Hydrosilylation of Olefins Catalysed by *trans*-Di-μ-hydrido-bis(tricyclohexylphosphine)bis(silyl)diplatinum Complexes

By **Michael Green, John L. Spencer, F. Gordon A. Stone,*** and **Constantinos A. Tsipis,** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

The diplatinum complexes $[\{Pt(SiR_3)(\mu\text{-}H)[(C_6H_{11})_3P]\}_2]$ catalyse the addition of silanes R_3SiH (R = Me, Et, $PhCH_2$, Ph, OEt, or Cl) to pent-1-ene, hex-1-ene, styrene, allyl chloride, and 2-methylpropene. Reactivity of the silanes is qualitatively in the order: $Me_2EtSiH \simeq Me_2PhSiH \simeq Me_2(PhCH_2)SiH \geqslant ClMe_2SiH > Me_3SiH > Cl_3SiH \gg Et_3SiH \geqslant (EtO)_3SiH$, except for allyl chloride for which it is $Cl_3SiH > Cl_2MeSiH > Me_2PhSiH \gg ClMe_2SiH$. The hydrosilylations are frequently strongly exothermic, proceeding in high yield with a catalyst : reactant ratio of 10^{-4}—10^{-6} : 1. Hexa-1,5-diene, octa-1,7-diene, and 4-vinylcyclohexene also react readily with silanes using the same catalyst system. Hexa-1,5-diene and octa-1,7-diene afford the bis(silicon) adducts, but with 4-vinylcyclohexene only the exocyclic double bond is hydrosilylated. Catalytic addition of silanes to bicyclo[2.2.1]heptene is also described, *exo*-addition products being formed in 60—85% yield. The addition of Me_3GeH to hex-1-ene and to styrene is catalysed by $[\{Pt(GeMe_3)(\mu\text{-}H)[(C_6H_{11})_3P]\}_2]$.

FROM the versatile reagent bis(cyclo-octa-1,5-diene)platinum [1] it is possible to prepare bis(ethylene)(trialkylphosphine)platinum complexes, for example, $[Pt(C_2H_4)_2\{(C_6H_{11})_3P\}]$.[2] The latter reacts with trisubstituted silanes or germanes to give the μ-hydrido-bridged species $[\{Pt(MR_3)(\mu\text{-}H)[(C_6H_{11})_3P]\}_2]$ (R = Me, Et, $PhCH_2$, Ph, OEt, or Cl).[3] These diplatinum complexes catalyse the addition of silanes and germanes across unsaturated carbon–carbon and –oxygen bonds, and herein we describe their use in the hydrosilylation of several olefins, as well as two examples of hydrogermylation.

RESULTS AND DISCUSSION

Complexes of Group 8 metals are useful catalysts for hydrosilylation,[4] and each of the nine metals except osmium have some activity in this respect. However, hexachloroplatinic(IV) acid or Speier's catalyst [5] remains the most commonly used catalyst in this field, having the advantage that only a small amount of the platinum compound is needed (*ca.* 10^{-5} mol per mol of silane). Nevertheless, the use of $H_2PtCl_6{\cdot}6H_2O$ has certain disadvantages including insolubility in hydrocarbon solvents, the frequent necessity to heat the reaction mixture to ensure complete addition, and an induction period before hydrosilylation commences. The latter effect is probably related to the fact that the acid is not the true catalyst. An initial reduction of the platinum(IV) complex by the silane is necessary to afford a platinum(II) d^8 species which can then undergo with the reactants a series of oxidative-addition and reductive-elimination steps.[4,6] The induction period can then be understood in terms of the need to produce a square-planar d^8 platinum complex containing labile ligands and vacant co-ordination sites. Various triphenylphosphine-platinum(0) d^{10} complexes known to have a marked tendency to undergo oxidative-addition reactions can also function as hydrosilylation catalysts.[7,8] However, two triphenylphosphine ligands will be strongly held by the metal thus blocking co-ordination sites in the platinum(II) species produced from the d^{10} complexes in the oxidative-addition step. It seemed, therefore, that the diplatinum complexes $[\{Pt(SiR_3)(\mu\text{-}H)(R'_3P)\}_2]$, or their precursors $[Pt(C_2H_4)_2(R'_3P)]$, both of which contain only one phosphine ligand per metal centre, might be superior catalysts to the platinum species used previously. In a detailed study made with the tricyclohexylphosphine compounds this has been shown to be true.

Most of the hydrosilylation reactions catalysed by $[\{Pt(SiR_3)(\mu\text{-}H)[(C_6H_{11})_3P]\}_2]$ or by $[Pt(C_2H_4)_2\{(C_6H_{11})_3P\}]$ proceed exothermally immediately on mixing the reactants at room temperature. The catalyst : olefin or catalyst : silane ratio used was in the range 10^{-4}—10^{-6} : 1. Studies with pent-1-ene, hex-1-ene, styrene, and 2-methylpropene are summarised in Table 1.

The reactivity of the silanes in the hydrosilylation of pent-1-ene, hex-1-ene, or styrene is generally in the sequence: $Me_2EtSiH \simeq Me_2PhSiH \simeq Me_2(PhCH_2)SiH \geqslant ClMe_2SiH > Me_3SiH > Cl_3SiH \gg Et_3SiH \geqslant (EtO)_3SiH$. Triethyl- and triethoxy-silanes are the least reactive; for example, styrene does not react with triethoxysilane at room temperature and only slowly on heating.

It was observed qualitatively that in the hydrosilylation of allyl chloride, the reactivity of the silanes changed to: $Cl_3SiH > Cl_2MeSiH > Me_2PhSiH \geqslant ClMe_2SiH$. In these reactions the compounds $R_3SiCH_2CH_2Me$, R_3SiCl, and $MeCH{:}CH_2$ are formed, in addition to the desired $R_3SiCH_2CH_2CH_2Cl$ ($R_3Si = Cl_3Si$, Cl_2MeSi, Me_2PhSi, or $ClMe_2Si$). The proportion of the latter produced depends on the silane, increasing in the order $Me_2PhSiH < ClMe_2SiH < Cl_2MeSiH < Cl_3SiH$, while the amount of R_3SiCl formed decreases in the same order. Thus yields of $Cl_3SiCH_2CH_2CH_2Cl$ from room-temperature reactions were typically 70% with no induction period,

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[1] M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 271.

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[4] C. S. Cundy, B. M. Kingston, and M. F. Lappert, *Adv. Organometallic Chem.*, 1973, **11**, 253.

[5] J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Amer. Chem. Soc.*, 1957, **79**, 974; J. L. Speier and D. E. Hook, U.S.P. 2,823,218 (*Chem. Abs.*, 1959, **53**, 16965f).

[6] A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, 1965, **87**, 16.

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whereas $ClMe_2SiCH_2CH_2CH_2Cl$ formed only very slowly at room temperature, and at 70 °C with quantitative conversion of allyl chloride the crude yield from chlorodimethylsilane was only *ca.* 38% with concomitant formation of Me_2SiCl_2 (*ca.* 30%), $ClMe_2SiCH_2CH_2Me$ (*ca.* 15%), and unchanged $ClMe_2SiH$ (*ca.* 15%).

The various hydrosilylation reactions proceeded more slowly when a solvent (hexane or toluene) was used than when the solid catalyst $[\{Pt(SiR_3)(\mu\text{-}H)[(C_6H_{11})_3P]\}_2]$ was added to the reactants. In reactions catalysed by $H_2PtCl_6\cdot6H_2O$, as the number of chlorine atoms in the silyl group increases the reactivity of the silane in-

TABLE 1

Hydrosilylation of terminal olefins

Olefin (amount/mmol)	Silane (amount/mmol)	Catalyst[a]	Reaction time (t/h)[b]	Product (m/g)	Yield[c] (%)
Pent-1-ene (20)	Cl_3SiH (25)	A 1 cm^3; 3.8×10^{-4} mol dm^{-3} in toluene [1.9×10^{-5}]	4	$C_5H_{11}SiCl_3$ (2.9)	70
(23)	$ClMe_2SiH$ (16)	B 2 cm^3; 4.1×10^{-4} mol dm^{-3} in hexane [5.1×10^{-5}]	1	$C_5H_{11}SiMe_2Cl$ (2.0)	75
(20)	Me_2EtSiH (10)	B 0.5 cm^3; 4.1×10^{-4} mol dm^{-3} in hexane [2.1×10^{-5}]	0.3	$C_5H_{11}SiEtMe_2$ (1.35)	85
(20)	Me_2PhSiH (10)	B 0.5 cm^3; 4.1×10^{-4} mol dm^{-3} in hexane [2.1×10^{-5}]	1	$C_5H_{11}SiPhMe_2$ (1.85)	91
(20)	Et_3SiH (10)	B 1 cm^3; 4.1×10^{-4} mol dm^{-3} in hexane [4.1×10^{-5}]	6[d]	$C_5H_{11}SiEt_3$ (0.95)	51
(20)	$(EtO)_3SiH$ (10)	C 1 mg [7.8×10^{-5}]	17[d]	$C_5H_{11}Si(OEt)_3$ (2.15)	92
Hex-1-ene (20)	Cl_3SiH (25)	A 1 cm^3; 3.8×10^{-4} mol dm^{-3} in toluene [1.9×10^{-5}]	7[d]	$C_6H_{13}SiCl_3$ (3.1)	70
(20)	$ClMe_2SiH$ (16)	B 1 cm^3; 4.1×10^{-4} mol dm^{-3} in hexane [2.6×10^{-5}]	2	$C_6H_{13}SiMe_2Cl$ (2.4)	85
(32)	(20)	D 1 mg [3.7×10^{-5}]	0.75	(2.6)	83
(10)	Me_3SiH (15)	B 1 cm^3; 4.1×10^{-4} mol dm^{-3} in hexane [4.1×10^{-5}]	2	$C_6H_{13}SiMe_3$ (1.42)	90
(0)	Me_2EtSiH (10)	B 0.1 cm^3; 4.1×10^{-4} mol dm^{-3} in hexane [4.1×10^{-6}]	1	$C_6H_{13}SiEtMe_2$	85
(10)	(10)	E 4 mg [7.53×10^{-4}]	1	(1.56)	90
(16)	Me_2PhSiH (10)	B 0.5 cm^{-3}; 4.1×10^{-4} mol dm^{-3} in hexane [2.05×10^{-5}]	1	$C_6H_{13}SiPhMe_2$ (2.0)	90
(16)	$Me_2(PhCH_2)SiH$ (10)	D 4 mg [2.98×10^{-4}]	0.5	$C_6H_{13}Si(CH_2Ph)Me_2$ (2.06)	88
(16)	Et_3SiH (10)	B 1 cm^3; 4.1×10^{-4} mol dm^{-3} in hexane [4.1×10^{-5}]	6[d]	$C_6H_{13}SiEt_3$ (1.2)	60
(20)	$(EtO)_3SiH$ (10)	D 1 mg [7.45×10^{-5}]	24[d]	$C_6H_{13}Si(OEt)_3$ (1.36)	55[e]
(10)	(10)	C 25 mg [1.8×10^{-3}]	24[d]	(1.5)	60
Styrene (20)	Cl_3SiH (25)	A 1 mg [3.8×10^{-5}]	6	$PhCH_2CH_2SiCl_3$ (4.5)	94
(20)	Cl_2MeSiH (30)	D 1 mg [3.7×10^{-5}]	1	$PhCH_2CH_2SiMeCl_2$ (4.2)	96
(20)	$ClMe_2SiH$ (24)	D 1 mg [3.7×10^{-5}]	1	$\left.\begin{array}{l}PhCH_2CH_2SiMe_2Cl\\PhCH(SiMe_2Cl)Me\end{array}\right\}$ (3.65)(78% β-, 22% α-isomer)	92
(10)	Me_2EtSiH (10)	B 1 cm^3; 4.9×10^{-4} mol dm^{-3} in hexane [4.9×10^{-5}]	0.75	$PhCH_2CH_2SiEtMe_2$ (1.75)	92
(10)	Me_2PhSiH (10)	B 1 cm^3; 4.1×10^{-4} mol dm^{-3} in hexane [4.1×10^{-5}]	1.5	$PhCH_2CH_2SiPhMe_2$ (2.0)	83
(5)	$Me_2(PhCH_2)SiH$ (5)	D 0.5 mg [7.5×10^{-5}]	3.5	$PhCH_2CH_2Si(CH_2Ph)Me_2$ (1.15)	90
(10)	Et_3SiH (10)	F 1 cm^3; 5.0×10^{-4} mol dm^{-3} in hexane [5.0×10^{-5}]	3[d,f]	$PhCH_2CH_2SiEt_3$ (1.65)	75

TABLE 1 (*Continued*)

Olefin (amount/mmol)	Silane (amount/mmol)	Catalyst [a]	Reaction time (t/h) [b]	Product (m/g)	Yield [c] (%)
Allyl chloride (20)	Cl_3SiH (25)	A 2 cm^3; 3.8×10^{-4} mol dm^{-3} in toluene [3.8×10^{-5}]	2	$ClCH_2CH_2CH_2SiCl_3$ (2.95)	70 [g]
(10)	Cl_2MeSiH (10)	A 1 mg [7.6×10^{-5}]	8	$ClCH_2CH_2CH_2SiMeCl_2$ (1.0)	55 [h]
(20)	(25)	D 1 mg [3.72×10^{-5}]	20 [i]	(2.3)	60
(20)	$ClMe_2SiH$ (30)	B 2 cm^3; 4.1×10^{-4} mol dm^{-3} in hexane [2.0×10^{-5}]	17 [f]	$ClCH_2CH_2CH_2SiMe_2Cl$ (1.1)	32 [j]
(10)	Me_2PhSiH (20)	D 2 mg [1.5×10^{-4}]	43 [d]	$ClCH_2CH_2CH_2SiPhMe_2$	18 [k]
2-Methylpropene (15)	Me_2EtSiH (10)	B 1 cm^3; 4.1×10^{-4} mol dm^{-3} in hexane [4.1×10^{-5}]	20 [d]	$Me_2CHCH_2SiEtMe_2$ (0.93)	65

[a] A = [$\{Pt(SiCl_3)(\mu\text{-}H)[(C_6H_{11})_3P]\}_2$], B = [$\{Pt(SiEtMe_2)(\mu\text{-}H)[(C_6H_{11})_3P]\}_2$], C = [$\{Pt[Si(OEt)_3](\mu\text{-}H)[(C_6H_{11})_3P]\}_2$], D = [$\{Pt[Si(CH_2Ph)Me_2](\mu\text{-}H)[(C_6H_{11})_3P]\}_2$], E = [$Pt(C_2H_4)_2\{(C_6H_{11})_3P\}$], and F = [$\{Pt(SiEt_3)(\mu\text{-}H)[(C_6H_{11})_3P]\}_2$]. The concentration is given in square brackets expressed as a ratio of either catalyst : olefin or catalyst : silane, depending on which reactant is not in excess. [b] Upper limit; all the reactions occur at room temperature and are exothermic unless otherwise stated. [c] Pure product after distillation and expressed in terms of the reactant not in excess. Yields of crude product were somewhat higher. [d] Not detectably exothermic. [e] Hydrosilylation at 65 °C gave 90% yield of product. [f] Days. [g] Accompanied by 20% yield of Pr^nSiCl_3. [h] Accompanied by 38% yield of $MeSiCl_3$. [i] At 65 °C; $MeSiCl_3$ was also formed in this reaction. [j] Accompanied by 31% Me_2SiCl_2 and some Me_2Pr^nSiCl. [k] Product analysed by g.l.c. showed also Me_2Pr^nPhSi (24%), $Me_2PhSiCl$ (39%), and unchanged Me_2PhSiH.

TABLE 2

Hydrosilylation of some diolefins

Diolefin (amount/mmol)	Silane (amount/mmol)	Catalyst [a]	Reaction time (t/h) [b]	Product (m/g)	Yield [c] (%)
Hexa-1,5-diene (5)	$ClMe_2SiH$ (15)	D 1 mg [1.5×10^{-4}]	0.2	$ClMe_2Si(CH_2)_6SiMe_2Cl$ (1.3)	96
(5)	Me_2PhSiH (10)	B 1 mg [1.6×10^{-4}]	0.5	$Me_2PhSi(CH_2)_6SiPhMe_2$ (1.77)	100
Octa-1,7-diene (10)	Cl_3SiH (25)	A 1 mg [7.6×10^{-5}]	2	$Cl_3Si(CH_2)_8SiCl_3$ (2.9)	76 [d]
(10)	Cl_2MeSiH (25)	D 1 mg [7.4×10^{-5}]	1	$Cl_2MeSi(CH_2)_8SiMeCl_2$ (2.5)	74
(10)	$ClMe_2SiH$ (25)	D 1 mg [7.4×10^{-5}]	1.25	$ClMe_2Si(CH_2)_8SiMe_2Cl$ (2.4)	80 [e]
(5)	Me_3SiH (15)	B 1 cm^3; 4.1×10^{-4} mol dm^{-3} in hexane [8.2×10^{-5}]	2	$Me_3Si(CH_2)_8SiMe_3$ (1.1)	86
(5)	Me_2EtSiH (10)	B 1 mg [1.6×10^{-4}]	0.5	$Me_2EtSi(CH_2)_8SiEtMe_2$ (1.1)	80
(5)	Me_2PhSiH (13)	B 1 mg [1.6×10^{-4}]	0.5	$Me_2PhSi(CH_2)_8SiPhMe_2$ (1.7)	88
(5)	$Me_2(PhCH_2)SiH$ (10)	D 1 cm^3; 6.0×10^{-4} mol dm^{-3} in hexane [1.2×10^{-4}]	1.5	$Me_2(PhCH_2)Si(CH_2)_8Si(CH_2Ph)Me_2$ (1.95)	95
(5)	Et_3SiH (11)	D 15 mg [2.2×10^{-4}]	2 [f,g]	$Et_3Si(CH_2)_8SiEt_3$ (1.0)	60 [h]
(5)	$(EtO)_3SiH$ (10)	C 1 mg [1.6×10^{-4}]	24 [g]	$(EtO)_3Si(CH_2)_8Si(OEt)_3$ (1.4)	65
4-Vinylcyclohexene (10)	Cl_2MeSiH (15)	B 2 mg [1.6×10^{-4}]	0.5 [i]	cyclo-$C_6H_9{\cdot}CH_2CH_2SiMeCl_2$ (1.9)	82
(10)	$ClMe_2SiH$ (15)	B 2 mg [1.6×10^{-4}]	0.5 [i]	cyclo-$C_6H_9{\cdot}CH_2CH_2SiMe_2Cl$ (1.8)	89
(10)	Me_2PhSiH (10)	B 1 mg [8.2×10^{-5}]	0.5	cyclo-$C_6H_9{\cdot}CH_2CH_2SiPhMe_2$ (1.8)	75

[a] See footnote *a* in Table 1. [b] Upper limit; all the reactions occur at room temperature and are exothermic unless otherwise stated. [c] Pure product after distillation and expressed in terms of reactant not in excess. [d] N.m.r. indicated before distillation 87% 1 : 2 adduct and 13% $MeCH{:}CH(CH_2)_5SiCl_3$ and $MeCH{:}CH(CH_2)_2CH{:}CHMe$. [e] N.m.r. revealed <10% other products prior to distillation. [f] Days. [g] Not detectably exothermic. [h] N.m.r. revealed *ca.* 25% $MeCH{:}CH(CH_2)_5SiEt_3$ and $MeCH{:}CH(CH_2)_2CH{:}CHMe$ prior to distillation. [i] Reaction becomes strongly exothermic on warming to 40 °C.

creases.[9] This is similar to that observed in the present study for allyl chloride but in contrast to the sequence found with other olefins.

Yields of hydrosilylation products are generally greater using the catalysts [$\{Pt(SiR_3)(\mu\text{-}H)[(C_6H_{11})_3P]\}_2$] than with other complexes of metals of sub-group 8, for example H_2PtCl_6,[5,10] [$Fe(CO)_5$],[11] [$\{PtCl(\mu\text{-}Cl)(C_2H_4)\}_2$],[6] [$RhCl(Ph_3P)_3$],[12,13] or metallic platinum.[5,10] Moreover,

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[10] M. C. Musolf and J. F. Speier, *J. Org. Chem.*, 1964, **29**, 2519.

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[12] A. J. Chalk, *J. Organometallic Chem.*, 1970, **21**, 207.

[13] R. N. Haszeldine, R. V. Parish, and D. J. Parry, *J. Chem. Soc.* (*A*), 1969, 683.

these catalysts lead to the isomerisation of terminal olefins, whereas in the present work such isomerisation was not observed except to a small degree in the case of triethylsilane and hex-1-ene. With this relatively unreactive silane, isomerisation increased on heating the mixture to 70 °C or in the presence of air, the mixture turning brown. The isomerisation may be due to the formation of metallic platinum by decomposition of the catalyst $[\{Pt(SiR_3)(\mu\text{-}H)[(C_6H_{11})_3P]\}_2]$.

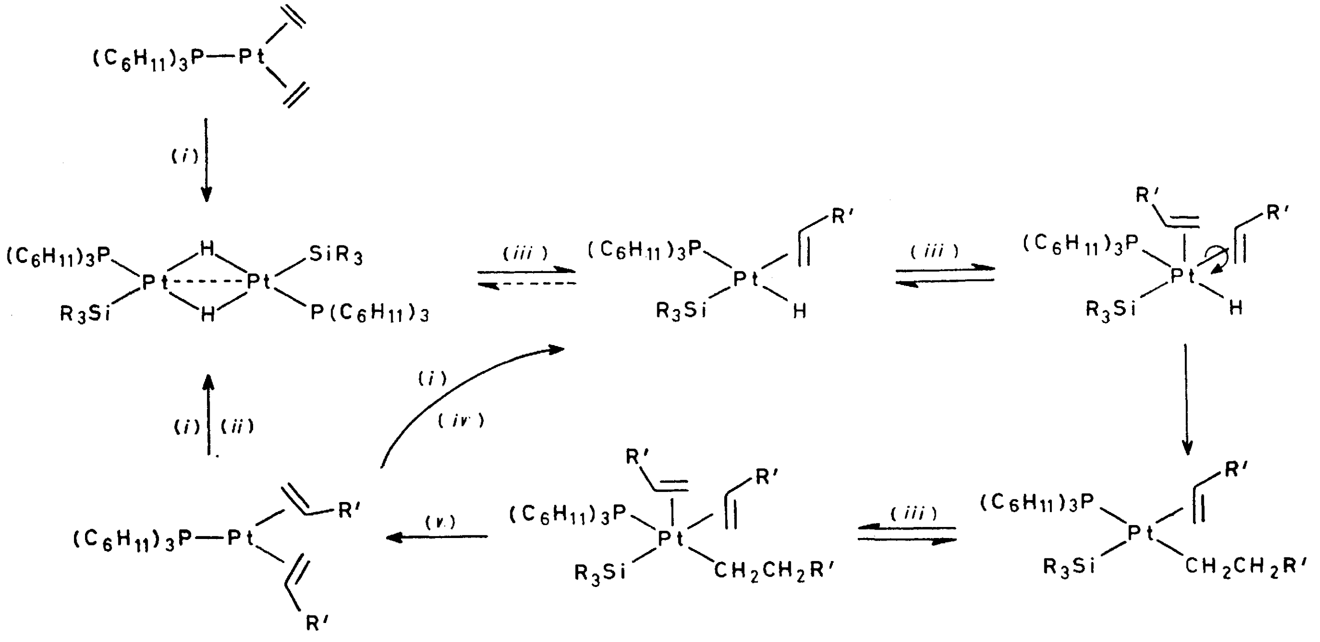
In the hydrosilylation of styrene only β-adducts were obtained with our catalyst system, except with chlorodimethylsilane when a mixture of the α- and β-adducts was formed. Addition of silanes to styrene when catalysed by H_2PtCl_6 [10] or nickel complexes [14] affords mixtures of the α- and β-isomers. The diplatinum catalysts used in the present study also differ from H_2PtCl_6 [15] in not promoting the addition of silanes to internal olefins or to cyclic olefins such as cyclohexene.

TABLE 3

Hydrosilylation of bicyclo[2.2.1]heptene

Silane	Catalyst [a]	Time (t/h)	Product [b]	Yield (%)	Analysis (%) [c] C	H
Cl_3SiH	A 2 mg [8.4×10^{-5}]	72 [d]	$C_7H_{11}SiCl_3$	58	36.8 (36.6)	4.9 (4.8)
Cl_2MeSiH	D 2 mg [9.0×10^{-5}]	5	$C_7H_{11}SiMeCl_2$	85	45.7 (45.9)	6.8 (6.7)
$ClMe_2SiH$	D 2 mg [1.9×10^{-4}]	0.5	$C_7H_{11}SiMe_2Cl$	80	56.9 (57.2)	9.2 (9.1)
Me_2PhSiH	B 1 mg [5.9×10^{-5}]	0.5	$C_7H_{11}SiPhMe_2$	75	78.4 (78.2)	9.7 (9.6)
Et_3SiH	D 2 mg [1.4×10^{-4}]	80	$C_7H_{11}SiEt_3$	76	74.5 (74.2)	12.9 (12.6)

[a] See footnote *a* in Table 1; catalyst concentration expressed as the ratio catalyst : bicyclo[2.2.1]heptene. [b] See text for structure. Calculated values are given in parentheses. [d] 8 h at 65 ° gives 76% yield.



SCHEME (*i*) R_3SiH; (*ii*) $-2R'CH{:}CH_2$; (*iii*) $R'CH{:}CH_2$; (*iv*) $-R'CH{:}CH_2$; (*v*) $-R_3SiCH_2CH_2R'$

The diplatinum complexes have the advantage of promoting the reactions of silanes with olefins at room temperature, in contrast to the other catalysts mentioned above. Moreover, in most cases the new platinum catalysts are not deactivated at the end of the reaction and can be used with fresh reactants.

Only two hydrogermylation reactions were investigated and these involved addition of trimethylgermane to hex-1-ene and to styrene. Both catalysed reactions proceeded more slowly than their silicon counterparts.

The hydrosilylation of the di-olefins hexa-1,5-diene, octa-1,7-diene, and 4-vinylcyclohexene was also investigated (Table 2). Reactions generally proceed rapidly at room temperature to give 2 : 1 silyl adducts in high yield. With Cl_3SiH or Et_3SiH and octa-1,7-diene, side reactions occurred involving isomerisation of the diene. Hydrosilylation of octa-1,7-diene with $ClMe_2SiH$ also produced small amounts (<10%) of $MeCH{:}CH(CH_2)_2CH{:}CHMe$

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and/or MeCH:CH$(CH_2)_5SiMe_2Cl$. Similar reactions catalysed by H_2PtCl_6 or platinum metal require high temperatures.[16-18] The hydrosilylations of 4-vinylcyclohexene occur exothermically with addition only to the exocyclic double bond (Table 2). The mild conditions are in striking contrast to previous work involving catalysis by H_2PtCl_6 or platinum on charcoal at 100—140 °C.[5,19]

With the strained cyclic olefin bicyclo[2.2.1]heptene, hydrosilylation occurred readily (Table 3) with Me_2PhSiH, $ClMe_2SiH$, Cl_2MeSiH, Cl_3SiH, and Et_3SiH, but $(EtO)_3SiH$ did not react. Reaction with Me_2PhSiH was strongly exothermic, while that with Et_3SiH was very slow at room temperature. The reactivity of the silanes thus parallels that found with terminal olefins but bicyclo[2.2.1]heptene is less reactive. Previous work with this olefin, using H_2PtCl_6 or platinum on charcoal as catalysts, gave low yields of products.[20,21]

TABLE 4

Analytical [a,b] and ^1H n.m.r. data for hydrosilylation products from mono-olefins

Compound	B.p. at 760 Torr (θ_c/°C)	Analysis (%) C	Analysis (%) H	^1H N.m.r. (τ) [c]
$C_5H_{11}SiCl_3$	167—169	29.6 (29.2)	5.3 (5.4)	9.08 (t, 3 H), 8.56 (m, 8 H)
$C_5H_{11}SiMe_2Cl$	157—159	51.6 (51.0)	10.8 (10.4)	9.75 (s, 6 H), 9.25 (m, 5 H), 8.79 (m, 6 H)
$C_5H_{11}SiEtMe_2$ [d]	160—162	68.1 (68.3)	14.1 (14.0)	10.19 (s, 6 H), 9.62 (m, 4 H), 9.21 (m, 6 H), 8.83 (m, 6 H)
$C_5H_{11}SiPhMe_2$	244—246	75.9 (75.7)	10.8 (10.7)	9.63 (s, 6 H), 9.07 (m, 5 H), 8.57 (m, 6 H), 2.54 (m, 3 H), 2.36 (m, 2 H)
$C_5H_{11}SiEt_3$ [e]	210—212	70.9 (70.9)	14.3 (14.1)	9.50 (m, 8 H), 9.06 (m, 12 H), 8.70 (m, 6 H)
$C_5H_{11}Si(OEt)_3$ [f]	203—205	56.1 (56.4)	11.4 (11.2)	9.38 (m, 2 H), 9.11 (t, 3 H), 8.76 (t, 9 H), 8.65 (m, 6 H), 6.16 (q, 6 H)
$C_6H_{13}SiCl_3$	189—191	33.2 (32.8)	6.2 (6.0)	9.10 (t, 3 H), 8.62 (m, 10 H)
$C_6H_{13}SiMe_2Cl$	179—181	54.0 (53.7)	10.7 (10.7)	9.74 (s, 6 H), 9.24 (m, 5 H), 8.79 (m, 8 H)
$C_6H_{13}SiMe_3$	162—164	68.1 (68.3)	14.0 (14.0)	10.16 (s, 9 H), 9.65 (m, 2 H), 9.24 (m, 3 H), 8.83 (m, 8 H)
$C_6H_{13}SiEtMe_2$	182—184	70.3 (69.7)	14.4 (14.0)	10.16 (s, 6 H), 9.60 (m, 4 H), 9.17 (m, 6 H), 8.80 (m, 8 H)
$C_6H_{13}SiPhMe_2$		76.6 (76.3)	11.0 (11.0)	9.60 (s, 6 H), 9.03 (m, 5 H), 8.56 (m, 8 H), 2.52 (m, 3 H), 2.34 (m, 2 H)
$C_6H_{13}Si(CH_2Ph)Me_2$ [g]		76.9 (76.8)	11.3 (11.2)	9.98 (s, 6 H), 9.41 (m, 2 H), 9.04 (t, 3 H), 8.63 (m, 8 H), 7.84 (s, 2 H), 2.81 (m, 5 H)
$C_6H_{13}SiEt_3$	229—230	72.4 (71.9)	14.2 (14.1)	9.49 (m, 8 H), 9.06 (t, 12 H), 8.70 (m, 8 H)
$C_6H_{13}Si(OEt)_3$ [h]	222—223	58.1 (58.0)	11.2 (11.4)	9.40 (m, 2 H), 9.12 (t, 3 H), 8.78 (t, 9 H), 8.67 (m, 8 H), 6.17 (q, 6 H)
$PhCH_2CH_2SiCl_3$	241—243	40.6 (40.1)	3.8 (3.8)	8.28 (m, 2 H), 7.12 (m, 2 H), 2.77 (m, 5 H)
$PhCH_2CH_2SiMeCl_2$	243—245	49.5 (49.3)	5.6 (5.5)	9.20 (s, 3 H), 8.42 (m, 2 H), 7.04 (m, 2 H), 2.66 (s, 5 H)
$PhCH_2CH_2SiMe_2Cl$ $PhCH(SiMe_2Cl)Me$	232—236 [i]	60.9 (60.4)	7.8 (7.6)	[j] 9.51 (s, 6 H), 8.71 (m, 2 H), 7.14 (m, 2 H), 2.68 (m, 5 H); 9.61 (s, 3 H), 9.58 (s, 3 H), 8.44 (d, 3 H), 7.48 (q, 1 H), 2.76 (m, 5 H)
$PhCH_2CH_2SiEtMe_2$	232—234	74.6 (74.9)	10.7 (10.5)	9.90 (s, 6 H), 9.38 (q, 2 H), 8.98 (m, 5 H), 7.26 (m, 2 H), 2.68 (m, 5 H)
$PhCH_2CH_2SiPhMe_2$ [k]	160—162 (15 Torr)	80.2 (79.9)	8.7 (8.4)	9.58 (s, 6 H), 8.75 (m, 2 H), 7.22 (m, 2 H), 2.68 (m, 5 H), 2.51 (m, 3 H), 2.34 (m, 2 H)
$PhCH_2CH_2Si(CH_2Ph)Me_2$		80.4 (80.2)	8.9 (8.7)	9.91 (s, 6 H), 9.02 (m, 2 H), 7.78 (s, 2 H), 7.31 (m, 2 H), 2.75 (br, 10 H)
$PhCH_2CH_2SiEt_3$		76.2 (76.3)	11.0 (11.0)	9.51—9.15 (m, 6 H), 9.15—8.76 (m, 11 H), 7.28 (m, 2 H), 2.68 (s, 5 H)
$Cl(CH_2)_3SiCl_3$	182—183	17.0 (17.0)	2.9 (2.9)	8.42 (m, 2 H), 7.96 (m, 2 H), 6.38 (t, 2 H)
$Cl(CH_2)_3SiMeCl_2$	186—188	25.0 (25.1)	5.0 (4.7)	9.40 (s, 3 H), 8.96 (m, 2 H), 8.21 (m, 2 H), 6.64 (t, 2 H)
$Cl(CH_2)_3SiMe_2Cl$		35.3 (35.1)	7.3 (7.1)	9.74 (s, 6 H), 9.26 (m, 2 H), 8.29 (m, 2 H), 6.67 (t, 2 H)
$Me_2CHCH_2SiEtMe_2$ [l]	138—140	66.8 (66.6)	14.3 (14.0)	10.13 (s, 6 H), 9.58 (m, 4 H), 9.16 (m, 9 H), 8.36 (m, 1 H)

[a] Calculated values are given in parentheses. [b] Molecular weights were obtained from mass spectra. [c] In $CDCl_3$. [d] *M* 158 (158). [e] *M* 186 (186). [f] *M* 206 (206). [g] *M* 234 (234). [h] *M* 248 (248). [i] Isomeric mixture (see text). [j] Spectra of β- and α-adducts, respectively. [k] *M* 240 (240). [l] *M* 144 (144).

The manner in which the diplatinum complexes function as catalysts for hydrosilylation may be as indicated in the Scheme. Cleavage of the hydrido-bridges in the diplatinum complexes by olefin would afford a square-planar platinum(II) species in which it seems reasonable to assume the olefin molecule would be *trans* to the R_3Si substituent because of the high *trans*-directing effect of this group.[22] It is possible that the resulting 16-electron square-planar complex then reacts with a further molecule of olefin to form a five-co-ordinate species which collapses *via* migration of the hydrogen on to the co-ordinated olefin. A similar sequence then leads to the reductive elimination of $R_3SiCH_2CH_2R'$ and the regeneration of the monophosphine-substituted platinum(0) complex. Oxidative addition with R_3SiH then completes the cycle.

EXPERIMENTAL

N.m.r. studies (^1H and ^{13}C) were made on Varian Associates HA100 and JEOL PFT-100 spectrometers. Infrared spectra were measured as neat liquids with a Perkin-Elmer 457 spectrophotometer. Mass spectra were determined with an A.E.I. MS902 instrument operating at 70eV.* Products of reactions were identified by analysis (Tables 3—5) and by ^1H n.m.r. (Tables 4 and 5) and by ^{13}C n.m.r.[23] G.l.c. techniques were also employed to identify products.

Hydrosilylation Reactions.—These were carried out in tubes (capacity *ca.* 100 cm^3) fitted with Westef stopcocks

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* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J; 1 Torr = (101 325/760) Pa.

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and a standard joint so that the reaction vessel could be attached to a vacuum system. The experimental results summarised in Tables 1 and 2 were obtained using procedures typified by the following reaction between Cl_3SiH and $CH_2{:}CHCH_2Cl$.

TABLE 5

Analytical [a] and ^1H n.m.r. data for hydrosilylation products from diolefins

Compound	Analysis (%) C	Analysis (%) H	^1H N.m.r. (τ) [b]
$ClMe_2Si(CH_2)_6SiMe_2Cl$	43.9 (44.3)	9.1 (8.9)	9.74 (s, 12 H), 9.34 (m, 4 H), 8.76 (m, 8 H)
$Me_2PhSi(CH_2)_6SiPhMe_2$	75.1 (74.5)	9.8 (9.7)	9.62 (s, 12 H), 9.14 (m, 4 H), 8.57 (m, 8 H), 2.54 (m, 6 H), 2.38 (m, 4 H)
$Cl_3Si(CH_2)_8SiCl_3$	26.0 (25.2)	4.5 (4.2)	8.58 (m, 16 H)
$Cl_2MeSi(CH_2)_8SiMeCl_2$	35.1 (35.3)	6.2 (6.5)	9.41 (s, 6 H), 9.05 (m, 4 H), 8.81 (m, 12 H)
$ClMe_2Si(CH_2)_8SiMe_2Cl$	48.0 (48.1)	9.4 (9.4)	9.56 (s, 12 H), 9.14 (t, 4 H), 8.63 (m, 12 H)
$Me_3Si(CH_2)_8SiMe_3$	65.0 (65.0)	13.4 (13.2)	10.11 (s, 18 H), 9.61 (t, 4 H), 8.79 (m, 12 H)
$Me_2EtSi(CH_2)_8SiEtMe_2$	67.0 (67.0)	13.6 (13.4)	10.16 (s, 12 H), 9.60 (m, 8 H), 9.16 (t, 6 H), 8.79 (m, 12 H)
$Me_2PhSi(CH_2)_8SiPhMe_2$	75.9 (75.3)	9.8 (10.0)	9.66 (s, 12 H), 9.18 (m, 4 H), 8.65 (m, 12 H), 2.58 (m, 6 H), 2.42 (m, 4 H)
$Me_2(PhCH_2)Si(CH_2)_8Si(CH_2Ph)Me_2$	76.2 (76.0)	10.2 (10.3)	9.90 (s, 12 H), 9.48 (m, 4 H), 8.68 (m, 12 H), 7.88 (s, 4 H), 3.06—2.60 (m, 10 H)
$Et_3Si(CH_2)_8SiEt_3$	70.1 (70.1)	14.0 (13.5)	9.65—9.37 (m, 16 H), 9.07 (t, 18 H), 8.71 (m, 12 H)
$(EtO)_3Si(CH_2)_8Si(OEt)_3$	55.1 (54.8)	11.1 (10.6)	9.40 (m, 4 H), 8.78 (t, unsym., 30 H), 6.15 (q, 12 H)
cyclo-$C_6H_9{\cdot}CH_2CH_2SiMeCl_2$	48.5 (48.4)	7.2 (7.2)	9.41 (s, 3 H), 9.01 (m, 2 H), 8.65 (m, 4 H), 8.37 (m, 2 H), 8.07 (m, 3 H), 4.44 (m, 2 H)
cyclo-$C_6H_9{\cdot}CH_2CH_2SiMe_2Cl$	58.8 (59.2)	9.3 (9.4)	9.84 (s, 6 H), 9.33 (m, 2 H), 8.71 (m, 4 H), 8.39 (m, 2 H), 8.07 (m, 3 H), 4.44 (m, 2 H)
cyclo-$C_6H_9{\cdot}CH_2CH_2SiPhMe_2$	78.8 (78.6)	9.8 (9.9)	9.65 (s, 6 H), 9.15 (m, 2 H), 8.61 (m, 4 H), 8.17 (m, 2 H), 7.87 (m, 3 H), 4.19 (m, 2 H), 2.55 (m, 3 H), 2.41 (m, 2 H)

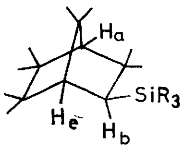
[a] Calculated values are given in parentheses. [b] In $CDCl_3$.

Allyl chloride (1.6 cm^3, 20 mmol) was treated with $[\{Pt(SiCl_3)(\mu\text{-}H)[(C_6H_{11})_3P]\}_2]$ (1 mg) and placed in the reaction vessel which was attached to the vacuum line. Trichlorosilane (25 mmol) was distilled into the reaction tube and the mixture was allowed to warm to room temperature. A strongly exothermic reaction took place. A ^1H n.m.r. spectrum and g.l.c. analysis of a representative sample indicated essentially complete consumption of allyl chloride, and formation of a mixture of $ClCH_2CH_2CH_2SiCl_3$ (82%) and Pr^nSiCl_3 (18%). Fractional distillation afforded 2.95 g (70% yield) of $ClCH_2CH_2CH_2SiCl_3$, identified by i.r. and ^1H and ^{13}C n.m.r. The Pr^nSiCl_3 was identified by independent synthesis (90% yield) from Cl_3SiH and propene using $[\{Pt(SiCl_3)(\mu\text{-}H)[(C_6H_{11})_3P]\}_2]$ as catalyst.

Reactions of Trimethylgermane.—(*a*) *With hex*-1-*ene*. Hex-1-ene (2.5 cm^3, 20 mmol) was treated with a solution (1 cm^3, 3.1×10^{-4} mol dm^{-3}) of $[\{Pt(GeMe_3)(\mu\text{-}H)[(C_6H_{11})_3P]\}_2]$ in hexane and trimethylgermane (10 mmol) was added, as described above. After 24 h a ^1H n.m.r. spectrum revealed quantitative consumption of Me_3GeH and some isomerisation of the excess of olefin. Fractional distillation afforded 1.65 g (80%) of $Me_3GeC_6H_{13}$ (Found: C, 53.3; H, 10.9. Calc. for $C_9H_{22}Ge$: C, 53.3; H, 10.9%). N.m.r. spectra in $CDCl_3$: ^1H, τ 10.01 (s, 9 H, CH_3Ge), 9.41 (m, 2 H, CH_2Ge), 9.22 (m, 3 H, CH_3), and 8.82 (m, 8 H, CH_2); ^{13}C (relative to Me_4Si) −2.38 (CH_3Ge), 14.27 (CH_3), 16.84 (CH_2Ge), 22.76 (ε-CH_2), 25.14 (β-CH_2), 31.74 (δ-CH_2), and 33.15 p.p.m. (γ-CH_2).

(*b*) *With styrene*. In a similar manner, styrene (0.6 cm^3, 5 mmol) and trimethylgermane (7.5 mmol) with the same catalyst for 48 h gave quantitative conversion of the styrene and afforded 0.85 g (76%) of $Me_3GeCH_2CH_2Ph$ (Found: C, 59.1; H, 8.1. Calc. for $C_{11}H_{18}Ge$: C, 59.3; H, 8.1%). N.m.r. spectra in $CDCl_3$: ^1H, τ 9.75 (s, 9 H, CH_3Ge), 8.81 (m, 2 H, CH_2Ge), 7.17 (m, 2 H, CH_2CH_2Ge), and 2.66 (m, 5 H, C_6H_5); ^{13}C, −2.38 (CH_3Ge), 18.64 (CH_2Ge), 31.26 (CH_2CH_2Ge), 125.52, 127.85, 128.28, and 144.98 p.p.m. (C_6H_5).

Hydrosilylation of Bicyclo[2.2.1]*heptene*.—Results of room-temperature reactions are summarised in Table 3. The products listed were identified as the *exo*-isomers in all cases from their i.r. and ^1H n.m.r. spectra. Analysis of the spectra of *exo*- and *endo*-isomers has revealed [20] that the former show characteristic i.r. bands near 1 209, 1 187, 1 147, and 1 137 cm^{-1}, and ^1H n.m.r. spectra with resonances:



τ *ca*. 9·45 (t, 1 H_b),
ca. 8·87–8·39 (m, br, 8 H), and
ca. 7·80 (m, br, H_a and H_e)

The spectra of the products are as follows.

$C_7H_{11}SiCl_3$. $\nu_{max.}$ at 2 950vs,br, 2 865vs, 1 455s, 1 317s, 1 300s, 1 254m, 1 213m, 1 197m, 1 150s, 1 134m, 1 122m, 1 040m, 1 000m, 977s, 917vs, 882s, 848m, 795s, 775m, 682vs, 595vs,br, 565vs, 500vs, and 476s cm^{-1}. τ 8.45—9.09 (m, br, 9 H), 7.77 (m, H_e), and 7.58 (m, H_a).

$C_7H_{11}SiMeCl_2$. $\nu_{max.}$ at 2 960vs,br, 2 875vs, 1 458s, 1 410m, 1 319s, 1 300s, 1 267vs, 1 215m, 1 200m, 1 150s, 1 135s, 1 122s, 1 039s, 1 005s, 978s, 918vs, 885vs, 851vs, 820vs, 795vs,br, 748vs, 660vs, 588vs, 550vs,br, and 500vs cm^{-1}. τ 9.45 (s, 3 H, CH_3Si), 9.08 (t, H_b, J 8.5 Hz), 9.03—8.39 (m, br, 8 H), 7.80 and 7.69 (m, H_a and H_e).

$C_7H_{11}SiMe_2Cl$. $\nu_{max.}$ at 2 950vs,br, 2 870vs, 1 458s, 1 410s, 1 320s, 1 300s, 1 260vs, 1 219m, 1 200m, 1 150m, 1 134m, 1 122s, 1 040m, 1 005w, 980s, 920vs, 885s, 850vs, 818vs, 793vs, 700s, 685s, 630s, and 495vs,br cm^{-1}. τ 9.78 (s, 6 H, CH_3Si), 9.34 (t, H_b), 8.90 (m, 4 H), 8.62 (m, 4 H), and 7.82 (m, H_a and H_e).

$C_7H_{11}SiPhMe_2$. $\nu_{max.}$ at 3 170s, 3 150m, 2 950vs,br, 2 860vs, 1 493m, 1 460s, 1 433vs, 1 318s, 1 300s, 1 250vs, 1 219m, 1 196m, 1 122vs, 1 035s, 1 008s, 980s, 930s, 918vs, 885vs, 852vs, 842vs, 820vs, 793vs, 775vs, 745vs, 710vs, 680s, 490vs, 430vs, and 420vs cm^{-1}. τ 9.68 (s, 6 H, CH_3Si), 9.10 (t, H_b), 8.91—8.27 (m, 8 H), 7.69 (m, H_a and H_e), and 2.57—2.41 (m, 5 H, C_6H_5).

$C_7H_{11}SiEt_3$. $\nu_{max.}$ at 2 940vs,br, 2 870vs, 1 460vs, 1 420vs, 1 385s, 1 318s, 1 303s, 1 256vs, 1 245vs, 1 218s, 1 198s, 1 160m, 1 150s, 1 130s, 1 120s, 1 080s, 1 020vs,br, 980vs, 918vs, 885vs, 850vs, 795vs, 739vs,br, and 575m cm^{-1}. τ 9.75—9.33 (m, 7 H), 9.16 (t, 9 H), 9.03—8.43 (m, 8 H), and 7.90 (m, H_a and H_e).

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