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HOMOGENEOUS CATALYSIS

VIII *. CARBENE-TRANSITION-METAL COMPLEXES AS HYDROSILYLATION CATALYSTS **

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Summary

Some carbene-transition-metal complexes, particularly those of rhodium(I) but also of ruthenium(II), have proved to be effective catalysts for the hydrosilylation (e.g., using $SiHEt_3$ or SiH_2Ph_2) of ketones (to afford silyl ethers) or alkynes. The addition of triethylsilane to phenylacetylene or diphenylacetylene, catalysed by *cis*-$[RhCl(COD)L^{Me}]$ or *trans*-$[RhCl(PPh_3)_2L^{Me}]$ (COD = cycloocta-1,5-diene, L^{Me} = $:\overline{CN(Me)(CH_2)_2N}Me$), proceeds stereoselectively via *trans*-addition; the stereochemistry of the hydrosilylation products and the catalytic enhancement observed in the presence of air or ultraviolet light suggests that the reaction proceeds via a radical intermediate. Diphenylsilane is catalytically converted into $(SiHPh_2)_2$, or $O(SiHPh_2)_2$ in presence of air, when for example *cis*-$[RhCl(COD)L^{Me}]$ is used.

Carbene-transition-metal complexes continue to attract considerable attention as mechanistic models for a variety of transition-metal catalysed reactions, e.g., olefin metathesis [2], Fischer–Tropsch synthesis [3], and olefin cyclopropanation [4]. Despite such interest comparatively few reports have appeared in the literature concerning the use of isolable carbene-transition-metal complexes as homogeneous catalysts. During our continuing study of the preparation and characterisation of carbene complexes of the type $[L_nM\{:\overline{CN(R)CH_2CH_2N}R\}_x]$, (I, abbreviated as $[L_nM(L^R)_x]$), a number of such complexes were found to be active hydrosilylation catalysts. A previous paper by Hill and Nile [5] describes the use of monocarbenerhodium(I) complexes of type I as hydrosilylation catalysts for a variety of organic substrates.

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* No reprints available. For Part VII, see ref. 1.

** Dedicated to Professor Raymond Calas on the occasion of his 70th birthday April 8, 1984 in recognition of his outstanding researches in organometallic chemistry during more than 30 years.

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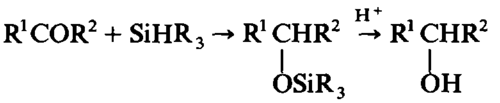
We report here the use of mono- or oligo-carbenemetal complexes of rhodium(I) or ruthenium(II) as active catalysts for the hydrosilylation of ketones or alkynes. In the latter case particular attention is drawn to (a) the stereochemistry of the addition products and (b) the photochemical enhancement observed.

Results and discussion

1. The hydrosilylation of ketones

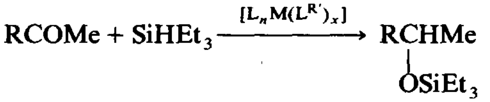
The hydrosilylation of a ketone is of synthetic interest, since acid or base hydrolysis of the so formed silyl ether provides a potentially mild, regioselective method for the reduction of ketones to secondary alcohols, eq. 1. This synthetic



$$R^1COR^2 + SiHR_3 \rightarrow \underset{\displaystyle OSiR_3}{R^1CHR^2} \xrightarrow{H^+} \underset{\displaystyle OH}{R^1CHR^2} \qquad (1)$$

method has recently been widely used as a catalytic procedure for the asymmetric reduction of a prochiral ketone to an optically active secondary alcohol, using a transition-metal complex containing chiral phosphine ligands [6,7].

A number of carbene-metal complexes of rhodium(I) or ruthenium(II) were examined as potential catalysts for the hydrosilylation of acetophenone or butan-2-one (R = Ph or Et) (eq. 2), the results of which are summarised in Tables 1 and 2 respectively.



$$RCOMe + SiHEt_3 \xrightarrow{[L_nM(L^{R'})_x]} \underset{\displaystyle OSiEt_3}{RCHMe} \qquad (2)$$

TABLE 1

HYDROSILYLATION OF ACETOPHENONE BY TRIETHYLSILANE CATALYSED BY SOME CARBENE-TRANSITION-METAL COMPLEXES [a]

Run	Catalyst	Time (h)	Temperature (°C) [b]	Solvent	Yield of silyl ether (%) [c]
1	*cis*-$[RhCl(COD)L^{Me}]$	4	120	–	92
2	*cis*-$[RhCl(COD)L^{Me}]$	1	110 [d]	PhMe	41
3	*cis*-$[RhCl(COD)L^{Me}]$	4	60	–	10
4	*cis*-$[RhCl(COD)L^{Me}]$	4	40 [d]	CH_2Cl_2	0
5	*cis*-$[RhCl(COD)L^{Ph}]$	4	110	–	97
6	*trans*-$[RhCl(PPh_3)_2L^{Me}]$	4	100	–	98
7	*trans*-$[RhCl(PPh_3)_2L^{Me}]$	4	40 [d]	CH_2Cl_2	53
8	*trans*-$[RhCl(PPh_3)_2L^{CH_2Ph}]$	4	120	–	23
9	*trans*-$[RhCl(PPh_3)_2L^{CH_2Ph}]$	4	40 [d]	CH_2Cl_2	10
10	*trans*-$[RhCl(CO)(L^{Me})_2]$	4	120	–	0
11	*trans*-$[RuCl_2(L^{Me})_4]$	4	100	–	70
12	*trans*-$[RuCl_2(L^{Me})_4]$	1.5	100	–	58
13	$[\overline{RuCl(PEt_3)_2L}^{p\text{-tol}}]$ [e]	4	120	–	7

[a] Acetophenone, 1.0 equivalent; triethylsilane, 1.25 equivalents; catalyst, 0.5 mol% (based on acetophenone), unless otherwise stated (see *e*). [b] If no solvent employed, figure denotes temperature of pre-heated oil bath. [c] Based on acetophenone, calculated by quantitative GLC. [d] Reflux temperature. [e] Catalyst, 1.6 mol%.

TABLE 2

HYDROSILYLATION OF BUTAN-2-ONE BY TRIETHYLSILANE CATALYSED BY SOME CARBENERHODIUM(I) COMPLEXES[a]

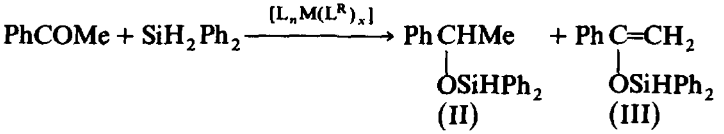
Run	Catalyst	Time (h)	Temperature (°C)[b]	Solvent	Yield of silyl ether (%)[c]
1	*cis*-$[\text{RhCl(COD)L}^{\text{Me}}]$	1.5	60	–	5
2	*cis*-$[\text{RhCl(COD)L}^{\text{Me}}]$	3.0	120	–	99
3	*cis*-$[\text{RhCl(COD)L}^{\text{Me}}]$	4.0	100	–	63
4	*trans*-$[\text{RhCl(PPh}_3)_2\text{L}^{\text{Me}}]$	5.0	100	PhMe	18
5	*trans*-$[\text{RhCl(PPh}_3)_2\text{L}^{\text{Me}}]$[d]	5.0	40[e]	CH_2Cl_2	50[f]

[a] Butan-2-one, 1.0 equivalent; triethylsilane, 1.28 equivalents; catalyst, 0.5 mol% (based on butan-2-one), unless stated otherwise (see note *d*). [b] If no solvent employed, figure denotes temperature of pre-heated oil bath. [c] Based on butan-2-one, calculated by quantitative GLC. [d] Butan-2-one, 2.1 equivalents; triethylsilane, 1.0 equivalent; catalyst, 0.2 mol% (based on butan-2-one). [e] Reflux temperature. [f] Based on triethylsilane.

The hydrosilylation of acetophenone, using as catalyst *cis*-$[\text{RhCl(COD)L}^{\text{R}}]$ (COD = cycloocta-1,5-diene, $\text{L}^{\text{R}} = {:}\overline{\text{CN(R)(CH}_2)_2\text{N}}\text{R}$, and R = Me or Ph) gave the required ether in essentially quantitative yield after 4 h at temperatures of 100–120°C. It is interesting to note that the catalytic activity of these complexes is markedly dependent upon temperature. In the case of the complex *cis*-$[\text{RhCl(COD)L}^{\text{Me}}]$, the yield of triethyl(1-phenylethoxy)silane after 4 h at 120°C is 92%, whereas at 60°C the yield is only 10%. The nature of the *N*-substituent of the carbene ligand also has a pronounced effect upon the catalytic activity of the complex. Thus, *trans*-$[\text{RhCl(PPh}_3)_2\text{L}^{\text{Me}}]$ gave an almost quantitative yield of the silyl ether after 4 h at 100°C (run 6), whilst the analogous complex *trans*-$[\text{RhCl(PPh}_3)_2\text{L}^{\text{CH}_2\text{Ph}}]$ afforded only 23% after 4 h at 120°C (run 8). The significant catalytic activity displayed by *trans*-$[\text{RuCl}_2(\text{L}^{\text{Me}})_4]$ is perhaps surprising, since this complex is almost totally insoluble under the reaction conditions employed. In contrast, the soluble, *ortho*-metallated ruthenium(II) complex $[\overline{\text{Ru}\text{Cl}\{\underline{\text{CN(C}_6\text{H}_4\text{Me-4)CH}_2\text{CH}_2\text{N}}\text{C}}_6\text{H}_3\text{Me-4}\}(\text{PEt}_3)_2]$ was only weakly active.

Data on the hydrosilylation of butan-2-one by triethylsilane, catalysed by some carbenerhodium(I) complexes, are summarised in Table 2. The marked dependence of catalytic activity upon temperature is once again exhibited by the complex *cis*-$[\text{RhCl(COD)L}^{\text{Me}}]$ (runs 1–3). Interestingly the reactivity of *trans*-$[\text{RhCl(PPh}_3)_2\text{L}^{\text{Me}}]$ is significantly improved by the use of dichloromethane as solvent (runs 4 and 5).

The hydrosilylation of ketones catalysed by carbenemetal complexes, whilst providing a potentially regioselective method for the preparation of secondary alcohols, unfortunately requires the use of somewhat forcing reaction conditions. The use of a dihydrosilane, however, allows the reduction to be performed under considerably milder conditions. The results of the hydrosilylation of acetophenone with diphenylsilane using carbene-transition-metal catalysts are shown in Table 3. The complexes *cis*-$[\text{RhCl(COD)L}^{\text{R}}]$ (R = Me or Ph) or *trans*-$[\text{RhCl(PPh}_3)_2\text{L}^{\text{CH}_2\text{Ph}}]$ have proved particularly effective, giving quantitative conversion of acetophenone after ca. 18 h at room temperature. In some instances however, significant amounts (runs 1, 2 and 4) of the corresponding silyl enol ether III (eq. 3) are produced, via a dehydrogenative hydrosilylation process, which accompanies the formation of the required silyl ether II.



$$\mathrm{PhCOMe} + \mathrm{SiH_2Ph_2} \xrightarrow{[\mathrm{L}_n\mathrm{M(L^R)}_x]} \underset{\text{(II)}}{\mathrm{PhCH(OSiHPh_2)Me}} + \underset{\text{(III)}}{\mathrm{PhC(OSiHPh_2){=}CH_2}} \tag{3}$$

The hydrosilylation of acetophenone with diphenylsilane, catalysed by a carbene-transition-metal complex, proceeds exothermically at room temperature with the liberation of gas (mainly dihydrogen) in the initial stages of the reaction. The detection (GLC) of trace amounts of triphenylsilane, from the resultant product mixtures, implies a redistribution of the phenyl substituents of diphenylsilane.

The redistribution of substituents on silicon is not uncommon and may be achieved either thermally [8] or under acid- [9] or base-catalysed [10] conditions. Diphenylsilane has been observed to undergo disproportionation both thermally, particularly in the presence of catalysts such as $H_2[PtCl_6]$ [8], and in a free-radical manner; e.g., at 130°C in the presence of a peroxide or by ultraviolet irradiation [11]. More recently, Ojima and co-workers have reported the redistribution of dihydrosilanes catalysed by tris(triphenylphosphine)chlororhodium(I), e.g., eq. 4 [12].

$$\mathrm{SiH_2Ph_2} \xrightarrow[80^\circ\mathrm{C/1h}]{[\mathrm{RhCl(PPh_3)_3}]} \underset{(45\%)}{\mathrm{SiH_2Ph_2}} + \underset{(8\%)}{\mathrm{SiHPh_3}} + \underset{\text{(trace)}}{\mathrm{SiH_3Ph}} + \underset{\text{(trace)}}{\mathrm{SiPh_4}} + \underset{(38\%)}{\mathrm{Ph_2HSiSiHPh_2}} \tag{4}$$

The use of a carbenerhodium(I) complex, *cis*-$[RhCl(COD)L^{Me}]$ or *trans*-$[RhCl(PPh_3)_2L^{Me}]$, with diphenylsilane, in the absence of acetophenone, gave similar results to those described above in eq. 4. The addition of a catalytic amount of *trans*-$[RhCl(PPh_3)_2L^{Me}]$ to diphenylsilane under an inert atmosphere results in the solidification of the reaction mixture within 18 h at room temperature. The major product, 1,1,2,2-tetraphenyldisilane (IV) has, in some cases, proved difficult to

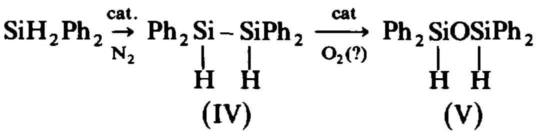
TABLE 3

HYDROSILYLATION OF ACETOPHENONE BY DIPHENYLSILANE CATALYSED BY SOME CARBENE-TRANSITION-METAL COMPLEXES [a]

Run	Catalyst	Time (h)	Temperature (°C)	Yield of silylated products	
				II	III
1	*cis*-$[RhCl(COD)L^{Me}]$	18	20	76	24
2	*cis*-$[RhCl(COD)L^{Me}]$	21	20 [c]	67	33
3	*cis*-$[RhCl(COD)L^{Ph}]$	24	20	98	2
4	*trans*-$[RhCl(PPh_3)_2L^{CH_2Ph}]$	24	20	86	14
5	*trans*-$[RuCl_2(L^{Me})_4]$	24	20	18	6

[a] Acetophenone, 1.0 equivalent; diphenylsilane, 1.25 equivalents; catalyst, 0.5 mol% (based on ketone). [b] Calculated by quantitative GLC; based on ketone. [c] Silane added to reaction mixture at −78°C in toluene and maintained at that temperature for 0.5 h before being allowed to warm slowly to room temperature.

isolate. A closer examination of this reaction indicated that the observed decomposition, during purification by crystallisation, occurred only in the presence of both catalyst and air. Monitoring the reaction by GLC revealed that the initially formed disilane IV reacted further to give the disiloxane V in the presence of air, eq. 5.



$$SiH_2Ph_2 \xrightarrow[N_2]{cat.} \underset{(IV)}{Ph_2\underset{H}{\overset{|}{Si}}-\underset{H}{\overset{|}{Si}}Ph_2} \xrightarrow[O_2(?)]{cat} \underset{(V)}{Ph_2\underset{H}{\overset{|}{Si}}O\underset{H}{\overset{|}{Si}}Ph_2} \qquad (5)$$

$(cat = [RhClL_2L']; (L_2 = COD, L' = L^{Me}$ or $L = PPh_3$, or $L = L' = PPh_3)$

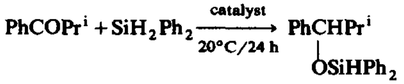
The concomitant disproportionation and disilane formation, observed during the hydrosilylation of acetophenone, are of very minor inconvenience, since the relative rate of hydrosilylation is much faster than either of these two processes. However, the formation of the undesired silyl enol ether III (eq. 3) can be a problem in some cases. Interestingly the carbene-transition-metal-catalysed addition of diphenylsilane to isopropyl phenyl ketone proceeds smoothly at room temperature with no observable trace of the corresponding silyl enol ether, despite the availability of an α-hydrogen. The results of the hydrosilylation of isopropyl phenyl ketone with diphenylsilane using some carbenerhodium(I) complexes are given in Table 4. It is noteworthy that the catalytic activities of the oligo-carbene complexes $[RhCl(L^{CH_2Ph})_3]$ (VI) and $[RhCl(L^{Et})_3]$ (VII) are very different. The reaction of carbon monoxide with each of the tris(carbene) complexes parallels this distinction in catalytic activity (eq. 6 [13] and 7 [14]). Carbon monoxide displaces a carbene ligand from the tris(carbene)rhodium(I) complex VI affording the neutral bis(carbene)rhodium(I) complex VIII, whereas displacement of the chloride ion from complex VII gives the cationic tris(carbene)rhodium(I) complex IX. This contrast in

$$\underset{(VI)}{[RhCl(L^{CH_2Ph})_3]} \xrightarrow[CH_2Cl_2]{CO} \underset{(VIII)}{[RhCl(CO)(L^{CH_2Ph})_2]} + \tfrac{1}{2}(L^{CH_2Ph})_2 \qquad (6)$$

$$\underset{(VII)}{[RhCl(L^{Et})_3]} \xrightarrow[CH_2Cl_2]{CO} \underset{(IX)}{[RhCO(L^{Et})_3]^+} Cl^- \qquad (7)$$

TABLE 4

THE HYDROSILATION OF ISOPROPYL PHENYL KETONE WITH DIPHENYLSILANE USING SOME CARBENERHODIUM(I) COMPLEXES [a]



$$PhCOPr^i + SiH_2Ph_2 \xrightarrow[20°C/24\ h]{catalyst} Ph\underset{OSiHPh_2}{\underset{|}{C}}HPr^i$$

Catalyst	Yield of silyl ether (%) [b]
trans-$[RhCl(PPh_3)_2L^{CH_2Ph}]$	45
cis-$[RhCl(COD)L^{Me}]$	72
cis-$[RhCl(COD)L^{Ph}]$	100
$[RhCl(L^{CH_2Ph})_3]$	65
$[RhCl(L^{Et})_3]$	0

[a] Isopropyl phenyl ketone, 1.0 equivalent; diphenylsilane, 1.25 equivalents; catalyst, 0.5 mol% (based on ketone). [b] Calculated by quantitative ^1H NMR; based on ketone.

behaviour towards substitution is representative of the relative labilities of the respective carbene ligands. The relative ease of displacement of the *N*-benzyl-substituted carbene ligand from complex VI can be correlated with its observed higher catalytic activity.

2. *The hydrosilylation of alkynes*

The hydrosilylation of alkynes has been studied by many workers, using a variety of catalysts and conditions. The nature and the distribution of the products obtained is dependent upon the ratio of the reactants, the reaction conditions, and the catalyst employed. The mode of addition of the silane, and hence the resultant stereochemistry of the product(s), depends largely upon the type of catalyst used. Homogeneous transition-metal catalysed hydrosilylation proceeds via *cis*-addition, whereas other processes, such as radical-initiated reactions, give products predominantly resulting from *trans*-addition.

The hydrosilylation of an alkyne catalysed by a rhodium(I) complex has been reported by several groups [15–18]. Particular attention has been paid to the stereochemistry of this reaction in the light of previously established mechanistic concepts. Tris(triphenylphosphine)chlororhodium(I) has been reported to catalyse the addition of a monohydrosilane to a terminal alkyne via a stereoselective *trans*-addition [16], i.e., *cis*-adduct formation (e.g., X with $R = Bu^n$, $R^1 = Ph$, and $R^2 = Me$), as in eq. 8. Ojima and co-workers have suggested that the *cis*-adduct

$$RC{\equiv}CH + SiHR^1R^2_2 \xrightarrow{[RhCl(PPh_3)_3]} \underset{(X)}{RCH{=}CHSiR^1R^2_2} \qquad (8)$$

R	R^1	R^2	*cis/trans*
Bu^n	Ph	Me	72/28
Ph	Ph	Me	77/23
Bu^n	Et	Et	76/24

results from *trans*-addition by a mechanism which involves a radical-like species as an intermediate or transition state. There is, however, the possibility that the *trans*-adduct, formed initially via *cis*-addition, isomerises to the *cis*-adduct during the course of the reaction. Nevertheless, Ojima et al. claim that no isomerisation of the *trans*-adduct occurred under the reaction conditions employed.

Watanabe and co-workers [17] have shown that, under certain conditions, complete isomerisation of the *cis*-isomer (X, $R = R^1 = Ph$, $R^2 = Me$) to the *trans*-silyl olefin occurred during the course of the hydrosilylation reaction. Control experiments established that the isomerisation only occurred in the presence of both the catalyst and the silane. In contrast, Haszeldine and co-workers [18] have shown that the *trans*-silyl olefin (X, $R = Bu^n$, $R^1 = R^2 = Et$), formed via *cis*-addition, isomerises to the *cis*-adduct on treatment with the catalyst, again only in the presence of the silane. The mechanism proposed involves the intermediacy of the known five coordinate hydridometal species, $[RhClH(SiEt_3)(PPh_3)_2]$, which had previously been shown to be an effective catalyst for the isomerisation of olefins [19,20].

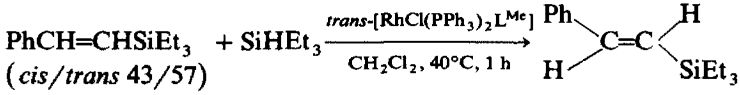
The catalytic activities of some carbenerhodium(I) complexes for the hydrosilylation of phenylacetylene were investigated, eq. 9, and the results of which are

$$PhC{\equiv}CH + SiHEt_3 \xrightarrow{[L_nRhL^R]} \underset{\left(\begin{array}{c}\textit{cis-}\text{ and }\textit{trans}\\ \text{isomers}\end{array}\right)}{PhCH{=}CHSiEt_3} + \underset{(\alpha\text{-adduct})}{Ph(SiEt_3)C{=}CH_2} \qquad (9)$$

summarised in Table 5. It is evident from these results that the complexes *cis*-[RhCl(COD)L^{Me}] or *trans*-[RhCl$(PPh_3)_2L^{Me}$] are very effective catalysts, affording essentially quantitative yields of the 1/1 adducts; the complex *cis*-[RhCl(COD)L^{Ph}], however, proved only weakly active. As previously observed with the hydrosilylation of acetophenone, the nature of the *N*-substituent of the carbene ligand can have a significant effect upon the catalytic activity of this type of complex.

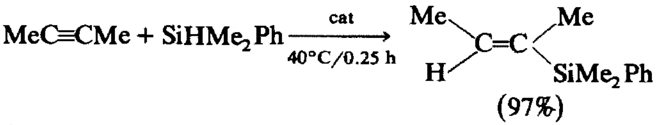
The isomeric ratios of the 1/1 adducts, produced by the catalyst *cis*-[RhCl(COD)L^{Me}], do not vary to any great extent with changes in catalytic concentration or temperature. It is interesting to note the large proportion of α-adduct formed in these reactions. Metal carbonyls, such as octacarbonyldicobalt(0), have also been reported to give high proportions of internal adducts [21]. However, for the rhodium(I) complexes [RhCl$(PPh_3)_3$] or *trans*-[RhCl(CO)$(PPh_3)_2$] α-adduct formation is relatively insignificant [17].

The hydrosilylation of phenylacetylene by triethylsilane, using as catalyst *cis*-[RhCl(COD)L^{Me}] or *trans*-[RhCl$(PPh_3)_2L^{Me}$], is extremely exothermic. Upon gently warming a mixture of the catalyst, alkyne, and silane to ca. 60°C, a violent reaction occurs. At lower temperatures, or in the absense of silane, phenylacetylene is slowly polymerised. GLC analysis of the reaction mixture directly after the subsidence of the exothermic reaction indicates an almost quantitative conversion of phenylacetylene. However, the isomeric distribution of the 1/1 adducts slowly changes upon further heating, the *cis*-adduct isomerising to the *trans*-silyl olefin, as previously observed by Watanabe and co-workers [17]. A mixture of the *cis*- and *trans*-silyl olefins was heated in the presence of the complex *trans*-[RhCl$(PPh_3)_2L^{Me}$] for 2 h at 40°C with no change in the isomeric ratio. However, in the presence of both catalyst and silane, complete isomerisation of the *cis*-adduct to the *trans*-product was observed after only 1 h at 40°C, as in eq. 10.



(10)

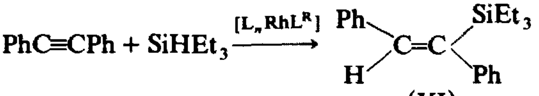
The hydrosilylation of an internal alkyne using as a catalyst a transition-metal complex, has received very little attention. In those cases previously reported, *cis*-addition occurred preferentially, e.g., eq. 11 [22]. The catalytic activities of the



(11)

$$\left(\text{cat} = \left[\{Pt[Si(CH_2Ph)Me_2](\mu\text{-}H)[(C_6H_{11})_3P]\}_2\right]\right)$$

carbenerhodium(I) complexes, *cis*-[RhCl(COD)L^{Me}] or *trans*-[RhCl$(PPh_3)_2L^{Me}$], for the hydrosilylation of diphenylacetylene by triethylsilane (eq. 12) were investigated,



(XI)

(12)

the results being summarised in Table 6. Both complexes are effective catalysts, giving modest yields of the *trans*-1/1 adduct by stereoselective *trans*-addition. It is

TABLE 5

HYDROSILYLATION OF PHENYLACETYLENE BY TRIETHYLSILANE CATALYSED BY SOME CARBENE RHODIUM(I) COMPLEXES[a]

Catalyst	Catalytic concentration[b] (mol%)	Time (h)	Temperature[c] (°C)	Overall yield of 1/1 adducts[b] (%)	Isomeric ratios		
					trans	*cis*	α
cis-[RhCl(COD)L^{Me}]	0.5	2.0	20	0[d]	0	0	0
	0.5	1.0	60	98	48	11	41
	0.5	1.0	100	98	48	11	41
	1.5	1.0	100	97	49	13	37
	5.0	1.0	100	96	54	10	35
cis-[RhCl(COD)L^{Ph}]	0.25[e]	0.5	100	0[d]	0	0	0
	0.5[f]	0.5	100	12[d]	6	3	3
trans-[RhCl(PPh_3)$_2$$L^{Me}$]	0.5	1.0	100	99	74	4	22

[a] Phenylacetylene, 1.0 equivalent; triethylsilane, 1.2 equivalents; unless stated otherwise (see notes *e* or *f*). [b] Based on phenylacetylene. [c] Temperature of pre-heated oil bath. [d] Poly(phenylacetylene) formed. [e] Triethylsilane, 0.5 equivalent. [f] Triethylsilane, 1.0 equivalent.

interesting to note the dramatic enhancement of catalytic activity observed in these reactions by the presence of air. A similar enhancement has been reported previously by Wilkinson and co-workers [23] for the hydrosilylation of hex-1-ene by trichlorosilane with a rhodium catalyst in the presence of traces of dioxygen.

More recently, the catalytic hydrosilylation of propene, hex-1-ene, or hex-1-yne, using the complex $[RhCl(PPh_3)_3]$, has been reinvestigated [24]. When all the reagents are carefully purified, hydrosilylation is completely inhibited. The reaction can be initiated, however, by dioxygen or t-butyl hydroperoxide. The role of dioxygen is considered to be its ability to remove triphenylphospine from the system by oxidation, generating a highly active catalyst with a low PPh_3/Rh ratio. Whilst the observed enhancement of catalytic activity, for the hydrosilylation of diphenylacetylene using a carbenemetal complex, can be rationalised by ligand oxidation, the stereochemistry of the resultant *trans*-silyl olefin (XI) requires a mechanism involving a radical intermediate. The *trans*-configuration of the silyl olefin XI, based on a comparison of its ^1H NMR data with those reported [22] for the corresponding *cis*-isomer, prompted a further examination of the carbenemetal catalysed hydrosilylation of alkynes in the presence of ultraviolet light.

3. *The photochemical enhancement of carbene-transition-metal complex-catalysed hydrosilylation reactions*

Despite the wealth of data available on transition-metal-catalysed hydrosilylation reactions, very few reports have been concerned with the effects of air and/or ultraviolet light upon catalytic activity and product stereochemistry. Faltynek [25] has recently reported the effects of dioxygen and near-ultraviolet radiation upon the activity of alkene hydrosilylation catalysed by $[RhCl(PPh_3)_3]$. Reaction rates were drastically increased when SiH- and vinylsilicon-functionalised siloxane mixtures

TABLE 6

HYDROSILYLATION OF DIPHENYLACETYLENE BY TRIETHYLSILANE CATALYSED BY SOME CARBENERHODIUM(I) COMPLEXES [a]

Catalyst		Reaction conditions [b] (°C/h)	Solvent	Yield of *trans* 1/1 adduct (%) [c]
cis-$[RhCl(COD)L^{Me}]$		20/1 [d]	PhMe	1
cis-$[RhCl(COD)L^{Me}]$		60/1	–	23
cis-$[RhCl(COD)L^{Me}]$		70/1	–	50
cis-$[RhCl(COD)L^{Me}]$	(i)	60/1	–	
	(ii)	20/24/air		100
trans-$[RhCl(PPh_3)_2L^{Me}]$		40/1	CH_2Cl_2	2
trans-$[RhCl(PPh_3)_2L^{Me}]$	(i)	40/1	CH_2Cl_2	
	(ii)	20/1/air		35
trans-$[RhCl(PPh_3)_2L^{Me}]$	(i)	40/1	CH_2Cl_2	
	(ii)	20/4/air		100
trans-$[RhCl(PPh_3)_2L^{Me}]$		20/1/air	CH_2Cl_2	29
trans-$[RhCl(PPh_3)_2L^{Me}]$		20/18/air	CH_2Cl_2	30

[a] Diphenylacetylene, 1.0 equivalent; triethylsilane, 1.14 equivalents; catalyst, 0.5 mol% (based on diphenylacetylene), unless otherwise stated (see note *d*). [b] Experiments performed under argon unless otherwise stated. [c] Yield determined by quantitative GLC, based on diphenylacetylene. [d] Triethylsilane, 1.25 equivalents.

were photolysed in the presence of air or soluble oxidising agents. Irradiation was shown to promote phosphine ligand dissociation and accelerate free ligand oxidation, eq. 13.

$$[\mathrm{RhCl(PPh_3)_3}] \xrightarrow{h\nu} [\mathrm{RhCl(PPh_3)_2}] + \mathrm{PPh_3} \xrightleftharpoons{h\nu/\frac{1}{2}\mathrm{O_2}} [\mathrm{RhCl(PPh_3)_2}] + \mathrm{P(O)Ph_3} \quad (13)$$

The hydrosilylation of a ketone or an alkyne by a monohydrosilane, catalysed by a carbenemetal complex, is particularly slow at ambient temperature. It appears that the conditions necessary for the formation of the required coordinatively unsaturated species, e.g. XII, cannot be achieved thermally to any appreciable extent at temperatures below ca. 40°C, eq. 14.

$$\textit{trans}\text{-}[\mathrm{RhCl(PPh_3)_2L^R}] \rightleftharpoons \underset{\text{(XII)}}{[\mathrm{RhCl(PPh_3)L^R}]} + \mathrm{PPh_3} \quad (14)$$

However, irradiation of a mixture of diphenylacetylene, triethylsilane, and catalyst (*cis*-[RhCl(COD)L^{Me}]) gave a 60% yield of the *trans*-adduct after only 1 h at 20°C. Similar reaction conditions in the absence of ultraviolet irradiation gave only a 1% yield of the *trans*-adduct (Table 6). No hydrosilylation products were formed by irradiation in the absence of catalyst.

The photolysed hydrosilylation of phenylacetylene by triethylsilane, using the complex *cis*-[RhCl(COD)L^{Me}], proceeded exothermically at room temperature. Within a period of 0.5 h, phenylacetylene was essentially quantitatively converted into hydrosilylation products and poly(phenylacetylene). No hydrosilylation products were detected in control experiments either in the absence of ultraviolet irradiation or in the absence of catalyst. Interestingly, no such catalytic enhancement is observed for the complex [RhCl(PPh_3)$_3$].

Experimental

General procedures

All experiments were performed under argon using freshly distilled, dry, degassed solvents, unless otherwise stated.

^{1}H NMR spectra were recorded on Varian T60 (60 MHz) or Perkin–Elmer R32 (90 MHz) spectrometers. IR spectra were recorded on Perkin–Elmer 457 or 597 spectrometers, as mulls or thin films between potassium bromide plates. Quantitative GLC measurements were carried out using a Pye-Unicam model (katharometer detector) gas chromatograph, using a 6 ft column of 5% SE30 on 100-120 mesh Chromosorb G. Melting points were recorded using an electrothermal melting point apparatus and are uncorrected.

Acetophenone, butan-2-one, isopropyl phenyl ketone, and phenylacetylene were dried over molecular sieves and distilled in an inert atmosphere prior to use. Diphenylacetylene was recrystallised from absolute ethanol and stored under argon. Triethyl- [26] and diphenyl-silane [27] were prepared by standard methods. The transition-metal complexes, [RhCl(PPh_3)$_3$] [28], *trans*-[RhCl(PPh_3)$_2L^R$] (R = Me [29,30] or CH_2Ph [14]), *cis*-[RhCl(COD)L^R] (R = Me or Ph [29]), [RhCl(L^R)$_3$] (R = Et [14] or CH_2Ph [13]), *trans*-[RhCl(CO)(L^{Me})$_2$] [31], [$RuCl_2$(L^{Me})$_4$] [32], and [RuCl(PEt_3)$_2L^{p\text{-tol}}$] [33] were prepared as reported in the literature. The experimental procedures for some typical hydrosilylation reactions are described below.

(a) Hydrosilylation of acetophenone with triethylsilane

trans-Tetrakis(1,3-dimethylimidazolidin-2-ylidene)dichlororuthenium(II) (13.3 mg) was added to a solution of acetophenone (0.567 g, 4.72 mmol) and triethylsilane (0.686 g, 5.90 mmol). The yellow suspension was stirred at 100°C for 4 h. GLC analysis at 220°C indicated a 70% yield of the required silyl ether.

(b) Hydrosilylation of acetophenone with diphenylsilane

The carbenerhodium(I) complex *cis*-cycloocta-1,5-diene(1,3-diphenylimidazolidin-2-ylidene)chlororhodium(I) (5.0 mg) was added to a stirred solution of acetophenone (0.26 g, 2.16 mmol) and diphenylsilane (0.50 g, 2.71 mmol). After 24 h at room temperature, GLC analysis indicated a 98% yield of the silyl ether II. Trace amounts of the silyl enol ether III and triphenylsilane were also detectable.

(c) Preparation of 1,1,2,2-tetraphenyldisilane

A mixture of diphenylsilane (1.36 g, 7.38 mmol) and *trans*-(1,3-dimethylimidazolidin-2-ylidene)bis(triphenylphosphine)chlororhodium(I) (22.4 mg) was stirred under an inert atmosphere for 18 h. Crystallisation of the resultant solid reaction mixture from n-hexane gave the disilane as colourless prisms, m.p. 75.5–76°C (lit. [34], 79–80°C); IR (Nujol): ν_{max} 2115s (SiH) cm^{-1}; ^1H NMR δ ($CDCl_3$): 7.78–7.02 (m, br, 20 H, C_6H_5), 5.16 (s, 2 H, SiH).

(d) Hydrosilylation of phenylacetylene

trans-(1,3-Dimethylimidazolidin-2-ylidene)bis(triphenylphosphine)chlororhodium(I) (52 mg) was added to a stirred solution of phenylacetylene (1.40 g, 13.7 mmol) and triethylsilane (1.83 g, 15.7 mmol). The mixture was then placed in a pre-heated oil bath at 100°C. The yellow catalyst quickly dissolved affording an orange solution. After ca. 2 min a very exothermic reaction occurred, yielding a dark-red solution. The solution was heated for a total of 1 h and analysed by GLC at 210°C; this indicated an overall yield of 99% of the 1/1 adducts in the following isomeric ratios: *trans* (74)/*cis* (4)/α(22).

(e) Hydrosilylation of diphenylacetylene

cis-Cycloocta-1,5-diene(1,3-dimethylimidazolidin-2-ylidene)chlororhodium(I) (24 mg) was added to a mixture of diphenylacetylene (2.45 g, 13.75 mmol) and triethylsilane (1.83 g, 15.74 mmol). After 1 h at 70°C, GLC analysis at 280°C indicated a 50% yield of the 1/1 adduct with no other detectable products. Removal of volatiles under reduced pressure, followed by fractional vacuum distillation, afforded *trans*-PhCH=C(Ph)$SiEt_3$ (b.p. 126–132°C/0.1 mmHg) as a pale yellow liquid. IR (neat): ν_{max} 1598s (C=C) (cm^{-1}); ^1H NMR δ($CDCl_3$): 7.25–6.75 (m, br, 10 H, C_6H_5), 6.66 (s, 1 H, CH=C), 1.1–0.3 [m, br, 15 H, $(C_2H_5)_3Si$].

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