

Catalytic hydrosilylation of acetylenes mediated by phosphine complexes of cobalt(I), rhodium(I), and iridium(I)

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Abstract

The complexes [Co(PPh₃)₃Cl] (**1**), [Co(PPh₃)₂(CO)₂Cl] (**2**), [Co(PMe₃)₃Cl] (**3**), [Co(PMe₃)₂(CO)₂Cl] (**4**), [Rh(dppe)(CO)Cl] (**5**), [Rh(PPh₂Me)₂(CO)Cl] (**6**), [Ir(dppe)(CO)Br] (**7**), and [Ir(PPh₂Me)₂(CO)Cl] (**8**) catalyse the hydrosilylation of a range of acetylenes including 1-hexyne, phenylacetylene, and 1-phenyl-1-propyne with triethylsilane. In the case of 1-hexyne and 1-phenyl-1-propyne, only the expected hydrosilylation products were observed; however, when the substrate was phenylacetylene, cyclotrimerisation and dimerisation products were observed in addition to the expected vinylsilanes. No hydrosilylation was observed with alkene substrates; however, in the presence of some metal complexes, there was double bond migration and *cis/trans*-isomerisation probably mediated by the formation of metal hydrides in the reaction mixture.

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1. Introduction

Organosilicones have proven to be a versatile class of compounds which have found applications as precursors to photoresistors, semiconductors, preceramics, reagents for organic synthesis, bioactive compounds [1–3], as well as being important industrially where such compounds are employed as adhesives, binders, and coupling agents [4]. Consequently, the synthesis of organosilicon compounds has become increasingly important. However, the methods employed to form Si–C bonds are still limited to a few reactions, including organic halide-based Wurtz-type or Grignard reactions with halosilanes, hydrosilylation, and the Rochow process [5].

The hydrosilylation of various functional groups catalysed by transition metal complexes provides convenient routes to organosilicon compounds. This reaction also serves as a unique and effective method for the selective reduction of carbon–heteroatom bonds (including asymmetric reduction) [4].

In general, the term ‘hydrosilylation’ is used to describe an addition reaction of hydrosilanes to double and triple bonds and, in the laboratory, hydrosilylation is a very convenient method for the synthesis of a range of organosilicon compounds. Although hydrosilylation sometimes takes place at high temperatures (> 300 °C) without any catalyst, the reaction is effectively promoted by ultraviolet light, γ -irradiation, electric discharge and catalysts such as peroxides, metals, metal salts, metal complexes, or, in some special cases, by amines. Among a variety of catalysts that promote the addition of hydrosilanes to carbon–carbon multiple bonds, hexachloroplatinic acid has been used most commonly. Group VII and VIII transition metal complexes, such as tertiary phosphine complexes of nickel, palladium, platinum and rhodium, are also effective [4,6,7].

Hydrosilylation is the addition of Si–H across an unsaturated bond such as C=C, C \equiv C, C=O, or C \equiv N. Although details of the mechanism are still controversial, transition-metal-catalysed reactions are generally rationalised in terms of the Chalk–Harrod mechanism [8] in which the alkene, alkyne, carbonyl compound, or imine initially coordinates to the metal to give a π -complex, which adds oxidatively to the Si–H bond of the hydrosilane. It has also been proposed [9] that the

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reaction could proceed via initial oxidative addition of the hydrosilane to the metal, followed by π -coordination of the alkene and then by insertion of the π -bound moiety into the M–Si bond.

Extensive studies of platinum-catalysed hydrosilylation reactions [8,10] have shown that electron-withdrawing groups on the hydrosilane increase the rate of hydrosilylation and electron-donating groups on the unsaturated moiety accelerate the rate of addition of hydrosilane [11].

Hydrosilylation of monosubstituted alkynes should give three isomeric products: β -(*Z*) **9**, β -(*E*) **10** and α **11** (Scheme 1).

This paper examines the catalytic hydrosilylation of 1-hexyne, phenylacetylene, and 1-phenyl-1-propyne with triethylsilane using the metal complexes [Co(PPh₃)₃Cl] (**1**), [Co(PPh₃)₂(CO)₂Cl] (**2**), [Co(PMe₃)₃Cl] (**3**), [Co(PMe₃)₂(CO)₂Cl] (**4**), [Rh(dppe)(CO)Cl] (**5**), [Rh(PPh₂Me)₂(CO)Cl] (**6**), [Ir(dppe)(CO)Br] (**7**), and [Ir(PPh₂Me)₂(CO)Cl] (**8**) at 65 °C.

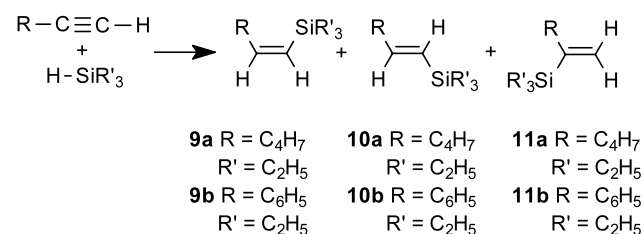
2. Experimental

The synthesis and manipulation of the air-sensitive phosphines and metal complexes was performed under an inert atmosphere of nitrogen either by performing reactions in a glove-box (nitrogen atmosphere) or using standard Schlenk or vacuum-line techniques.

All compressed gases were obtained from B.O.C. Gases. Nitrogen (>99.5%) and carbon monoxide (>99.0%) were used as received without further purification.

Phenylacetylene, 1-hexyne, 1-phenyl-1-propyne, 1-pentene, *cis*-2-pentene, *trans*-2-pentene, and triethylsilane were obtained from Aldrich and distilled immediately prior to use. Hexane, tetrahydrofuran (THF) and THF-*d*₈ were distilled from benzophenone over sodium wire. Deuterated solvents were degassed by three consecutive freeze–pump–thaw cycles, stored under vacuum in an ampoule, and distilled immediately prior to use.

Air-sensitive NMR samples were prepared in a nitrogen-filled glove-box or by vacuum transfer of solvent on a high vacuum line into an NMR tube fitted with a concentric teflon valve [12]. ¹H- and ¹³C-NMR



Scheme 1.

spectra were recorded on a Bruker AMX400 spectrometer or a Bruker DRX400 spectrometer at 400.13 and 100.62 MHz, respectively. In the presentation of NMR data, chemical shifts (δ) are quoted in ppm, the down-field direction being positive. ¹H-NMR chemical shifts are referenced to residual solvent resonances.

GC analyses were performed using a Hewlett Packard 5890A gas chromatograph equipped with a split–splitless capillary inlet and flame ionisation detector. Helium was used as the carrier gas at a head pressure of 110 kPa. The column used was an SGE 25QC2/BPX5-0.25. The profile used was as follows: initial oven temperature 60 °C; initial hold time 2 min; rate 10 °C min⁻¹; final oven temperature 300 °C; and, final time 20 min.

The metal complexes [Co(PPh₃)₃Cl] (**1**) [13], [Co(PPh₃)₂(CO)₂Cl] (**2**) [13], [Co(PMe₃)₃Cl] (**3**) [14], [Co(PMe₃)₂(CO)₂Cl] (**4**) [14], [Rh(dppe)(CO)Cl] (**5**) [15], [Rh(PPh₂Me)₂(CO)Cl] (**6**) [16], [Ir(dppe)(CO)Br] (**7**) [17], and [Ir(PPh₂Me)₂(CO)Cl] (**8**) [18] were synthesised following literature methods.

2.1. General protocol for the hydrosilylation of acetylenes

The hydrosilylation of acetylenes with triethylsilane was performed using 2 mol% of the metal complex in THF-*d*₈ (in the case of complexes **4**, **5**, **6**, **7**, and **8**) and heating the reaction mixture to 65 °C. For the paramagnetic metal complexes (**1**, **2**, and **3**), the reaction was heated for 24 h at 65 °C in THF before the solvent was removed in vacuo, the residue extracted with hexane and passed through a silica plug, eluting with hexane. In the case of the hydrosilylation of 1-hexyne and 1-phenyl-1-propyne, the relative proportion of products was determined by careful integration of the vinylic resonances in the ¹H-NMR spectrum. The relative proportion of products for the hydrosilylation of phenylacetylene was determined by careful integration of the ¹H-NMR spectrum and by GC analysis. The assignment for the β -(*Z*), β -(*E*), and α -vinylsilanes was based upon spectroscopic comparison with literature [19–21].

2.2. *cis*-1-(Triethylsilyl)-1-hexene (**9a**)

¹H-NMR (THF-*d*₈): δ 6.48 (dt, 1H, ³*J*_{1,2} = 14.1 Hz, ³*J*_{2,3} = 7.3 Hz), 5.50 (dt, 1H, ³*J*_{1,2} = 14.10 Hz, ⁴*J*_{1,3} = 1.30 Hz), 2.24 (m, 2H), 1.49 (m, 2H), 1.08 (m, 14H), 0.74 (q, ³*J*_{CH₂-CH₃} = 7.8 Hz, 6H) ppm.

2.3. *trans*-1-(Triethylsilyl)-1-hexene (**10a**)

¹H-NMR (THF-*d*₈): δ 6.17 (dt, 1H, ³*J*_{1,2} = 18.6 Hz, ³*J*_{2,3} = 6.3 Hz), 5.67 (dt, 1H, ³*J*_{1,2} = 18.6 Hz, ⁴*J*_{1,3} = 1.5 Hz), 2.27 (m, 2H), 1.70–1.50 (m, 2H), 1.06 (m, 14H), 0.69 (q, ³*J*_{CH₂-CH₃} = 7.8 Hz, 6H) ppm.

2.4. 2-(Triethylsilyl)-1-hexene (**11a**)

$^1\text{H-NMR}$ (THF- d_8): δ 5.76 (dt, 1H, $^2J_{\text{gem}} = 3.1$ Hz, $^4J_{1,3} = 1.6$ Hz), 5.42 (dt, 1H, $^2J_{\text{gem}} = 3.1$ Hz, $^4J_{1,3} = 1.3$ Hz), 2.26 (m, 2H), 1.70–1.50 (m, 2H), 1.08 (m, 14H), 0.71 (q, $^3J_{\text{CH}_2-\text{CH}_3} = 7.8$ Hz, 6H) ppm.

2.5. *cis*-2-(Triethylsilyl)styrene (**9b**)

$^1\text{H-NMR}$ (THF- d_8): δ 7.56 (d, 1H, $^3J_{\text{HC}=\text{CH}} = 15.4$ Hz, PhCH=), 7.38–7.29 (m, 5H, Ph), 5.87 (d, 1H, $^3J_{\text{HC}=\text{CH}} = 15.4$ Hz, =CH(SiEt₃)), 0.91 (t, 9H, $^3J_{\text{CH}_2-\text{CH}_3} = 7.8$ Hz, CH₃), 0.58 (q, 6H, $^3J_{\text{CH}_2-\text{CH}_3} = 7.8$ Hz, CH₂) ppm.

2.6. *trans*-2-(Triethylsilyl)styrene (**10b**)

$^1\text{H-NMR}$ (THF- d_8): δ 7.38–7.29 (m, 5H, Ph), 7.10 (d, 1H, $^3J_{\text{HC}=\text{CH}} = 15.4$ Hz, PhCH=), 6.56 (d, 1H, $^3J_{\text{HC}=\text{CH}} = 15.4$ Hz, =CH(SiEt₃)), 1.01 (t, 9H, $^3J_{\text{CH}_2-\text{CH}_3} = 7.8$ Hz, CH₃), 0.58 (q, 6H, $^3J_{\text{CH}_2-\text{CH}_3} = 7.8$ Hz, CH₂) ppm.

2.7. 1-(Triethylsilyl)styrene (**11b**)

$^1\text{H-NMR}$ (THF- d_8): δ 7.38–7.29 (m, 5H, Ph), 5.98 (d, 1H, $^2J_{\text{H}-\text{C}=\text{H}} = 3.1$ Hz, =CH₂), 5.70 (d, 1H, $^2J_{\text{H}-\text{C}=\text{H}} = 3.1$ Hz, =CH₂), 0.98 (t, 9H, $^3J_{\text{CH}_2-\text{CH}_3} = 7.8$ Hz, CH₃), 0.70 (q, 6H, $^3J_{\text{CH}_2-\text{CH}_3} = 7.8$ Hz, CH₂) ppm.

2.8. 1,2,4-Triphenylbenzene (**13**)

This product was identified and characterised by GC/MS.

2.9. 1,3,5-Triphenylbenzene (**14**)

$^1\text{H-NMR}$ (THF- d_8): δ 7.97 (s, 3H), 7.88 (d, $^3J = 7.40$ Hz, 6H), 7.57 (t, $^3J = 7.40$ Hz, 6H), 7.46 (t, $^3J = 7.40$ Hz, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ -NMR (THF- d_8): δ 144.5, 143.3, 130.8, 129.4, 129.3, 126.9 ppm.

2.10. *trans*-1,4-Diphenylbut-3-en-1-yne (**15**)

$^1\text{H-NMR}$ (THF- d_8): δ 7.56 (m, 6H, Ph), 7.43 (m, 4H, Ph), 7.15 (d, $^3J_{1,2} = 16.2$ Hz, 1H, CH=C≡), 6.60 (d, $^3J_{1,2} = 16.2$ Hz, 1H, Ph-C=CH-) ppm. $^{13}\text{C}\{^1\text{H}\}$ -NMR (THF- d_8): δ 143.4, 138.7, 133.4, 130.7, 130.6, 130.4, 130.1, 128.3, 125.8, 110.1, 93.5, 91.0 ppm.

2.11. *cis*-1,4-Diphenylbut-3-en-1-yne (**16**)

This product was identified by GC/MS.

2.12. *cis*-1-Phenyl-2-(triethylsilyl)-1-propene (**17**)

$^1\text{H-NMR}$ (THF- d_8): δ 7.41–7.22 (m, 5H, Ph), 6.21 (q, 1H, $^4J_{\text{H}-\text{C}=\text{C}-\text{CH}_3} = 6.5$ Hz, CH=), 1.67 (d, 3H, $^4J_{\text{H}-\text{C}=\text{C}-\text{CH}_3} = 6.5$ Hz, =CCH₃), 1.04 (t, 9H, $^3J_{\text{CH}_3-\text{CH}_2} = 7.8$ Hz, CH₃), 0.72 (q, 6H, $^3J_{\text{CH}_3-\text{CH}_2} = 7.8$ Hz, CH₂) ppm.

2.13. *trans*-1-Phenyl-2-(triethylsilyl)-1-propene (**18**)

$^1\text{H-NMR}$ (THF- d_8): δ 7.41–7.22 (m, 5H, Ph), 6.88 (q, 1H, $^4J_{\text{H}-\text{C}=\text{C}-\text{CH}_3} = 1.7$ Hz, CH=), 2.05 (d, 3H, $^4J_{\text{H}-\text{C}=\text{C}-\text{CH}_3} = 1.7$ Hz, =CCH₃), 1.13 (t, 9H, $^3J_{\text{CH}_3-\text{CH}_2} = 7.8$ Hz, CH₃), 0.84 (q, 6H, $^3J_{\text{CH}_3-\text{CH}_2} = 7.8$ Hz, CH₂) ppm.

2.14. General protocol for the hydrosilylation of alkenes

The hydrosilylation of alkenes was attempted using 2 mol% of the metal complexes **1–8** in THF- d_8 and heating the reaction mixture at 65 °C. When the paramagnetic metal complexes were used, the volatiles were removed by trap-to-trap distillation under reduced pressure into an NMR tube at –180 °C. The ratio of *cis*-2-pentene to *trans*-2-pentene was determined by careful integration of equivalent peaks in the $^1\text{H-NMR}$ spectrum.

3. Results and discussion

3.1. Hydrosilylation of 1-hexyne

Table 1 summarises the hydrosilylation of 1-hexyne with triethylsilane catalysed by a range of metal complexes. The hydrosilylation of 1-hexyne resulted in the formation of three isomeric vinylsilanes, β -(*Z*) **9a**, β -(*E*) **10a**, and α -**11a** (Scheme 1).

The cobalt complexes studied were, in general, ineffective as catalysts for the hydrosilylation of 1-hexyne. The only Co complex which displayed any catalytic activity was [Co(PPh₃)(CO)₂Cl] (**2**) which formed the β -(*E*)- and β -(*Z*)-vinylsilanes exclusively; however, the yield was only 8% (two turnovers) after 24 h at 65 °C (Entry 2, Table 1).

The rhodium complexes, [Rh(dppe)(CO)Cl] (**5**) and [Rh(PPh₂Me)₂(CO)Cl] (**6**), proved effective catalysts for the hydrosilylation of 1-hexyne. In the case of [Rh(dppe)(CO)Cl] (**5**), only 79% of the 1-hexyne was converted to products after 20 h at 65 °C, with the major product being the β -(*Z*)-vinylsilane (Entry 5, Table 1). Complete conversion to products was achieved, after 54 h at 65 °C, when [Rh(PPh₂Me)₂(CO)Cl] (**6**) was used as the catalyst (Entry 6, Table 1). In this case the major product was the β -(*Z*)-vinylsilane, with no α -isomer observed.

Table 1
Distribution of products obtained from the catalytic hydrosilylation of 1-hexyne with triethylsilane at 65 °C

| Entry | Catalyst ^a | Time (h) | Yield ^b (%) | Vinylsilanes (%) | | | 12 (%) |
|-------|---|----------|------------------------|------------------|-----------|-------|--------|
| | | | | β-(Z) 9a | β-(E) 10a | α-11a | |
| 1 | [Co(PPh ₃) ₃ Cl] (1) | 24 | 0 | 0 | 0 | 0 | 0 |
| 2 | [Co(PPh ₃) ₂ (CO) ₂ Cl] (2) | 24 | 8 | 0 | 5 | 3 | 0 |
| 3 | [Co(PMe ₃) ₃ Cl] (3) | 24 | 0 | 0 | 0 | 0 | 0 |
| 4 | [Co(PMe ₃) ₂ (CO) ₂ Cl] (4) | 24 | 0 | 0 | 0 | 0 | 0 |
| 5 | [Rh(dppe)(CO)Cl] (5) | 20 | 79 | 38 | 19 | 19 | 3 |
| 6 | [Rh(PPh ₂ Me) ₂ (CO)Cl] (6) | 54 | 100 | 71 | 25 | 0 | 5 |
| 7 | [Ir(dppe)(CO)Br] (7) | 20 | 100 | 53 | 35 | 7 | 6 |
| 8 | [Ir(PPh ₂ Me) ₂ (CO)Cl] (8) | 36 | 100 | 12 | 65 | 10 | 13 |

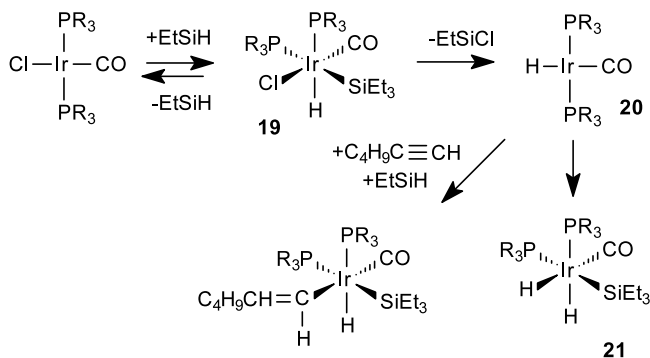
^a All reactions were performed using 2 mol% of catalyst.

^b Yields based on 1-hexyne.

The most effective catalyst for the hydrosilylation of 1-hexyne was the complex [Ir(dppe)(CO)Br] (7), which achieved complete conversion of the 1-hexyne to hydrosilylated products after 20 h at 65 °C, and producing the β-(Z)-vinylsilane as the major product (Entry 7, Table 1). The complex [Ir(PPh₂Me)₂(CO)Cl] (8) also proved effective, producing the β-(E)-isomer as the major product (Entry 8, Table 1).

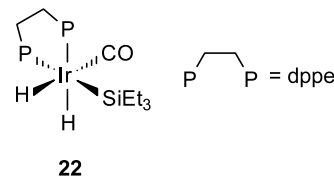
The *trans*-complexes, [Rh(PPh₂Me)₂(CO)Cl] (6) and [Ir(PPh₂Me)₂(CO)Cl] (8), display greater stereoselectivity than their *cis*-analogues, [Rh(dppe)(CO)Cl] (5) and [Ir(dppe)(CO)Br] (7). In the case of the rhodium complexes, both 5 and 6 favoured the formation of the β-(Z)-vinylsilane 9a: complex 5 achieved 38% conversion to 9a, while the *trans* complex 6 achieved 71% conversion. In the case of the iridium complexes, the stereospecificities are different: the *cis*-complex 7 produces the β-(Z)-vinylsilane 9a as the major product, whereas the *trans*-complex 8 primarily produces the *trans*-vinylsilane 10a.

The reduction of 1-hexyne to 1-hexene (12) was also observed with rhodium and iridium catalysts. This product can be rationalised by the possible formation of rhodium or iridium dihydrides by the stepwise addition of two equivalents of silane to starting metal complexes (Scheme 2). The hydridosilyl complex (19),



Scheme 2.

formed by the oxidative addition of hydrosilane, can eliminate a chlorosilane to form an iridium (or rhodium) dihydride (20) which could directly trap the terminal acetylene or react with excess hydrosilane to form the dihydridosilyliridium(III) complex 21 [22]. The formation of an iridium or rhodium dihydride in the reaction medium provides the avenue for reduction of the terminal alkyne to compete with hydrosilylation. An iridium complex 22 (analogous to 21) has been observed in the reaction of [Ir(dppe)(CO)X] (X = Cl, Br) with triethylsilane [23].



22

3.2. Hydrosilylation of phenylacetylene

Table 2 summarises the hydrosilylation of phenylacetylene with triethylsilane catalysed by a range of metal complexes. The hydrosilylation of phenylacetylene resulted in the formation of three isomeric vinylsilanes, β-(Z) 9b, β-(E) 10b, and α-11b (Scheme 1). However, there were also two other competing reaction pathways: the cyclotrimerisation of the phenylacetylene to form 1,2,4-triphenylbenzene (13) and 1,3,5-triphenylbenzene (14) (Scheme 3); and the tail-to-tail dimerisation of the phenylacetylene to form *trans*-1,4-diphenylbut-1-en-3-yne (15) and *cis*-1,4-diphenylbut-1-en-3-yne (16) (Scheme 4) [24].

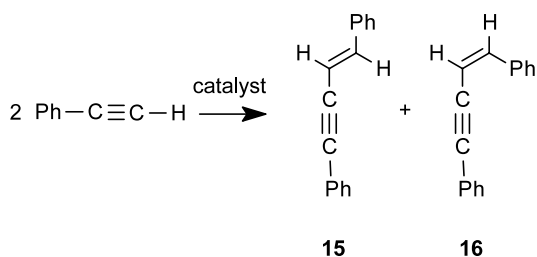
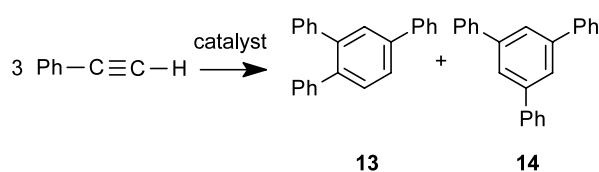
Of the cobalt complexes examined, the most effective hydrosilylation catalyst was [Co(PPh₃)₃(CO)₂Cl] (2) which converted all of the phenylacetylene substrate to products after 24 h at 65 °C. Vinylsilanes comprised 79% of the product mixture with the α-vinylsilane being the major product (Entry 2, Table 2). The other cobalt

Table 2
Distribution of products obtained from the catalytic hydrosilylation of phenylacetylene with triethylsilane

| Entry | Catalyst ^a | Temperature (°C) | Time (h) | Yield ^b (%) | Vinylsilanes (%) | | | Triphenylbenzenes (%) | | Dimers (%) | |
|-------|--|------------------|----------|------------------------|------------------------|-------------------------|-----------------------|-----------------------|------------------|------------------------|----------------------|
| | | | | | β -(Z) 9b | β -(E) 10b | α - 11b | 1,2,4- 13 | 1,3,5- 14 | <i>trans</i> 15 | <i>cis</i> 16 |
| 1 | [Co(PPh ₃) ₃ Cl] (1) | 65 | 24 | 100 | 6 | 10 | 19 | 0 | 8 | 57 | <1 |
| 2 | [Co(PPh ₃) ₂ (CO) ₂ Cl] (2) | 65 | 24 | 100 | 5 | 18 | 56 | 0 | 21 | 1 | <1 |
| 3 | [Co(PMe ₃) ₃ Cl] (3) | 65 | 24 | 100 | <1 | <1 | <1 | 1 | 19 | 78 | <1 |
| 4 | [Co(PMe ₃) ₂ (CO) ₂ Cl] (4) | 65 | 18 | 89 | <1 | 2 | <1 | <1 | 7 | 76 | 13 |
| 5 | [Rh(dppe)(CO)Cl] (5) | 40 | 24 | 100 | 41 | 22 | 29 | <1 | 5 | <1 | 3 |
| 6 | [Rh(dppe)(CO)Cl] (5) | 65 | 16 | 100 | 48 | 21 | 23 | 1 | 6 | 0 | 1 |
| 7 | [Rh(dppe)(CO)Cl] (5) | 80 | 4 | 100 | 51 | 20 | 18 | 2 | 9 | 0 | <1 |
| 8 | [Rh(PPh ₂ Me) ₂ (CO)Cl] (6) | 65 | 18 | 100 | 4 | 19 | 45 | 3 | 8 | 19 | 3 |
| 9 | [Ir(dppe)(CO)Br] (7) | 65 | 16 | 100 | 19 | 67 | 14 | <1 | <1 | 0 | <1 |
| 10 | [Ir(PPh ₂ Me) ₂ (CO)Cl] (8) | 65 | 18 | 100 | 28 | 10 | 62 | <1 | <1 | <1 | <1 |

^a All reactions were performed using 2 mol% of catalyst.

^b Yields based on phenylacetylene.



complexes produced *trans*-1,4-diphenylbut-1-en-3-yne (**15**) as the major product. In the case of [Co(PMe₃)₃Cl] (**3**) and [Co(PMe₃)₂(CO)₂Cl] (**4**), only traces of the hydrosilylation products were identified (Entries 3 and 4, Table 2).

The most effective catalysts for hydrosilylation of phenylacetylene were the complexes [Rh(dppe)(CO)Cl] (**5**) and [Ir(dppe)(CO)Br] (**7**). At 65 °C both complexes achieved total conversion of the phenylacetylene to products after 16 h: complex **5** producing the β -(Z)-vinylsilane **9b** as the major product (Entry 6, Table 2), while complex **7** formed the β -(E)-vinylsilane **10b** as the predominant product (Entry 9, Table 2). With these catalysts, only traces of dimerisation and cyclotrimerisation products were observed.

Catalytic reactions with [Rh(dppe)(CO)Cl] (**5**) were also performed at 40 °C and 80 °C to establish the effect of varying temperature (Entries 5, 6, and 7, Table 2). In all cases, the β -(Z)-isomer **9b** was the major product;

however, the proportion of the β -(Z)-isomer **9b** increased with increasing temperature with a corresponding systematic decrease in the amount of the α -isomer **11b** formed. The proportion of the β -(E)-isomer **10b** formed remained relatively constant with temperature.

The complexes [Rh(PPh₂Me)₂(CO)Cl] (**6**) and [Ir(PPh₂Me)₂(CO)Cl] (**8**) also effectively catalysed the hydrosilylation of phenylacetylene. Both complexes achieved complete conversion to products within 18 h at 65 °C. When [Rh(PPh₂Me)₂(CO)Cl] (**6**) was used, the major product was the α -vinylsilane **11b**; however, dimerisation and cyclotrimerisation products comprised 33% of the product mixture (Entry 8, Table 2). The complex [Ir(PPh₂Me)₂(CO)Cl] (**8**) converted 99% of the phenylacetylene to vinylsilanes, with **11b** being the major product (Entry 10, Table 2).

3.3. Hydrosilylation of 1-phenyl-1-propyne

Table 3 summarises the hydrosilylation of 1-phenyl-1-propyne with triethylsilane catalysed by a range of metal complexes. 1-Phenyl-1-propyne is a non-terminal acetylene and the hydrosilylation with triethylsilane can result in the formation of four possible vinylsilanes, β -(Z) **17**, β -(E) **18**, α -(Z) **23**, and α -(E) **24** (Scheme 5).

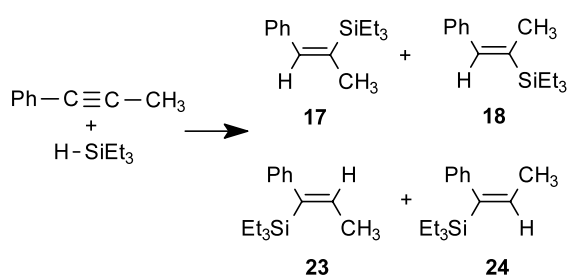
When the cobalt complexes [Co(PPh₃)₃Cl] (**1**), [Co(PPh₃)₂(CO)₂Cl] (**2**), [Co(PMe₃)₃Cl] (**3**), and [Co(PMe₃)₂(CO)₂Cl] (**4**), and the rhodium complex [Rh(PPh₂Me)₂(CO)Cl] (**6**) were heated for 24 h at 65 °C in the presence of 1-phenyl-1-propyne with triethylsilane, no reaction was observed. Similarly, the complex [Ir(PPh₂Me)₂(CO)Cl] (**8**) showed little activity, achieving only a 3% yield of vinylsilanes after 36 h at 65 °C (Entry 8, Table 3). This is probably due to the fact that the internal triple bond is inherently more crowded and this reduces the reactivity of the alkyne.

The most effective catalyst for the hydrosilylation of 1-phenyl-1-propyne with triethylsilane was the rhodium

Table 3
Distribution of products obtained from the hydrosilylation of 1-phenyl-1-propyne with triethylsilane at 65 °C

| Entry | Catalyst ^a | Time (h) | Yield (%) | Vinylsilanes (%) | |
|-------|--|----------|-----------|------------------|----|
| | | | | 17 | 18 |
| 1 | [Co(PPh ₃) ₃ Cl] (1) | 24 | 0 | 0 | 0 |
| 2 | [Co(PPh ₃) ₂ (CO) ₂ Cl] (2) | 24 | 0 | 0 | 0 |
| 3 | [Co(PMe ₃) ₃ Cl] (3) | 24 | 0 | 0 | 0 |
| 4 | [Co(PMe ₃) ₂ (CO) ₂ Cl] (4) | 24 | 0 | 0 | 0 |
| 5 | [Rh(dppe)(CO)Cl] (5) | 20 | 100 | 38 | 62 |
| 6 | [Rh(PPh ₂ Me) ₂ (CO)Cl] (6) | 24 | 0 | 0 | 0 |
| 7 | [Ir(dppe)(CO)Br] (7) | 54 | 54 | 37 | 17 |
| 8 | [Ir(PPh ₂ Me) ₂ (CO)Cl] (8) | 36 | 3 | 2 | 1 |

^a 2 mol% of the metal complex was used.

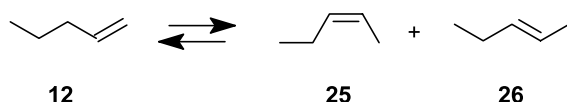


complex [Rh(dppe)(CO)Cl] (**5**), where 100% conversion to vinylsilanes was achieved at 65 °C in 20 h. In this case, only the β-(*Z*) **17** and β-(*E*) **18** vinylsilanes were observed in yields of 38 and 62%, respectively (Entry 5, Table 3). The iridium analogue, [Ir(dppe)(CO)Br] (**7**), afforded a 54% yield of vinylsilanes after 54 h at 65 °C, with only the β-(*Z*) **17** and β-(*E*)-vinylsilanes **18** observed (Entry 7, Table 3).

3.4. Attempted hydrosilylation of 1-pentene

When the hydrosilylation of 1-pentene was attempted in the presence of the complexes [Co(PPh₃)₃Cl] (**1**), [Co(PPh₃)₂(CO)₂Cl] (**2**), and [Co(PMe₃)₂(CO)₂Cl] (**4**) no reaction was observed after 24 h at 65 °C.

When the complexes [Co(PMe₃)₄Cl] (**3**), [Rh(dppe)(CO)Cl] (**5**), [Rh(PPh₂Me)₂(CO)Cl] (**6**), [Ir(dppe)(CO)Br] (**7**), and [Ir(PPh₂Me)₂(CO)Cl] (**8**) were used to mediate the hydrosilylation of alkenes, no hydrosilylation products were detected after 24 h at 65 °C. However, the isomerisation of 1-pentene to a mixture of *cis*-2-pentene **25** and *trans*-2-pentene **26** was observed (Scheme 6).



When [Co(PMe₃)₄Cl] (**3**) was used as the catalyst, the ratio of **25:26** was 58:42 (24 h; 65 °C). After additional heating (24 h; 65 °C) the ratio remained unchanged. After 24 h at 65 °C, complex **5** achieved the ratio of **25:26** of 22:78, while a ratio of 28:72 was obtained when **7** was used. Similar ratios of **25** and **26** were obtained over the same time period when the complexes **6** and **8** were used. A trace of 1-pentene was still present in the reaction mixtures after heating for 36 h, irrespective of the metal complex employed and this probably reflects an equilibration between all of the isomers of pentene. The triethylsilane remained unreacted throughout the course of the reactions.

The isomerisation of *cis*-2-pentene by [Rh(dppe)(CO)Cl] (**5**) in the presence of triethylsilane (40 h; 65 °C), afforded a ratio of **25:26** of 16:84 with a trace of 1-pentene (<1%). When the same isomerisation was performed using **7**, the ratio of **25:26** was 27:73 with ca. 2% 1-pentene after 72 h. The isomerisation of *trans*-2-pentene by [Rh(dppe)(CO)Cl] (**5**) under the same conditions (72 h, 65 °C) resulted in a **25:26** ratio of 12:88 with the formation of <1% 1-pentene; the complex [Ir(dppe)(CO)Br] (**7**) produced a ratio of **25:26** of 5:95 with only a trace of 1-pentene (<1%).

The isomerisation of alkenes will result in the formation of the thermodynamically more favourable *trans*-isomer. In the isomerisation of 2-pentenes, the rhodium complexes [Rh(dppe)(CO)Cl] (**5**) and [Rh(PPh₂Me)₂(CO)Cl] (**6**) display a greater turnover rate than the iridium complexes [Ir(dppe)(CO)Br] (**7**) and [Ir(PPh₂Me)₂(CO)Cl] (**8**), based upon the rate of conversion of *cis*-2-pentene to the thermodynamically more favoured *trans*-2-pentene. Complex **5** shows the lowest *cis:trans* ratio of 2-pentenes for the isomerisation of 1-pentene after 24 h.

When the metal complexes, [Rh(dppe)(CO)Cl] (**5**) or [Ir(dppe)(CO)Br] (**7**), was added to 1-pentene (in the absence of triethylsilane) no isomerisation was observed after 3 days at 65 °C. It is most likely that a metal hydride such as **20**, formed by the reduction of the metal halide by the silane, is the critical intermediate in the

isomerisation and that bond migration occurs by reversible hydride addition/elimination to the metal centre [25].

4. Conclusions

A range of metal complexes in the Co–Rh–Ir triad were examined for their ability to catalyse the thermal hydrosilylation of acetylenes with triethylsilane. The most effective complex examined was the rhodium complex [Rh(dppe)(CO)Cl] (**5**) which successfully catalysed the hydrosilylation of both terminal and non-terminal acetylenes and both aliphatic and aromatic acetylenes. In general, cobalt complexes examined exhibited much less catalytic activity for hydrosilylation of acetylenes, than the corresponding rhodium and iridium compounds, although for aromatic acetylenes the cobalt complexes were more effective in catalysing competitive dimerisation and cyclotrimerisation processes.

None of the complexes examined successfully hydrosilylated alkenes; however, the complexes [Co(PMe₃)₃Cl] (**3**), [Rh(dppe)(CO)Cl] (**5**), [Rh(PPh₂Me)₂(CO)Cl] (**6**), [Ir(dppe)(CO)Br] (**7**), and [Ir(PPh₂Me)₂(CO)Cl] (**8**) were effective catalysts for the isomerisation of alkenes. Alkene isomerisation only occurs in the presence of the silyl hydride and the active isomerisation catalyst is probably a metal hydride formed in situ from the reaction between the metal complex and the silane.

In this study, the range of metal complexes examined as potential catalysts for alkyne hydrosilylation was limited and the reaction conditions were generally not optimised. However, the results obtained demonstrate that the product distribution is sensitive to changes in the metal catalyst as well as reaction conditions and this lays the foundation for work both searching out better catalyst systems and optimising reaction conditions towards desired product distributions.

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References

- [1] R. West, *J. Organomet. Chem.* 300 (1986) 327.
- [2] E.W. Colvin, *Silicon in Organic Synthesis*, Butterworth, London, 1981.
- [3] R.J. Fessenden, J.S. Fessenden, *Adv. Organomet. Chem.* 18 (1980) 275.
- [4] I. Ojima, in: S. Patai, Z. Rappoport (Eds.), *The Chemistry of Organic Silicon Compounds*, Wiley, London, 1989 (Chapter 25).
- [5] T. Sakakura, Y. Tokunaga, T. Sodeyama, M. Tanaka, *Chem. Lett.* (1987) 2375.
- [6] J.A. Reichl, D.H. Berry, *Adv. Organomet. Chem.* 43 (1998) 197.
- [7] T. Hiyama, T. Kusumoto, in: I. Fleming (Ed.), *Comprehensive Organic Synthesis*, vol. 8, Pergamon Press, Oxford, 1991.
- [8] (a) J.F. Harrod, A.J. Chalk, *J. Am. Chem. Soc.* 86 (1964) 1776; (b) A.J. Chalk, J.F. Harrod, *J. Am. Chem. Soc.* 87 (1965) 16; (c) J.F. Harrod, A.J. Chalk, *J. Am. Chem. Soc.* 87 (1965) 1133; (d) J.F. Harrod, A.J. Chalk, *J. Am. Chem. Soc.* 88 (1966) 3491.
- [9] (a) I. Ojima, K. Hidai, *Asymmetric hydrosilylation and hydrocarbonylation*, in: J.D. Morrison (Ed.), *Asymmetric Synthesis*, vol. 5, Academic Press, New York, 1985 (Chapter 4); (b) M.A. Schroeder, M.S. Wrighton, *J. Organomet. Chem.* 128 (1977) 345; (c) M. Brookhart, B.E. Grant, *J. Am. Chem. Soc.* 115 (1993) 2151; (d) Y. Wakatsuki, H. Yamazaki, M. Nakano, Y. Yamamoto, *J. Chem. Soc. Chem. Commun.* (1991) 703.
- [10] A.J. Chalk, J.F. Harrod, in: I. Wender, P. Pino (Eds.), *Organic Synthesis via Metal Carbonyls*, Wiley, New York, 1977, p. 673.
- [11] V.D. Sheludyakov, et al., *Zh. Obshch. Khim.* 55 (1985) 1544.
- [12] Purchased from J. Young Ltd, Cat. No. VNMR/5.
- [13] M. Aresta, M. Rossi, A. Sacco, *Inorg. Chim. Acta* 3 (1969) 227.
- [14] (a) H.-F. Klein, *Angew. Chem. Int. Ed. Engl.* 10 (1971) 343; (b) H.-F. Klein, H.H. Karsch, *Inorg. Chem.* 14 (1975) 473.
- [15] A.R. Sanger, *J. Chem. Soc. Dalton Trans.* (1977) 120.
- [16] S.E. Boyd, L.D. Field, T.W. Hambley, M.G. Partridge, *Organometallics* 12 (1993) 1720.
- [17] (a) B.J. Fisher, R. Eisenberg, *Inorg. Chem.* 23 (1984) 3216; (b) C.E. Johnson, R. Eisenberg, *J. Am. Chem. Soc.* 107 (1985) 3148.
- [18] (a) J.P. Collman, J.W. Kang, *J. Am. Chem. Soc.* 89 (1967) 844; (b) L.D. Field, E.T. Lawrenz, A.J. Ward, *Polyhedron* 18 (1999) 3031.
- [19] M.A. Esteruelas, M. Oliván, L.A. Oro, J.I. Tolosa, *J. Organomet. Chem.* 487 (1995) 143.
- [20] I. Ojima, N. Clos, R.J. Donovan, P. Ingallina, *Organometallics* 9 (1990) 3127.
- [21] S. Elgafi, Ph.D. Thesis, University of Sydney, 1996.
- [22] See for example: (a) M.A. Bennett, R. Charles, P.J. Fraser, *Aust. J. Chem.* 30 (1977) 1201. (b) F. Glocking, M.D. Wilbey, *J. Chem. Soc. (A)* (1970) 1675. (c) F. Glocking, G.J. Irwin, *Inorg. Chim. Acta* 6 (1972) 355. (d) J. Chalk, *J. Chem. Soc. Chem. Commun.* (1969) 1207.
- [23] C.E. Johnson, R. Eisenberg, *J. Am. Chem. Soc.* 107 (1985) 6531.
- [24] L.D. Field, A.J. Ward, *Aust. J. Chem.* 52 (1999) 1085.
- [25] (a) R.H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, Wiley, New York, 1988; (b) S.G. Davies, *Organotransition Metal Chemistry: Applications to Synthesis*, Pergamon Press, Oxford, 1982.