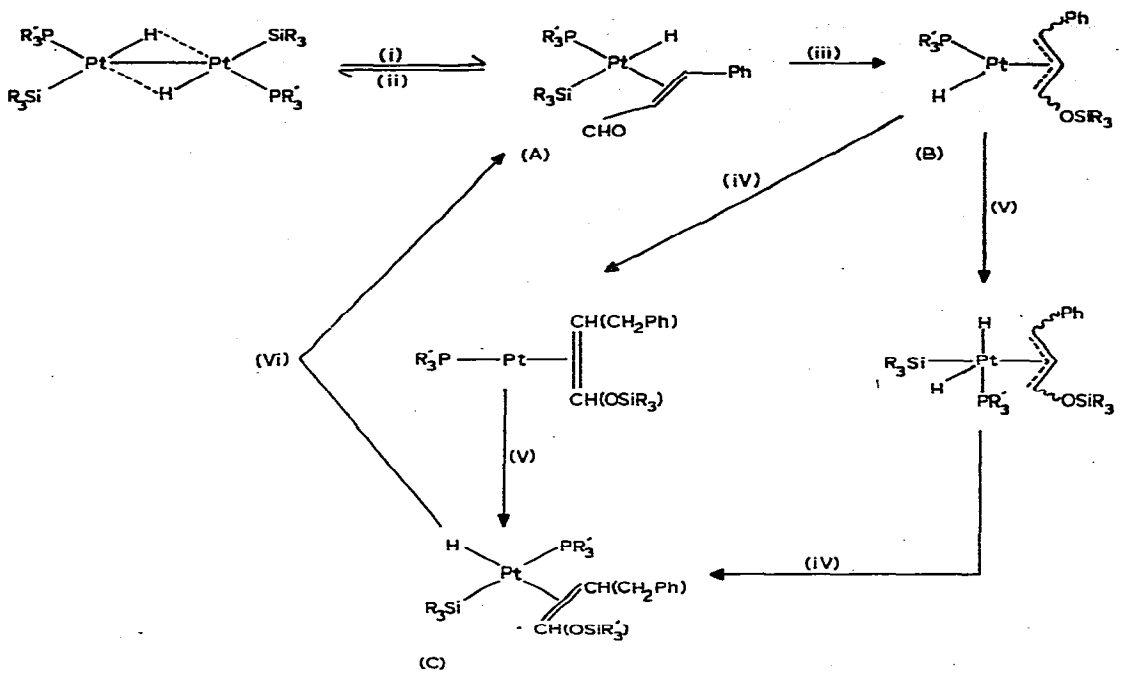
other hand, for II partial decoupling revealed no $^{1}H—^{13}C$ coupling for the resonances at 117.7 and 116.9 ppm in the spectra of the two isomers but the corresponding signals at 135.1 and 135.0 ppm gave rise to doublets, as expected for a MeC : CH group. This experiment also served to show that the carbon atom in the C : C group bonded to oxygen resonated at lower field than its partner as expected.

An interesting feature of the ^{13}C data of Table 2 is that for each isomeric pair the signals of the two C : C atoms are found at lower field in the *trans* isomers of I, IV, V, IX, and XI than in the *cis* isomers. This trend seems to be essentially followed by the compounds containing MeC : CH groups, suggesting that the isomer-spectra assignments for II, III and VI in Table 2 are correct.

The choice of silane is an important factor in the rates of hydrosilylation of alkenes and alkynes using the diplatinum complexes as catalysts [2]. Similarly, experiments with PhCH : CHCHO and Et_3SiH, $EtMe_2SiH$, $MePh_2SiH$, and $(EtO)_3SiH$ under identical conditions (solutions in toluene, 25°C, 1 hour, with $[\{(Pt(\mu\text{-}H)(SiMe_2Ph)[P(C_6H_{11})_3]\}_2]$ as catalyst) revealed, as measured by GLC traces, a reactivity sequence $MePh_2SiH > EtMe_2SiH > Et_3SiH >> (EtO)_3SiH$. In fact triethoxysilane did not react under the conditions of the experiment. The qualitative order of reactivity is similar to that found previousiy [2]. At the higher temperature of 60°C complete conversion to products within 15 minutes was observed for reactions involving $MePh_2SiH$ and $EtMe_2SiH$, whereas Et_3SiH took 45 minutes for completion. Only trace products were noted with $(EtO)_3SiH$. Use of diplatinum complexes as catalysts with PPh_3 ligands instead of $P(C_6H_{11})_3$ slightly slowed the rate of hydrosilylation at 25°c, but at 60°C and above no difference was observed. It appears from the work described herein that the diplatinum compounds $[\{(Pt(\mu\text{-}H)(SiR_3)(PR'_3)\}_2]$ operate effectively as catalysts for C=O hydrosilylation at lower temperatures than $[H_2PtCl_6]$ (120—140°C) [8].

It has been suggested [2] that hydrosilylation of alkenes and alkynes using the diplatinum complexes as catalysts involves a mechanism wherein the alkene or alkyne initially promotes bridge-cleavage of the diplatinum compounds to afford platinum(+II) species. Transfer of hydride to the η^2-bonded alkyne gives a platinum—carbon σ-bond intermediate which then, with the $Pt—SiR_3$ group present, reductively eliminates to give product and regenerate platinum(0). A similar initial formation of a mono-platinum species could operate in the reactions described herein; see Scheme 1, with cinnamaldehyde as example. Indeed, it was observed that the presence of tetrahydrofuran inhibits the hydrosilylation of the α,β-unsaturated aldehydes and ketones, presumably by virtue of occupying the coordination site on platinum required in the first step.

Following formation of the η^2-platinum complex (A), internal attack by the R_3Si ligand on the carbonyl function could afford an η^3-allylplatinum complex (B). There are then two routes (Scheme 1) whereby the platinum η^2-complex $[Pt(H)(SiR_3)(PR'_3)(\eta^2\text{-}PhCH_2CH : CHOSiR_3)]$ (C) can be attained, either via a 14-electron Pt(0) or via an 18-electron Pt(+IV) species. Replacement of $PhCH_2CH : CHOSiR_3$ by PhCH : CHCHO, perhaps via a penta-coordinated intermediate, would then afford the hydrosilylated product and regenerate (A) to continue the cycle. In either of the steps involving transfer of hydride from platinum to the allylic ligands, to afford an η^2-complex, formation of two



SCHEME 1. Proposed reaction sequence for the hydrosilylation of PhCH : CHCHO; (i) +PhCH : CHCHO, (ii) —PhCH : CHCHO, (iii) R_3Si group transfer, (iv) H transfer could yield *cis*- or *trans*-olefin isomers in this step, (v) +R_3SiH, (vi) + PhCH : CHCHO, —$PhCH_2CH$: $CHOSiR_3$.

isomers is possible; hence explaining the observed results. Moreover, it will be noted that it is the stereochemistry of the allyl group which dictates the geometry of the final product. Thus if the $OSiR_3$ group is in the *anti* position, then the *cis* isomer ensues. Conversely, the *trans* isomer results if the $OSiR_3$ is in the *syn* configuration.

Experimental

NMR studies (^1H and ^{13}C) were made on JEOL PS-100 and PFT-100 MHz spectrometers. Infrared measurements were made on thin films or as Nujol mulls with a Perkin-Elmer 457 spectrophotometer, and mass spectra were determined with an AEI MS 902 instrument operating at 70 eV. All experiments were carried out under nitrogen.

Hydrosilylation experiments were carried out as described previously [2]. Reaction vessels were glass tubes fitted with Westef grease-less stopcocks and a standard joint so that the vessel could be attached to a vacuum line. Reactants were mixed in a 1 : 1 mol ratio to which 2 mg of catalyst was added so that the catalyst : reactant ratio was circa 10^{-5}. In many reactions the reactants were heated at 100° C overnight but in general hydrosilylation was complete in less than 1 hour even at 60° C.

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