Journal of Organometallic Chemistry 177 (1979) 153—161
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HOMOGENEOUS CATALYSIS

VII *. THE CATALYSIS OF ISOPRENE HYDROSILYLATION USING METAL ATOMS **

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(Received April 30th, 1979)

Summary

The catalysis of isoprene hydrosilylation using transition-metal atoms has been investigated Hydrosilylation by co-condensation of nickel, cobalt, or iron vapour at —196° C with isoprene and triethoxysilane proceeded both regio- and stereo-selectively to afford (*Z*)-1-triethoxysilyl-2-methyl-2-butene Nickel, in particular, was a very active catalyst, giving quantitative yields below 0° C Other first-row transition metals did not cause hydrosilylation, either alone, or in the presence of a co-catalyst, $[Et_2AlCl]_2$

Introduction

To date only two examples of the use of metal atoms in catalysis have been reported· the oligomerisation of butadiene [1], and the formation of cyclic olefins or aromatic compounds from acetylenes [2] The use of metal atoms in catalysis has now been extended to the hydrosilylation of isoprene Several transition-metal complexes, especially those of Group 8 metals, have proved to be effective catalysts for the addition of organosilicon hydrides to conjugated dienes Previous data on the hydrosilylation of isoprene using transition-metal catalysts are summarised in Table 1

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[*] For Part VI see ref 26

[**] Dedicated to Professor H Normant on the occasion of his 72nd birthday on June 25th 1979

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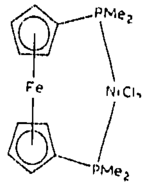
TABLE 1

HYDROSILYLATION OF ISOPRENE CATALYSED BY TRANSITION METAL COMPLEXES

Catalyst	Catalyst concentration (mol/mol silane)	Silane	Temp (°C)	Time (h)	Yields of major products (%) [a]				Ref
					1,4 addn		1,2 addn		
					(I)	(II)	(III)/(IV)	(V)/(VI)	
$[Cr(CO)_6]$	'catalytic'	$HSiMe_3$	30	several days	60	40			3
$[Co(acac)_3]/AlEt_3$ [d]	2×10^{-2}	$HSi(OEt)_3$	20	6	14				1
$[Co_2(CO)_8]$	1.5×10^{-2}	$HSiMe(OSiMe_3)_2$	20	12	31		24/0		5
$[Rh_2(OAc)_4]$ [e]	2×10^{-2}	$HSiEt_3$	20	ca 4	——	45 [f]	——		26
$[Rh(PPh_3)_3Cl]$	7×10^{-4}	$HSiMeCl_2$	130	15	19 [g]	41			7 27
$[Rh(PPh_3)_3Cl]$	7×10^{-4}	$HSi(OEt)_3$	110	2	24 [g]	58			7,27
$[Rh(acac)_3]$	5×10^{-2}	$HSiEt_3$	60	15	94 [j]			5 [k]	26
$[Rh(acac)_3]$	5×10^{-2}	$HSi(OEt)_3$	60	15	89 [j]				26
$[Ni(dmpf)Cl_2]$ [c]	10^{-3}–10^{-4}	$HSiMeCl_2$	105	192	44	33			8
$[Ni(acac)_2]/AlEt_3$ [d]	2×10^{-2}	$HSi(OEt)_3$	20	2	94				1
$[Ni(acac)_2]/AlEt_3$ [d]	2×10^{-2}	$HSiEt_3$	20	4	97				1
$NiCl_2/AlEt_3$	2×10^{-2}	$HSiEt_3$	20	6	95				1
$[Ni(CO)_3(PPh_3)]$	4×10^{-3}	$HSiCl_3$	130	4	96				9
$[Ni(1,5\ C_8H_{12})_2]$	4×10^{-3}	$HSi(OEt)_3$	150	3	65	35			9
$[Ni(PPh_3)_2Cl_2]$	4×10^{-3}	$HSiEt_3$	150	3	13	11		23	9
$[Pd(PhCN)_2Cl_2]$	4×10^{-3}	$HSiCl_3$	80	4	73 [g]				9
$[Pd(PhCN)_2Cl_2]$	4×10^{-3}	$HSi(OEt)_3$	100	6	5	35		14	9
$[Pd(PPh_3)_4]$	10^{-3}	$HSiCl_3$	110	6	83	1			10
$[Pd(PhCN)_2Cl_2]/(PPh_3)$	2×10^{-3}	$HSiMeCl_2$	70	6	95 [g]				11 27
$[Pd(PhCN)_2Cl_2]/(PPh_3)$	2×10^{-3}	$HSi(OEt)_3$	70	6	0				11,27
$[Pd(PPh_3)_2Cl_2]$	4×10^{-3}	$HSiCl_3$	80	4	100 [g]				9
$[Pd(PPh_3)_2Cl_2]$	4×10^{-3}	$HSi(OEt)_3$	100	6	1	22			9
$H_2[PtCl_6]$	4×10^{-3}	$HSiCl_3$	80	1	95			5	9
$H_2[PtCl_6]$	3×10^{-5}	$HSiMeCl_2$	165	17	51				12
$H_2[PtCl_6]$	4×10^{-3}	$HSi(OEt)_3$	150	3	20	68			9
$H_2[PtCl_6]$	4×10^{-3}	$HSi(Et)_3$	150	3	80	20			9
$[Pt(C_2H_4)(PPh_3)_2]$		$HSiMeCl_2$	80				[b] [h]	[b] [i]	13
$[Pt(PPh_3)_4]$	4×10^{-4}	$HSiMeCl_2$	15–82	25			38 [h]	38 [i]	11

[a] Products are shown in Scheme 1 and the yield given is with respect to the silane [b] No quantities given

[c] $Ni(dmpf)Cl_2$

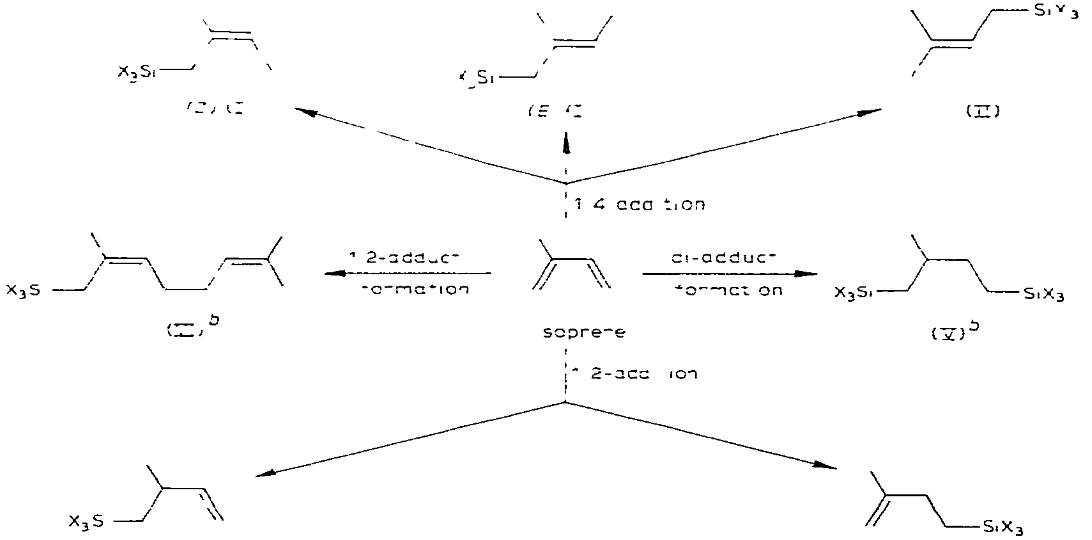


[d] acac = acetylacetonate [e] OAc = acetate [f] 1:1 adducts, unknown isomer distribution [g] (Z) isomers shown by nuclear Overhauser effect (NOE) [h] IV only [i] V only [j] 1,4 adduct(s) unknown stereoisomer distribution [k] 1,2 adducts, unknown isomer distribution

Results and discussion

The activity of transition-metal atoms as catalysts for the hydrosilylation of isoprene was examined No attempts were made to isolate products other than those of hydrosilylation The yields of polymeric products were estimated by inspection. Addition of a monohydrosilane to isoprene can, in principle, afford a wide variety of products (Scheme 1) It is evident that the hydrosilylation of isoprene would enable a rigorous examination of both the regio- and stereoselectivity of catalysts using transition-metal atoms and would allow valuable comparisons to be made with the catalysis achieved using transition-metal complexes

SCHEME 1 POSSIBLE PRODUCTS OF THE HYDROSILYLATION OF ISOPRENE BY A MONOHYDROSILANE $HSiX_3$



(I) 1-silyl-2-methyl-2-butene (II) 1-silyl-3-methyl-2-butene (III) 1-silyl-2-methyl-4-butene (IV) 4-silyl-2-methyl-1-butene (V) 1 4-disilyl-2-methylbutane (VI) 1-silyl-2 7-dimethyl-2 6-octadiene
a Internal isomers are not shown b Other isomers are possible

The majority of hydrosilylation catalysts previously known either with isoprene as substrate, or with other olefins or dienes, have contained a Group 8 metal. It is clear from Table 2 that hydrosilylation catalysis using metal atoms of the first-row transition series occur only for Group 8 metals Nickel, in particular, exhibited remarkable catalytic activity giving high yields at temperatures below 0°C and with a short reaction time. Such reactivity is far greater than that observed with chloroplatinic acid [9], where comparable yields are only obtained after 3 h at 150°C.

Manganese is known to be less reactive as a metal vapour due to its rapid aggregation [16] to produce "massive" metal and would be expected to have poor catalytic activity The low activities of chromium, vanadium, and titanium as hydrosilylation catalysts were thought initially to be due to their ability to form stable metal—arene complexes [16] under the conditions of the reaction This, in fact, is not the case, since changing the solvent from toluene to

TABLE 2

RESULTS OF THE METAL VAPOUR CATALYSIS EXPERIMENTS ON THE HYDROSILYLATION OF ISOPRENE

Metal	Amount of metal evaporated [a] (mg)	Isoprene/silane ratio [b]	Solvent	Temp (°C)	Time [f] (h)	Yield [e] of I (%)	Amount of polymerisation [g]
Ni	12	4.0 [c]	PhMe	110	8	0	Some
Ni	14	5.3 [d]	PhMe	<0		51	Some
Ni	14	3.6	PhMe	<0		79	None
Ni	28	3.6	PhMe	<0		98	None
Ni	61	3.6	MeC_6H_{11}	<0		100	None
Ni [h]	27	3.6	PhMe	<0		0	Considerable
Co	28	3.6	PhMe	0		13	None
Co	28	3.6	PhMe	110	6	28	Considerable
Fe	36	3.6	PhMe	<0		trace	None
Fe	36	3.6	PhMe	110	5	23	Considerable
Mn	20	3.6	PhMe	<0		0 [j]	None
Cr	14	3.6	PhMe	<0		0	None
Cr	14	3.6	PhMe	110	6	0	Some
Cr	12	3.6	MeC_6H_{11}	<0		0	Considerable
Cr	35	3.6	None	<0		0	Considerable
Cr/Et_2AlCl [i]	16	3.6	PhMe	<0		0	Some
Cr/Et_2AlCl [i]	16	3.6	PhMe	110	6	0	Considerable
V	37	3.6	PhMe	<0		trace	Considerable
V	31	3.6	MeC_6H_{11}	<0		0	Considerable
V/Et_2AlCl [i]	33	3.6	PhMe	<0		trace [j]	None
Ti	24	3.6	PhMe	<0		trace [j]	None
Ti	15	3.6	MeC_6H_{11}	<0		0	Some
Ti/Et_2AlCl [i]	23	3.6	PhMe	<0		0	None
Ti/Et_2AlCl [i]	23	3.6	PhMe	110	6	trace	Considerable

[a] Catalyst concentration ranged from $1-5 \times 10^{-2}$ mol/mol silane [b] $HSi(OEt)_3$ unless stated otherwise [c] $HSiEt_3$ [d] $HSiMe(OSiMe_3)_2$ [e] Determined by quantitative GLC with respect to silane [f] Reflux time after removal from the reaction vessel [g] Not characterised qualitative value given [h] Ni and PhMe co-condensed at −196°C to form a slurry silane/isoprene mixture added at ca −30°C [i] 0.5 mmol co catalyst added. 0.1 M Et_2AlCl in PhMe (5 cm^3) [j] No change after 6 h reflux

methylcyclohexane only produced an increased quantity of polymeric material

It has been shown [1] that co-condensation of atoms of V, Cr, Mn, Fe, Co, or Ni with butadiene in benzene catalysed oligomerisation Addition of co-catalysts, such as alkylaluminium halides, gave increased yields, mainly of the cyclic trimers. In contrast, the co-condensation of Cr, Ti, or V atoms with isoprene, silane, toluene, and a solution of diethylaluminium chloride in toluene, produced no hydrosilylated products.

Some, but not all, of the transition-metal catalysts used previously are very sensitive to a change in the nature of the silane (Table 1) In hydrosilylation the reactivity of the silane is dependent upon the nature of the unsaturated substrate and the catalyst employed. The catalysis of nickel metal atoms also exhibited a wide range of activity dependent upon the silane used, but generally followed the sequence:

$$HSi(OEt)_3 > HSiMe(OSiMe_3)_2 >> HSiEt_3$$

The electronegativity of the substituents and hence the polarity of the Si—H bond is thought to be important since oxidative addition of silane is commonly

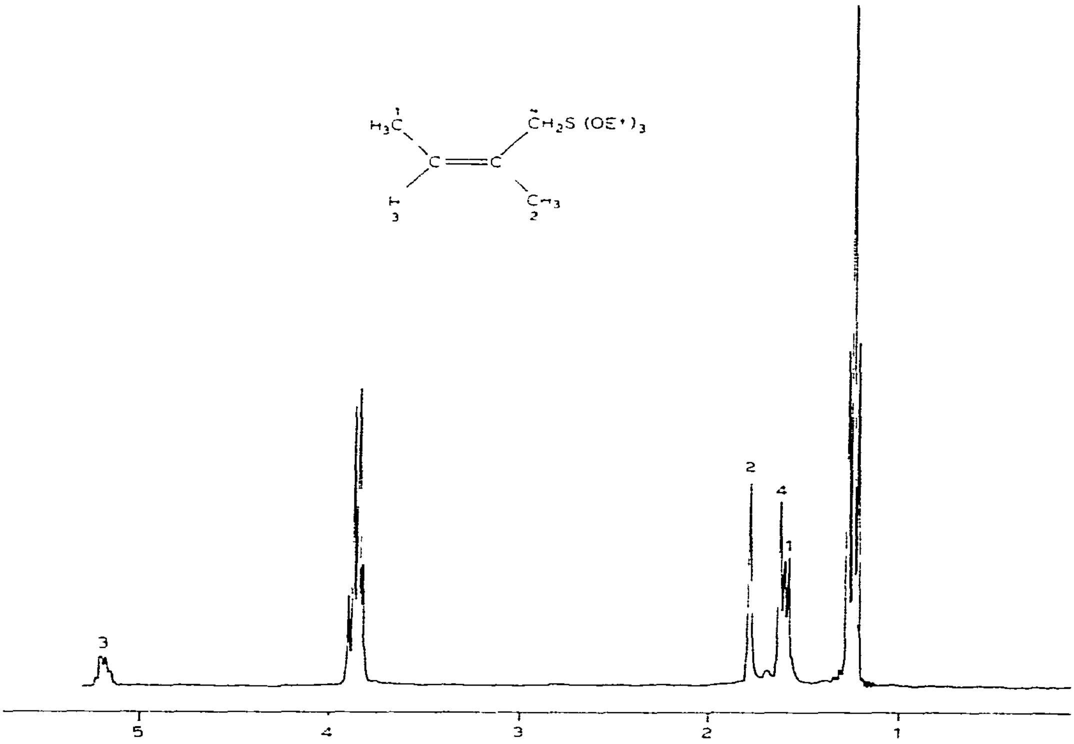


Fig 1 The ^{1}H NMR spectrum (300 MHz) of (Z)-1-triethoxysilyl-2-methyl-2-butene

held to be a key step in the catalytic pathway The increase in the rate of the reaction with decrease of electron density in the Si—H bond has been observed for many catalytic systems

No attempts were made to optimise the conditions for the metal atom catalysis experiments and hence the concentration of the derived catalyst should be regarded as an upper limit The concentrations of the metal atom derived catalysts used are comparable with those reported for other transition-metal catalysts (Table 1)

The metal atom catalysed hydrosilylation of isoprene with triethoxysilane, using Ni, Co, or Fe atoms, gave the same 1,4-addition adduct with no other detectable products The ^{1}H NMR spectrum at 60 MHz indicated that the product was 1-triethoxysilyl-2-methyl-2-butene (I, X = OEt) It was not possible to elucidate the geometry of the olefin from the 60 MHz spectrum. GLC analysis gave a single peak, implying that only one geometric isomer had been formed. However, the ^{1}H NMR spectrum at 300 MHz shows signals due to the protons numbered 1—4 (Fig 1).

The chemical shifts, δ, and spin—lattice relaxation times, T_1, are listed in Table 3. Irradiation of proton 3 produced an 8% enhancement of methyl group 2 (nuclear Overhauser effect). Calculation of the enhancement expected for the two geometric isomers gave maximum values of 13% for the (*Z*)-isomer, and 3% for the (*E*)-isomer. These values led to the assignment of the 1,4-addition product as (*Z*)-1-triethoxysilyl-2-methyl-2-butene (I, X = OEt) The (*Z*)-isomer was

TABLE 3

CHEMICAL SHIFTS δ AND SPIN—LATTICE RELAXATION TIMES T_1 FOR (Z)-1-TRIETHOXYSILYL-2-METHYL-2-BUTENE

Assignment [a]		δ (ppm)	T_1 (s)
1	CH_3	1 600	2 59
2	CH_3	1 791	1 87
3	H	5 196	3 61
4	CH_2	1 631	2 04

[a] For numbering see Fig 1

also prepared by an independent chemical route (Z)-1-Trichlorosilyl-2-methyl-2-butene (I, X = Cl), obtained by the hydrosilylation of isoprene with trichlorosilane [9], was refluxed for 48 h with a large excess of triethyl orthoformate The physical and chemical properties of the 1,4-adduct formed from the catalytic experiments and the product prepared independently from the butene (I X = Cl) were identical in every respect.

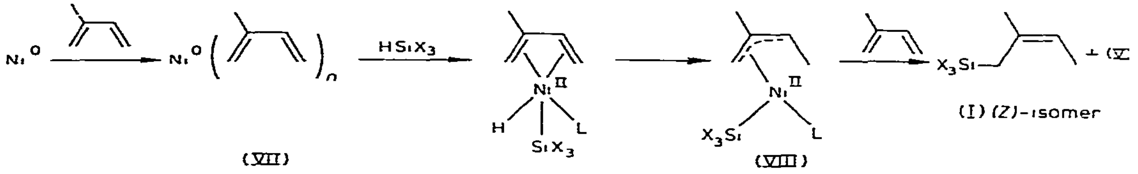
Previous catalysts have rarely achieved a comparable degree of regio- and stereo-selectivity. This selectivity is particularly unexpected for the catalysts derived from Co and Fe atoms, since the hydrosilylation of isoprene with these metals invariably produced mixtures previously [4,5]

Mechanism

Metals, either finely divided [17] or supported [18] on carbon or alumina have been used as catalysts for the hydrosilylation of dienes or olefins To ensure that the results obtained were not simply the consequence of a finely divided metal acting as a catalyst, a reactive Ni/PhMe slurry was prepared [19] by co-condensing nickel vapour and toluene at —196° C. The silane/isoprene mixture was then added to a slurry at ca —30° C No hydrosilylation products were detected from this mixture This suggests that the metal does not participate as activated massive metal, but as atoms, small clusters, or complexes derived therefrom.

A possible mechanism for the catalytic hydrosilylation of isoprene using catalysts derived directly from metal atoms is shown in Scheme 2 for Ni atoms

SCHEME 2 PROPOSED MECHANISM FOR THE HYDROSILANONE OF ISOPRENE BY CATALYSTS DERIVED FROM Ni VAPOUR (L = ALL OTHER LIGANDS CO-ORDINATED TO Ni)



The mechanism is very similar to that proposed for the hydrosilylation of 1,3-dienes using Ziegler-type catalysts such as $[M(acac)_n]$-$AlEt_3$ [4] (M = Cr, Mn, Fe, Co, or Ni). In view of our current findings, the hydrosilylation of isoprene with triethoxysilane using a $[Ni(acac)_2]$-$AlEt_3$ Ziegler system was reinvestigated

The product previously reported has now also been shown to be the (*Z*)-isomer (I. X = OEt)

The proposed mechanism involves oxidative addition of the silane to a nickel(0) species (VII), followed by the subsequent formation of a π-allyl intermediate (VIII) The fact that only one isomer is finally produced suggests that the insertion of isoprene into the Ni—H bond is extremely regioselective Such insertions are well-known for metal hydrides [20—22] and are very specific. The π-allyl intermediate VIII then affords the (*Z*)-isomer (I, X = OEt) upon reductive elimination Similar mechanisms have been proposed for the hydrosilylation of isoprene using other transition-metal catalysts [7,9,11,26] It seems unlikely that the solvent plays a major role in the mechanistic pathway, since change in the solvent (from toluene to methylcyclohexane) had little effect on the yield, rate, or product formed

It appears that the extraordinarily mild reaction conditions inevitably used in metal atom catalysis may encourage the formation of the kinetic product, in those cases where more than one product may be formed Hence the high degree of specificity found there may have some generality

Experimental

General procedures

All experiments were carried out under argon or in vacuo, using freshly distilled, dry, degassed solvents

^{1}H NMR spectra were recorded on a Varian T60 spectrometer IR spectra were obtained with a Perkin—Elmer 457 grating spectrometer as thin films Quantitative GLC measurements were carried out using a Pye-Unicam model 104 (katharometer detector) gas chromatograph, using a 6 ft column of 5% SE30 on 100—120 mesh Chromasorb at 150°C.

Isoprene was purchased from Koch-Light Ltd , and was dried over molecular sieves and distilled in an inert atmosphere prior to use Triethyl- [23], triethoxy- [24], and bis(trimethylsiloxy)methyl- [6] silanes were prepared by standard methods Metal samples were used as supplied titanium rod (12 5 mm in

TABLE 4

DETAILS OF ISOPRENE HYDROSILYLATION CATALYSIS EXPERIMENTS

Silane	Amount of silane (cm^3 mmol)	Amount of isoprene (cm^3 mmol)	Volume of solvent [a] (cm^3)	Metal vapours used [e]
$HSiEt_3$	4 25	10, 100	6	Ni
$HSiMe(OSiMe_3)_2$	4, 15	8 80	8	Ni
$HSi(OEt)_3$	4 22	8, 80	8	Ni Co Fe Mn Cr, V, or Ti
$HSi(OEt)_3$	4 22	8, 80	8	Ni [c]
$HSi(OEt)_3$	4 22	8 80	None	Cr
$HSi(OEt)_3$	4 22	8 80	8 [b]	Ni, Cr V or Ti
$HSi(OEt)_3$	4 22	8 80	8 [d]	Cr V or Ti

[a] Normally toluene [b] MeC_6H_{11} [c] Ni and PhMe co-condensed at —196°C to form a slurry silane/isoprene mixture added to the slurry at —30°C [d] Co-catalyst added 0 1 *M* Et_2AlCl in PhMe (5 cm^3, 0 5 mmol co-catalyst) [e] 0 2—0 7 mmol vaporised see Table 2 for the exact amount of metal vaporised in each case

TABLE 5

SAMPLE POWER RATINGS USED FOR METAL VAPORISATION IN THE CATALYSIS EXPERIMENTS

Metal	Quantity evaporated [a] (mg)	Power rating [b] (W)	High tension voltage (kV)	Emission current (mA)	Vaporisation time (min)
Ni	27	270	3.0	90	20
Co	28	52	1.3	40	15
Fe	36	70	1.4	50	15
Mn	20	30	1.2	25	10
Cr	12	51	1.7	30	15
V	31	225	3.0	75	30
Ti	23	175	2.5	70	30

[a] Amount evaporated is not only dependent upon the power rating but inter alia also on how accurately the electron beam is focussed, the degree of thermal contact between metal sample and copper hearth and the pressure in the reaction vessel during co-condensation. [b] Equal to emission current × high tension voltage.

diameter, Alpha Products), vanadium rod (12.5 mm in diameter, Metals Research Ltd.), chromium granules (Balzers Ltd.), manganese granules (B.D.H. Ltd.), iron rod (12.5 mm in diameter, soft steel), cobalt granules (Hopkins and Williams Ltd.), and nickel rod (12.5 mm in diameter, Metals Research Ltd.).

The metal atom catalysis experiments were carried out using a G.V. Planar VSP 101 metal vapour synthesiser with an EBSI electron beam source (a commercial model based upon an apparatus described elsewhere [25]).

Typically, a first-row transition metal was vaporised and co-condensed with a silane/isoprene/solvent solution over a period of 20—30 min at −196°C. The quantities of each reagent used for these experiments are listed in Table 4 and power ratings required for suitable rates of evaporation of the different transition metals are shown in Table 5. In some cases $[Et_2AlCl]_2$ in toluene was also added, as a co-catalyst. In the instances where a co-catalyst was used, the two solutions were introduced into the reaction vessel simultaneously via different inlet tubes, in order to avoid side-reactions due to pre-mixing. The co-condensate, which was usually coloured, was allowed to warm to ca. −30°C and was then siphoned off anaerobically into a graduated Schlenk tube. An aliquot was removed and the yield and distribution of hydrosilylated products determined by quantitative GLC.

In those cases where very little or no hydrosilylation had occurred, the mixture was refluxed for ca. 6 h. Another aliquot was removed and quantitative GLC performed once again. The particular conditions for each experiment and the yields of hydrosilylated products are given in Table 2. The viscosity of the co-condensate upon melting and the design of the reaction vessel did not allow for complete recovery of the reaction mixture. Losses are estimated to be ca. 10—20% of the total volume added. The yields have therefore been determined from the volume of co-reactants added during the condensation, rather than from the volume of the solution recovered at the end of the experiment.

Hydrosilylation of isoprene catalysed by nickel atoms

A weighed sample of nickel rod was placed on the copper hearth of the election beam furnace The reaction vessel was evacuated and rotated whilst being cooled to —196°C. The electron beam gun was activated and suitably adjusted until evaporation of nickel metal was observed A solution of isoprene (4 cm^3, 40 mmol), triethoxysilane (2 cm^3, 11 mmol), and methylcyclohexane (4 cm^3) was co-condensed with the metal vapour over a period of 30 min The matrix was allowed to melt, warm to ca —30°C, and be collected The amount of nickel evaporated was calculated from the weight loss of the electron beam furnace At ca —5°C an exothermic reaction occurred GLC analysis indicated that the reaction had proceeded quantitatively After removal of volatile materials under reduced pressure at room temperature, distillation gave the hydrosilylation product as a colourless liquid, b p 94—95°C/15 mmHg. The product was identified as (*Z*)-1-triethoxysilyl-2-methyl-2-butene (I, X = OEt, from its ^{1}H NMR spectrum at 60 and 300 MHz

Acknowledgment

We thank Dr F. Heatly for the 300 MHz ^{1}H spectra and Dr J.A Connor for arranging that these be run at the University of Manchester, S R C for studentships (to AJC and JJM) and in association with Dow Corning Ltd , for a CASE award (to RKM), and for purchasing the MVS apparatus

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