

Trimethylsilylcyclooctadiene-transition metal complexes: metal-catalysed protodesilylation of cyclic vinylsilanes, and transfer hydrogenation promoted by the displaced silyl group

Balachandra S. Bandodakar and Gopalpur Nagendrappa

Department of Chemistry, Bangalore University (Central College Campus), Bangalore-560 001 (India)

(Received August 21, 1991)

Abstract

Complexes of 1-trimethylsilyl-1,5-cyclooctadiene (TMS-COD, **2**) with Ag^{I} , Rh^{I} , Pd^{II} and Pt^{II} have been prepared and characterised. The distortion in their structures in comparison with the near symmetrical structures of the corresponding 1,5-cyclooctadiene (COD, **1**) complexes, which is obviously attributable to the presence of vinylic SiMe_3 group, is clearly indicated by their ^1H and ^{13}C NMR spectral characteristics. The silver complex is somewhat unstable, but the other complexes are quite stable. An unstable Cu^{I} complex that could not be satisfactorily characterised was also obtained. If appropriate conditions for the preparation of Rh and Pd complexes are not maintained, desilylation occurs, accompanied by reduction of COD to cyclooctene by transfer of hydrogen from the solvent alcohol. The displaced silicon containing moiety seems to enhance the transfer hydrogenation. Attempts to prepare Ru^{II} complex resulted in the formation of a complex of desilylated diene (Ru^{II} -COD).

Introduction

Diene π -transition metal complexes have an important role in transition metal coordination chemistry, but reports on complexes of dienes bearing a silyl substituent at vinylic positions are scarce. Vinyltrimethylsilane, divinyltrimethylsilane and tetravinylsilane have commonly been used as ligands in most of these investigations, and their complexes with metals such as Cu^{I} , Pt^{II} , Pt^0 , Fe, Cr, Mo, W, Mn, Ni^0 and Rh^{I} have been prepared and characterised [1–11]. Recently, 2-trimethylsilyl-2,5-norbornadiene complex of molybdenum has been reported [9]. It is noteworthy that no palladium complex with a vinylsilane ligand has so far been prepared and characterised.

Studies of vinylsilane- π complexes have been undertaken in order to compare their spectral properties, structural features and stability with those having no silicon containing moiety and to investigate the influence of the silyl substituent on

Correspondence to: Dr. G. Nagendrappa, Department of Chemistry, Bangalore University, (Central College Campus), Bangalore-560 001, India.

the nature of metal-olefin bond and also the reactivity of the silyl-substituted double bond after complexation [6].

One of the more frequently used chelating dienes is *cis,cis*-1,5-cyclooctadiene (COD, **1**) [12], and its transition metal complexes have played a significant role in the development of diene π -transition metal coordination chemistry. Recent reports deal with the conformational characteristics of medium ring dienes relative to the most stable conformation of the free diene and related energy changes on chelation with palladium [13]. The presence of a bulky but relatively labile SiMe₃ group in the vinylic position of the ligand can significantly influence the formation and stability of the complexes and the conformation of the ligand in the complexes [14].

Because of our interest both in medium ring vinylsilanes [15] and cyclodiene-metal complexes [16], we have synthesised 1-trimethylsilyl-1,5-cyclooctadiene (TMS-COD, **2**) [17] and prepared and studied its complexes with several transition metals. We have found that PdCl₂ is an excellent catalyst for protodesilylation of 1-cycloalkenylsilanes in alcohols, and that catalytic hydrogen transfer from alcohols to COD takes place smoothly.

Results and discussion

Preparation of complexes

1-Trimethylsilyl-1,5-cyclooctadiene (**2**) was prepared from 1-bromo-1,5-cyclooctadiene [18] by the procedure reported previously [19]. The complexes of **2** with Ag^I, Rh^I, Pd^{II} and Pt^{II} were prepared by standard procedures. The Ag^I complex was obtained by stirring **2** with AgNO₃ in aqueous solution. The Rh^I complex was prepared by displacing either ethylene from tetraethylenedirhodium dichloride or carbon monoxide from tetracarbonyldirhodium dichloride. The latter method gives purer material and is more convenient. The Pd^{II} complex was made by displacing benzonitrile from (PhCN)₂PdCl₂ with diene. The Pt^{II} complex was prepared by stirring the diene **2** with K₂PtCl₄ in acetic acid.

All the complexes gave satisfactory elemental analysis. When treated with aqueous KCN solution each liberated pure TMS-COD (**2**) showing that the ligand diene **2** remained unchanged during the formation of the complexes. However, attempts to prepare Rh^I and Ru^{II} complexes by treating RhCl₃ and RuCl₃ with **2** in refluxing ethanol gave only the corresponding complexes of COD (**1**) since TMS-COD (**2**) underwent protodesilylation readily under these conditions. A similar reaction with PdCl₂ gave no identifiable complex but instead protodesilylation to COD took place and continuation of the reaction led to reduction of COD to cyclooctene. No desilylated olefin-coupling product was observed, in contrast to the outcome for some vinylsilanes [20].

Stability and solubility of the complexes

The Ag^I complex was not very stable, although it could be isolated and handled without difficulty and could even be dried under vacuum for 1 h. It did however, decompose slowly. The rhodium, palladium and platinum complexes remained unchanged during many months under normal laboratory conditions. All the complexes were soluble in organic solvents such as CH₂Cl₂, CHCl₃, CCl₄ and ether, indicating that they have monomeric or dimeric structures.

Table 1

The ^1H NMR spectra of TMS-COD (2) and its complexes ^a

Entry	Compound	Olefinic protons			Methylene protons ^b	SiMe ₃ ^c	
		H ₂ ^d	H ₅	H ₆			
1	TMS-COD (2)	5.91 (t, <i>J</i> = 5.6 Hz)	5.54	5.54	2.29–2.45 (2H ₃ + 2H ₄ + 2H ₇) 2.50 (2H ₈ , t, <i>J</i> = 6.5 Hz)	0.05	
2	Cu ^I complex (3)	5.85	5.46	5.46	2.15–2.40 (2H ₃ + 2H ₄ + 2H ₇) 2.45 (2H ₈)	0.00	
					Inner ^e	Outer ^f	
3	Ag ^I complex (4)	6.17 (t, <i>J</i> = 5.2 Hz)	5.87	5.87	2.51–2.58(4H)	2.42–2.50(4H)	0.12
4	Rh ^I complex (5)	4.45	3.94	4.52	2.30–2.62(H ₃ + H ₇) 2.10–2.30(H ₄) 2.62–2.91(H ₈)	1.35–1.72(H ₃ + H ₄) 1.78–2.10(H ₇ + H ₈)	0.20(3H) 0.26(6H)
5	Pd ^{II} complex (6)	6.49	6.06	6.44	2.75–2.88(H ₃ + H ₄ + H ₇) 3.11(H ₈ , sextet)	2.48(H ₃) 2.53(H ₄) 2.58(H ₇) 2.64(H ₈)	0.39
6	Pt ^{II} complex (7)	5.86	5.36	5.72	2.48–2.61(H ₃ + H ₄ + H ₇) 2.76(H ₈)	2.20–2.48(H ₃ + H ₄) 1.90–2.20(H ₇ + H ₈)	0.36

^a Solvent: CDCl₃, except Cu^I complex for which DMSO-*d*₆ was used; chemical shifts are in δ (ppm) relative to tetramethylsilane and CHCl₃. ^b All signals were not clearly resolved multiplets except where multiplicity is specified. ^c All are 9-proton singlets except for Rh^I complex. ^e Subscript corresponds to the number of C-atom to which the proton is attached. ^e Protons projecting inside the tub conformation. ^f Protons projecting out of the tub conformation.

Infrared spectra

The pure ligand, TMS-COD (2), shows a weak band at 1648 cm⁻¹ and a medium strong band at 1618 cm⁻¹ assigned to C₅=C₆ and C₁=C₂ double bonds, respectively. These bands have shifted to 1518, 1480 and 1475 cm⁻¹ in Pd, Pt and Rh complexes, indicating strong complexation. In contrast, in the case of the Ag complex there is only a small shift and the olefin band appears as a weak signal at around 1615 cm⁻¹, indicating weak complexation. Two strong bands at ~1245 cm⁻¹ and ~840 cm⁻¹ appear in the diene 2 and in all its complexes, (with slight variations in their positions) showing the presence of SiMe₃ group [3].

^1H NMR spectra (Table 1)

In the spectrum of diene 2 the C₂-proton signal is well separated from the C₅–C₆ proton signal, and the signal of C₈ protons is overlapped by that due to C₃, C₄ and C₇ protons.

The ^1H NMR spectrum of the Ag^I complex shows slight downfield shifts of varying magnitude for all the proton signals. For example, the signal due to the protons on C₅ and C₆ are more shifted (by 0.34 ppm) than that for the C₂ proton (0.26 ppm) indicating that the double bond with a SiMe₃ substituent (C₁=C₂) forms a weaker coordination bond with Ag^I than the unsubstituted one (C₅=C₆). The methylene protons show two 4-proton multiplets, assignable to four inner

protons and four outer protons of the ligand in its tub conformation in the complex.

The ^1H NMR of Rh^{I} complex is not as simple. The C_5 and C_6 proton peaks are well separated (0.58 ppm) and one of them overlaps with the $\text{C}_2\text{-H}$ peak at δ 4.45. There are three peaks (corresponding to 1, 2 and 1 protons) assignable to inner protons and three peaks (corresponding to 2, 1 and 1 protons) assignable to outer protons. None of these peaks is well resolved, and all are somewhat broad. The signals due to olefinic protons and the outer methylene protons exhibit large upfield shifts. In contrast, the SiMe_3 signal shows downfield shift and is split into two signals, one at δ 0.26 (6H) and the other at δ 0.20 (3H), indicating that two of the methyl groups are more deshielded than the other one; this could be due either to restricted rotation around the C-Si bond in the complex [1] or to the presence of two isomeric dimeric Rh^{I} complexes.

The Pd^{II} complex gives a clean proton NMR spectrum. Although we obtained 2D COSY and 2D $^{13}\text{C}\text{-}^1\text{H}$ shift correlation spectra (400 MHz), chemical shifts could not be unequivocally assigned to all the individual protons, but some shift patterns are discernible. The olefinic protons exhibit a large downfield shift and the methylene and SiMe_3 protons also show downfield shift. The inner methylene protons show larger shifts than the outer protons. The $\text{C}_6\text{-H}$ signal seems to be shifted more (0.91 ppm) than $\text{C}_2\text{-H}$ (0.58 ppm) and $\text{C}_5\text{-H}$ (0.52 ppm). Among the methylene protons, the inner $\text{C}_8\text{-proton}$ signal (sextet) is well separated and shows the largest shift (0.61 ppm). The other three inner protons appear as one multiplet (δ 2.84). The overlapping multiplets in the range δ 2.48–2.64 are due to the outer protons, but their assignment to individual protons (Table 1) is only tentative.

The Pt^{II} complex shows shift patterns similar to those of Pd^{II} complex, but the trends are a little different. The $\text{C}_2\text{-H}$ and $\text{C}_5\text{-H}$ signals are shifted to slightly higher field, whereas the $\text{C}_6\text{-H}$ signal is shifted to lower field. The methylene protons show trends similar to those for the Pd^{II} complex.

The ^1H NMR spectra of all the complexes clearly indicate that the diene **2** in the complexes is rigidly held in the tub form so that two distinct groups of inner and outer protons are recognisable [21a]. Even among the inner protons, $\text{C}_8\text{-H}$ is more deshielded, since it gives a signal well separated from those of the other three inner protons. The protons of the $\text{Si}(\text{CH}_3)_3$ group are also deshielded.

The formation of such complexes is assumed to change the hybridisation of the double bonded carbon from sp^2 towards sp^3 , resulting in an upfield shift of the proton signals [4,5,10,22]. This upfield shift of the proton signals is not always seen, as demonstrated by the spectra of palladium and silver complexes of the diene **2**. Such variations have also been observed in the case of complexes of unsilylated ligands [21]. This contrasting behaviour was revealed by ^{13}C NMR spectroscopy.

^{13}C NMR spectra (Table 2)

The diene **2** shows four olefinic, four methylene and one SiMe_3 ^{13}C signals. The assignments are made by comparing the chemical shifts with those for 1,5-cyclooctadiene [13b]. We have recorded ^{13}C spectra for Ag^{I} , Rh^{I} , Pd^{II} and Pt^{II} complexes. The spectrum of Rh^{I} complex is somewhat complicated, showing more than twice the expected number of signals in the olefinic and the methylene regions. However, the elemental analysis was correct for a 1 : 1 complex and ligand displacement by KCN gave only pure **2**. Thus, the complexity of this spectrum seems to be due to

Table 2

¹³C NMR spectra of TMS-COD (2) and its complexes ^a

Entry	Compound	Olefinic carbons				Methylene carbons				Si(CH ₃) ₃
		C ₁	C ₂	C ₅	C ₆	C ₃	C ₄	C ₇	C ₈	
1	TMS-COD (2)	140.54	137.48	128.60	128.80	30.70	27.76	28.77	29.36	-1.54
2	Ag ^I complex (4)	141.20	133.65	126.94	127.65	31.07	27.48	29.08	29.49	-1.32
3	Rh ^I complex (5) ^b									
4	Pd ^{II} complex (6)	140.88	118.36	114.00	120.36	35.00	30.44	32.21	32.89	0.93
5	Pt ^{II} complex (7)	119.23	101.70	97.51	104.78	35.43	30.45	31.85	32.79	1.17

^a Solvent is CDCl₃; chemical shifts (ppm) relative to tetramethylsilane and CDCl₃. ^b See Experimental section for ¹³C spectral data.

the fact that the complex is in a dimeric (or oligomeric) form in which the ligands can have more than one relative orientation. The other three complexes, i.e., those of Ag^I, Pd^{II} and Pt^{II}, gave very clean spectra. In all the spectra, the olefinic C₂, C₅ and C₆ signals are shifted to higher field and the methylene carbon signals to lower field. The magnitude of the shift in the vinylic carbon signals is indicative of the strength of the metal- π bond coordination. The direction of the shift of the C₁ signal is not the same for all the complexes. This signal shows a slight downfield shift in the case of the Ag^I and Pd^{II} complexes, but a large upfield shift in the case of the Rh^I (128.35 ppm) and Pt^{II} (119.23 ppm) complexes. One other important feature is that the C₅ and C₆ signals are well separated in the spectra of the complexes whereas in the ligand they are very close (separated by only 0.2 ppm). In each complex, the shift for the C₂ signal is the largest, followed by those for the C₅, C₆ and C₁. This observation, considered along with the ¹H NMR and IR spectral data, provides insight into the structural features of the complexes.

Both the double bonds of the diene 2 are involved in the complex formation. The bulky SiMe₃ group in the vinylic position does not completely block coordination of the double bond bearing it but pushes the metal ion away towards C₂ and C₅, as would be expected, causing distortion in the structure of the complexes in comparison to those of the corresponding COD complexes.

Cu^I complex

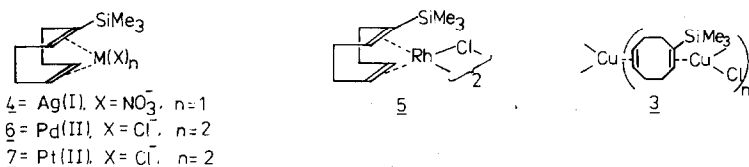
Attempts to prepare the Cu^I complex by mixing Cu₂Cl₂ with 2 in hexane gave an unstable compound insoluble in most organic solvents. It gave pure 2 on ligand

Table 3

Transition metal catalysed protodesilylation of cyclic vinylsilanes

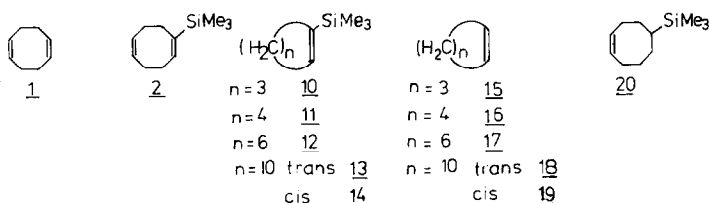
Vinylsilane	Time (h) taken for desilylation		Product
	PdCl ₂ /EtOH	RhCl ₃ ·3H ₂ O/EtOH	
2	7	10	1 + 17 (50/50)
	24	19	17
10	10	28	15
11	10	24	16
12	11	45	17
13 + 14	12	14	18 + 19

displacement reaction. No satisfactory elemental analysis could be obtained, and the IR and ^1H NMR (in $\text{DMSO}-d_6$) data indicate only weak coordination. Thus, its identity could not be established with certainty, but it is tentatively assigned structure **3**.



Protodesilylation (Table 3)

Palladium chloride catalysed protodesilylation of diene **2** in ethanol was faster than that of 1-trimethylsilylcyclooctene (**12**), which was desilylated at a rate comparable to the rates for 1-trimethylsilylcyclopentene (**10**), 1-trimethylsilylcyclohexene (**11**) and 1-trimethylsilylcyclododecene (**13** + **14**). Diene **2** was desilylated completely in less than 7 h, whereas the other cyclic vinylsilanes (**10**–**14**) required 10–12 h. The more facile desilylation of **2** than of the other 1-trimethylsilylcycloalkenes (**10**–**14**) seems to be due to the strong complexing ability of **2**. Rhodium chloride in refluxing ethanol also brought about desilylation of **2** and **10**–**14**, but not as smoothly as palladium chloride. The protodesilylation appears to be stereospecific, since the isomeric composition of the mixture of *cis*- and *trans*-cyclododecenes obtained on desilylation corresponds to the **13/14** ratio in the starting mixture (**13/14** = 60:40) [23].



Catalytic transfer hydrogenation

We observed that desilylation of **2** to **1** in ethanol with either palladium chloride or rhodium chloride was followed by reduction of **1** to cyclooctene (**17**). Cyclooctene began to appear after about 1 h from the start of desilylation, and about 50% reduction had taken place by the time the desilylation was complete. This indicates that protodesilylation precedes reduction. The reduction could also be brought about by using propan-2-ol, but slightly more slowly. The reduction in ethanol and propan-2-ol gave acetaldehyde and acetone, respectively, in proportion to the amount of **1** reduced. No further reduction of cyclooctene to cyclooctane was observed in any case even after long reaction times. These reductions are undoubtedly brought about by catalytic transfer of hydrogen from alcohol to COD [24]. Palladium chloride is a more efficient transfer hydrogen catalyst than rhodium chloride.

The formation of cyclooctene (**17**) from TMS-COD (**2**) was much faster than when COD (**1**) was subjected to the reduction under the same conditions. Reduc-

tion did not precede desilylation, since (i) desilylation was faster than reduction (see above), and (ii) neither 1-trimethylsilylcyclooctene (**12**) nor 5-trimethylsilylcyclooctene (**20**) was observed at any stage of the reaction. Further, COD (**1**) underwent reduction faster when mixed with **2** than when used alone. These results showed that the silyl group was in some way responsible for this rate enhancement. To check this we reduced COD (**1**) in the presence of 1-trimethylsilylcyclopentene (**10**), and surprisingly the reduction of **1** now occurred at about the same rate as when **1** was reduced in the presence of **2** or **2** was reduced alone. This leaves no doubt about the role the "silyl" group is playing in promoting the hydrogen transfer process. Since the silyl group need not be present within the molecule undergoing reduction for such rate enhancement, it is possible that some sort of bonding between the metal and the displaced silyl group takes place to form a catalyst that promotes hydrogen transfer. The exact nature of this new catalytic intermediate cannot at present be defined.

In conclusion 1-trimethylsilylcycloocta-1,5-diene forms complexes with transition metals readily under conditions that do not bring about desilylation. The metal is pushed away from the SiMe₃ group, resulting in structural changes that are reflected in the spectral characteristics of the complexes. The silicon-containing species displaced during the protodesilylation enhance the catalytic activity of palladium in reducing COD to cyclooctene through hydrogen transfer from alcohols.

Experimental

Melting points were determined in open capillaries and are uncorrected. Infrared spectra were recorded on Nicolet 5DXC FT-IR and Beckman 4260 instruments using KBr discs for solids and as film for liquids. ¹H and ¹³C NMR spectra were recorded on a Bruker AC-250 spectrometer and COSY and shift correlation spectra on a Bruker 400 MHz NMR spectrometer. Chemical shifts are given in δ ppm relative to tetramethylsilane or chloroform as internal standard. Mass spectra were recorded on a Hewlett-Packard 5985 B instrument. Gas chromatographic analyses were performed on a Varian Vista 6000 GC using (2 m \times 3.2 mm) 10% OV 101, 15% FFAP and 3% OV 17 columns with temperature programme (80–100°C with 5°C/min increase). Elemental analyses were carried out by the Department of Chemistry, Central College, and the Department of Organic Chemistry, Indian Institute of Science, Bangalore, Regional Research Laboratory, Trivandrum and Analytische Laboratorien, Gummiesbach, Germany.

1-Bromo-1,5-cyclooctadiene was prepared as described previously [18]. Alcohols were dried by standard procedure [25]. Tetrahydrofuran (THF) was distilled from sodium/benzophenone and chlorotrimethylsilane was distilled from sodium before use. The complexes were dried in vacuum at about 1.5 Torr over anhydrous CaCl₂.

1-Trimethylsilyl-1,5-cyclooctadiene (2)

To a stirred mixture of 5.20 g (0.27 mol) of sodium wire and 12.00 g (0.11 mol) of chlorotrimethylsilane in 20 ml of THF at room temperature was added, during 15 min, 8.50 g (0.04 mol) of 1-bromo-1,5-cyclooctadiene in 20 ml of THF. The mixture was refluxed for 15 h on an oil bath at 65°C then allowed to cool. The residual sodium and solid products were filtered off through a plug of glass wool

and washed with ether (25 ml). The combined filtrates and washings were carefully washed with saturated aq. NaHCO_3 (50 ml), water (2×50 ml) and finally with saturated aq. NaCl (50 ml) and dried (MgSO_4). After removal of the solvent, the residue was distilled under reduced pressure to give 7.05 g (87%) of 1-trimethylsilyl-1,5-cyclooctadiene, b.p. $75^\circ/5.0$ Torr. IR: 3011, 2954, 2882, 2831, 1648, 1618, 1246, 833, 749, 688 cm^{-1} . MS m/e (rel. abundance): 180 (M^+ , 0.9), 165 (3.3), 152 (0.3), 137 (30), 123 (0.6), 106 (17.9), 91 (5.6), 73 (100), 59 (26.8), 45 (19.4), 27 (1.4).

Copper(I) complex (3)

Diene **2** (0.20 g, 1.10 mmol) was added to a suspension of 0.06 g (0.30 mmol) of freshly prepared Cu_2Cl_2 in hexane (0.50 ml). The mixture was stirred for 5 h and the solid was then filtered off, washed with 1.5 ml of hexane, and dried; yield 0.10 g (86%); m.p. 232°C (decomp.). IR: 3015, 2937, 2883, 2830, 1618, 1500, 1457, 1426, 1371, 1246, 999, 838, 747, 716, 627 cm^{-1} (anal. not satisfactory).

Silver(I) complex (4)

To a stirred solution of 0.18 g (1.10 mmol) of AgNO_3 in 2 ml of water was added 0.21 g (1.10 mmol) of **2**. The mixture was stirred for 10 min, then the solid formed was filtered off, washed with water (1 ml) and cold absolute ethanol (1.5 ml), and dried; yield 0.28 g (73%); m.p. 100°C (decomp.). IR: 3011, 2991, 2882, 2831, 1619, 1379, 1246, 839, 749, 687 cm^{-1} . Anal. Found: C, 37.2; H, 5.43; N, 4.17. $\text{C}_{11}\text{H}_{20}\text{SiAgNO}_3$ calc.: C, 37.7; H, 5.71; N, 4.02%.

Rhodium(I) complex (5)

(a) *Via μ -dichlorotetraethylene dirhodium.* To the orange ethylene complex of rhodium formed by bubbling ethylene through a stirred solution of 0.10 g (0.48 mmol) of $\text{RhCl}_3\text{H}_2\text{O}$ in 2 ml of methanol was added 0.88 g (0.48 mmol) of **2**. The mixture was stirred for a further 10 min, then the yellow solid was filtered off, washed with petroleum ether ($60\text{--}80^\circ\text{C}$), and dried; yield 0.085 g (56%).

(b) *Via μ -dichlorotetracarbonyl dirhodium.* $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ was prepared by the published procedure [26]. To a clear solution of 0.06 g (0.31 mmol) of $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ in 3 ml of benzene was added 0.07 g (0.38 mmol) of **2** and the mixture was stirred for 10 min. The solution was concentrated under reduced pressure and the residue treated with 2 ml of ethanol and the mixture cooled in ice to give a yellow solid, which was filtered off, washed with 1 ml of cold absolute ethanol, and dried; yield 0.07 g (71%); m.p. $169\text{--}170^\circ\text{C}$ (decomp.). IR: 3005, 2942, 2926, 2767, 1348, 1241, 884, 836 cm^{-1} . ^{13}C NMR: (CDCl_3) 0.38, 0.46, 29.99, 32.40, 32.94, 33.11, 33.27, 75.91, 76.12, 76.24, 79.10, 79.23, 85.32, 85.53, 85.92, 86.12, 86.44, 86.69, 86.83, 87.08, 128.35. Anal. Found: C, 41.24; H, 6.36. $\text{C}_{11}\text{H}_{20}\text{SiRhCl}$ calc.: C, 41.45; H, 6.32%.

Palladium(II) complex (6)

To a clear solution of 0.20 g (0.52 mmol) of $(\text{PhCN})_2\text{PdCl}_2$ in 5 ml of benzene was added 0.102 g (0.57 mmol) of **2**. The solution was stirred for 10 min, and the yellow solid precipitated, then filtered off, washed with 2 ml of dry hexane, and dried; yield 0.11 g (58%); m.p. 160°C . IR: 2952, 2930, 2898, 2892, 1518, 1483, 1463, 1422, 1343, 1249, 1243, 1186, 988, 895, 844 cm^{-1} . Anal. Found: C, 36.70; H, 5.60. $\text{C}_{11}\text{H}_{20}\text{SiPdCl}_2$ calc.: C, 36.90; H, 5.59%.

Platinum(II) complex (7)

To a solution of K_2PtCl_4 (0.12 g, 0.28 mmol) in 6 ml of 2 *N* acetic acid was added to 0.12 g (0.66 mmol) of **2**. The solution was stirred for 5 h and the product then precipitated by addition of 3 ml of ethanol, and filtered off. Cooling the filtrate in ice-water gave a second crop of white shiny complex. The combined product was dried; yield 0.075 g (60%); m.p. 200°C (decomp.). IR: 2892, 2886, 2833, 2832, 1480, 1448, 1250, 1242, 902, 864, 843, 763, 753, 737, 682, 630 cm^{-1} . Anal. Found: C, 29.36; H, 4.39; Cl, 16.09. $\text{C}_{11}\text{H}_{20}\text{SiPtCl}_2$ calc.: C, 29.58; H, 4.52; Cl, 15.89%.

Reaction of 2 with $\text{RhCl}_3 \cdot \text{H}_2\text{O}$ in refluxing ethanol: formation of 8 through desilylation

To 0.20 g (0.96 mmol) of $\text{RhCl}_3 \cdot \text{H}_2\text{O}$ in 10 ml of absolute ethanol was added 0.92 g (5.11 mmol) of **2**, and the mixture refluxed on a water bath at 90°C for 1 h. The orange solid formed was filtered off and dried; yield 0.13 g (55%); m.p. 256°C (darkening at 220°C). IR: 2990, 2930, 2880, 2825, 1460, 1415, 1325, 1290, 1125, 1080, 985, 960 cm^{-1} . ^1H NMR: (CDCl_3) δ 1.2–2.2 (m, 4H), 2.2–2.8 (m, 4H), 4.0–4.5 (m, 4H) ppm.

Reaction of 2 with $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ in refluxing ethanol: formation of 9 through desilylation

To 0.20 g (0.96 mmol) of $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ in 10 ml of absolute ethanol was added 0.35 g (1.94 mmol) of **2**. The mixture was refluxed for 6 h on a water bath at 90°C then the dark brown solid was filtered off, washed with 1 ml absolute ethanol, and dried; yield 0.175 g (65%); m.p. 200°C (decomp.). IR: 2935, 2880, 2875, 1630, 1460, 1440, 1330, 990 cm^{-1} .

Olefin displacement reaction

Each of the complexes **3–9** (40–50 mg) was dissolved in 1 ml of CCl_4 . A solution of 0.10 g of KCN in 1 ml of water was added and the mixture stirred for 15 min. The CCl_4 layer was separated, washed with water, dried, and concentrated. The purity of the product was checked by GLC and its identity was established in the usual way in each case. Complexes **3–7** gave pure TMS-COD (**2**) whereas **8** and **9** gave COD (**1**).

Protodesilylation of cyclic vinylsilanes using PdCl_2 and RhCl_3

A mixture of 0.15 g of each of the vinylsilanes **2**, **10**, **11**, **12** and (**13** + **14**) and 0.3 equiv. of PdCl_2 or $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in 2 ml of ethanol was refluxed on a water bath (90°C). Each reaction was monitored by GLC until the desilylation was complete. The products were identified as (**1** + **17**), **15**, **16**, **17** and (**18** + **19**), respectively, by comparing their properties with those of the authentic samples.

Catalytic transfer hydrogenation promoted by silyl group

To a solution of 1,5-cyclooctadiene or 1-trimethylsilyl-1,5-cyclooctadiene (0.20 g) in 2 ml of ethanol or propan-2-ol was added PdCl_2 (0.3 equiv.). The mixture was heated at 90°C and the reaction monitored by GLC until the reduction to cyclooctene was complete. Continuation of the heating did not cause any further change.

Reduction of COD to cyclooctene in presence of 1-trimethylsilylcyclopentene

A similar procedure was carried out with a mixture of 0.10 g of **1** and 0.02 g of 1-trimethylsilylcyclopentene (**10**) (4 : 1 equiv.). The reaction was found to take same time as in the case of TMS-COD. Use of a higher proportion of **10** did not result in any significant enhancement of the rate of reduction.

Acknowledgements

This work was funded by Department of Science and Technology, Government of India, New Delhi. BSB thanks U.G.C., New Delhi for a fellowship. Thanks are also due to Chairman, Department of Organic Chemistry, I.I.Sc., Bangalore and Professor K. Griesbaum and Dr. H. Röttelle, Karlsruhe University, Germany, for spectra.

References

- 1 A. Christofides, M. Ciriano, J.L. Spencer and F.G.A. Stone, *J. Organomet. Chem.*, 178 (1979) 273.
- 2 L.S. Isaeva, T.A. Peganova, P.V. Petrovski, F.F. Kayumov, F.G. Yusupova and V.P. Yur'ev, *J. Organomet. Chem.*, 248 (1983) 375.
- 3 E.M. Haschke and J.W. Fitch, *J. Organomet. Chem.*, 57 (1973) C 93.
- 4 J.W. Fitch, D.P. Flores and J.E. George, *J. Organomet. Chem.*, 29 (1971) 263.
- 5 (a) R.D. Kelly and G.B. Young, *J. Organomet. Chem.*, 361 (1989) 123; (b) R.D. Kelly and G.B. Young, *Polyhedron*, 8 (1989) 433.
- 6 I. Haiduc and V. Popa, *Adv. Organomet. Chem.*, 15 (1977) 113.
- 7 (a) U. Schubert, *J. Organomet. Chem.*, 358 (1988) 215; (b) U. Schubert and J. Grönen, *Organometallics*, 6 (1987) 2458.
- 8 (a) A.J. Pearson and M.S. Holder, *J. Organomet. Chem.*, 383 (1990) 307; (b) L.A. Paquette, R.G. Daniels and R. Gleiter, *Organometallics*, 3 (1984) 560.
- 9 T.J. Chow and C.C. Cheng, *J. Organomet. Chem.*, 368 (1989) 323.
- 10 J.W. Fitch, E.B. Ripplinger, B.A. Shouldersand, S.D. Sorey, *J. Organomet. Chem.*, 352 (1988) C 25.
- 11 J.W. Fitch and W. Osterloh, *J. Organomet. Chem.*, 213 (1981) 493.
- 12 P.M. Maitlis, P. Espinet and M.J.H. Russel, in G. Wilkinson (Ed.), *Comprehensive Organometallic Chemistry*, Vol. VI, Pergamon Press, New York, 1982, p. 363.
- 13 (a) A.C. Albeniz, P. Espinet, Y. Jeannin, M. Philoche-Levisalles and B.E. Mann, *J. Am. Chem. Soc.*, 112 (1990) 6594; (b) M.F. Rettig, R.W. Wing and G.R. Wiger, *J. Am. Chem. Soc.*, 103 (1981) 2980; (c) L. Benckekroun, P. Herpin, M. Julia and L. Saussine, *J. Organomet. Chem.*, 128 (1977) 275.
- 14 For the steric influence of SiMe₃ group in organic reactions, see: J.R. Hwu and N. Wang, *Chem. Rev.* 89 (1989) 1599.
- 15 (a) G. Nagendrappa, *Tetrahedron*, 38 (1982) 2479; (b) G. Nagendrappa and T.J. Vidyapati, *J. Organomet. Chem.*, 280 (1985) 31; (c) B.S. Bandodakar and G. Nagendrappa, *Tetrahedron Lett.*, 30 (1989) 7461.
- 16 (a) G. Nagendrappa and D. Devaprabhakara, *J. Organomet. Chem.*, 17 (1969) 182; (b) G. Nagendrappa, G.C. Joshi and D. Devaprabhakara, *J. Organomet. Chem.*, 27 (1971) 421 and other papers of these authors cited therein.
- 17 The vinylsilyl diene **2** has been reported but without any details of preparation or physical properties: A.P. Davis, G.J. Hughes, P.R. Lowndes, C.M. Robbins, E.J. Thomas and G.H. Whitham, *J. Chem. Soc. Perkin Trans. 1*, (1981) 1934.
- 18 B.S. Bandodakar and G. Nagendrappa, *Synthesis*, (1990) 843.
- 19 G. Nagendrappa, *Synthesis*, (1980) 704.
- 20 (a) K. Karabelas and A. Hallburg, *J. Org. Chem.*, 53 (1988) 4909; (b) W.P. Weber, R.A. Felix, A.K. Willard and K.E. Koenig, *Tetrahedron Lett.*, (1971) 4701; (c) K. Yamamoto, K. Shinohara, T.O. Ohuchi and M. Kumada, *Tetrahedron Lett.*, (1974) 1153.
- 21 (a) H. Takahshi and J. Tsuji, *J. Am. Chem. Soc.*, 90 (1968) 2387; (b) P. Heimbach and M. Molin, *J. Organomet. Chem.*, 49 (1973) 483; (c) W. Partenheimer and B. Durham, *J. Am. Chem. Soc.*, 96 (1974) 3800.

- 22 M.L. Maddox, S.L. Stafford and H.D. Kaesz, *Adv. Organomet. Chem.*, 3 (1965) 47.
- 23 D. Mansuy, J. Pusset and J.C. Chottard, *J. Organomet. Chem.*, 110 (1976) 139.
- 24 For metal catalysed hydrogen transfer to 1,5-cyclooctadiene, see: (a) P. Kvintovics and B. Heil, *J. Organomet. Chem.*, 361 (1989) 117; (b) J. Kašpar, R. Spogliarich and M. Graziani, *J. Organomet. Chem.*, 281 (1985) 299; (c) J.J. Eisch, S.R. Sexmith and K.C. Fichter, *J. Organomet. Chem.*, 382 (1990) 273; (d) Review on transfer hydrogenation: R.A.W. Johnstone and A.H. Wilby, *Chem. Rev.*, 85 (1985) 129.
- 25 B.S. Furniss, A.J. Hannaford, V. Rogers, P.W.G. Smith, A.R. Tatchell, *Vogel's Textbook of Practical Organic Chemistry*, IVth edition, Longman (ELBS) London, 1978, p. 268.
- 26 A.J. Deeming and P.J. Sharrat, *J. Organomet. Chem.*, 99 (1975) 447.