Synthesis, Reactions and Catalytic Activities of σ- and η^3-Allylbis(triphenylstibine)rhodium(III) Complexes

Chong Shik Chin,* Sang Young Shin and Changjin Lee
Department of Chemistry, Sogang University, CPO Box 1142, Seoul 100–611, Korea

Reaction of $[\mathrm{RhCl(CO)(SbPh_3)_2}]$ **1** with $\mathrm{CH_2{=}CHCH_2Br}$ **2a** gives the σ-allylrhodium(III) complex $[\mathrm{Rh}(\sigma\text{-}\mathrm{CH_2CH{=}CH_2})\mathrm{Cl(Br)(CO)(SbPh_3)_2}]$ **3**, while reactions of **1** with allyl halides and $\mathrm{AgClO_4}$ give η^3-allylrhodium(III) complexes $[\mathrm{Rh}(\eta^3\text{-allyl})\mathrm{X(CO)(SbPh_3)_2}]\mathrm{ClO_4}$ **4** [allyl = $\mathrm{CH_2CHCH_2}$, $\mathrm{CH_2CHCHMe}$ (X = Br or Cl), $\mathrm{CH_2CMeCH_2}$, or $\mathrm{CH_2CHCHPh}$ (X = Cl)]. The complex $[\mathrm{Rh}(\eta^3\text{-}\mathrm{CH_2CHCH_2})\mathrm{Br(CO)(SbPh_3)_2}]\mathrm{ClO_4}$ can also be prepared by the reaction of **3** with $\mathrm{AgClO_4}$. The complex $[\mathrm{Rh}(\eta^3\text{-}\mathrm{CH_2CHCH_2})\mathrm{Cl(CO)(SbPh_3)_2}]\mathrm{ClO_4}$ reacts with alcohols, amines and triphenylphosphine to give **1** and allyl ethers, diallylamines and allylphosphonium perchlorate, respectively. Reactions of allyl halides with alcohols and amines are catalysed by the η^3-allyl complexes **4** in the presence of $\mathrm{ClO_4^-}$.

Metal–allyl compounds have been prepared and studied since they are known to be key intermediates in various organic reactions.[1] Rhodium is one of the metals whose allyl compounds have been investigated.[1e,f] Phosphines[1e,f,2] and arsines[2b,e] were employed to stabilize the allylrhodium moiety, but there has been no report on rhodium–allyl–stibine complexes. We now report the synthesis, reactions and catalytic activities of $[\mathrm{Rh}(\sigma\text{-}\mathrm{CH_2CH{=}CH_2})\mathrm{Cl(Br)(CO)(SbPh_3)_2}]$ and $[\mathrm{Rh}(\eta^3\text{-allyl})\mathrm{X(CO)(SbPh_3)_2}]\mathrm{ClO_4}$ (X = Br or Cl).

Results and Discussion

Synthesis.—Reaction of $[\mathrm{RhCl(CO)(SbPh_3)_2}]$ **1** with $\mathrm{CH_2{=}CHCH_2Br}$ **2a** gives a σ-allyl complex $[\mathrm{Rh}(\sigma\text{-}\mathrm{CH_2CH{=}CH_2})\mathrm{Cl(Br)(CO)(SbPh_3)_2}]$ **3** [equation (1)]. Complex **3** could be

$$\underset{\mathbf{1}}{[\mathrm{RhCl(CO)(SbPh_3)_2}]} + \underset{\mathbf{2a}}{\mathrm{CH_2{=}CHCH_2Br}} \longrightarrow \underset{\mathbf{3}}{[\mathrm{Rh}(\sigma\text{-}\mathrm{CH_2CH{=}CH_2})\mathrm{Cl(Br)(CO)(SbPh_3)_2}]} \qquad (1)$$

obtained from the reaction of **1** only with **2a**: reactions of **1** with other allyl bromides such as $\mathrm{MeCH{=}CHCH_2Br}$ **2b** and allyl chlorides **2c**–**2g** in the absence of $\mathrm{AgClO_4}$ yield a mixture of uncharacterized rhodium complexes.

On the other hand the η^3-allyl complexes **4** could be obtained from the reactions of both allyl bromides **2a** and **2b** and allyl chlorides **2c**–**2g** with **1** and $\mathrm{AgClO_4}$ which abstracts $\mathrm{Cl^-}$ from **1** to provide a co-ordination site for the η^3-allyl group [see equation (2)]. Complexes **4** are stable in the solid state and in solution under nitrogen at room temperature. Complex **3** decomposes to unknown compound(s) in solution within several hours even under $\mathrm{N_2}$.

$$\mathbf{1} + \underset{\mathbf{2}}{\mathrm{RCHCR'CHR''X}} \xrightarrow[-\mathrm{AgCl}]{\mathrm{AgClO_4}} \underset{\mathbf{4}\ (\mathbf{4d} = \mathbf{4f})}{[\mathrm{Rh}(\eta^3\text{-}\mathrm{RCHCR'CHR''})\mathrm{X(CO)(SbPh_3)_2}]\mathrm{ClO_4}} \qquad (2)$$

a R = R′ = R″ = H, X = Br
b R = Me, R′ = R″ = H, X = Br
c R = R′ = R″ = H, X = Cl
d R = Me, R′ = R″ = H, X = Cl
e R = R″ = H, R′ = Me, X = Cl
f R = R′ = H, R″ = Me, X = Cl
g R = Ph, R′ = R″ = H, X = Cl

The complexes were characterized by ^{1}H, ^{13}C NMR and IR spectral data, elemental analyses and conductance measurements. All the newly prepared rhodium(III)–allyl compounds in this study show the typical signals at the appropriate regions in their ^{1}H, ^{13}C NMR and IR spectra as do well characterized σ- or η^3-allylmetal compounds.[1–3] For example, the ^{1}H NMR spectrum of the σ-$\mathrm{CH_2CH{=}CH_2}$ complex **3** shows four different chemical shifts for the allyl protons ($\mathrm{H_A}$ to $\mathrm{H_D}$) while the η^3-allyl complexes **4a** and **4c** show only three for $\mathrm{H_A}$ to $\mathrm{H_C}$ (see Table 1). The ^{13}C NMR spectrum of **3** gives three different chemical shifts for the allyl carbons $\mathrm{C^1}$–$\mathrm{C^3}$ while **4a** and **4c** give only two for $\mathrm{C^1}$ and $\mathrm{C^2}$ (see Table 2). Coupling between ^{103}Rh and allylic ^{13}C also clearly distinguishes σ- from η^3-allylrhodium complexes: a relatively large coupling (17 Hz) is observed for only one carbon (Rh–$\mathrm{CH_2}$) in complex **3** whereas coupling is observed for two carbons (Rh–$\mathrm{CH_2}$ and –CH) in complexes **4a** and **4c** with relatively small values, 4.9 and 5.1 Hz (see Table 1). The two η^3-allyl complexes **4d** and **4f** obtained in the reactions of **1** with $\mathrm{MeCH{=}CHCH_2Cl}$ **2d** and $\mathrm{CH_2{=}CHCH(Me)Cl}$ **2f** were found to be identical according to spectral data as expected, which also supports the formulation η^3-$\mathrm{CH_2CHCHMe}$. The lower ν(CO) for complex **3** than for **4a** and **4c** suggests that the σ-$\mathrm{CH_2CH{=}CH_2(Br)(Cl)}$ moiety is a more effective electron-donating group to rhodium than is η^3-$\mathrm{CH_2CHCH_2(X)}$ (X = Br or Cl). The absorption due to ν(Rh–Cl) and ν(Rh–Br) of **3** and **4** may appear in the 200–300 cm^{-1} region,[4a] but are obscured by $\mathrm{SbPh_3}$ bands.[4b]

Complex **3** is readily converted into **4a** (but not **4c**) by reaction with $\mathrm{AgClO_4}$ [equation (3)]. The formation of **4a** was

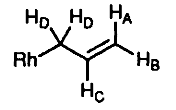
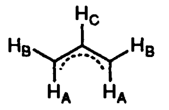
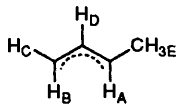
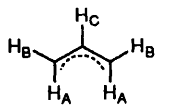
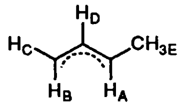
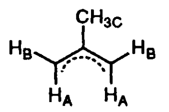
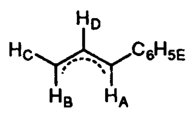
$$\mathbf{3} + \mathrm{AgClO_4} \longrightarrow \mathbf{4a} + \mathrm{AgCl} \qquad (3)$$

unambiguously confirmed by elemental analysis and spectral data (^{1}H, ^{13}C NMR and IR) which clearly distinguish the bromo- **4a** from the chloro-complex **4c** (see Tables).

It has been also found that the addition of $\mathrm{AgClO_4}$ always yields AgCl (rather than AgBr) in reactions of complex **1** with allyl bromides **2a** and **2b** [equation (2)]. This may suggest initial chloride abstraction from rhodium by $\mathrm{Ag^+}$ followed by oxidative addition of the allyl halides **2**. Separate experiments were carried out in order to verify the initial abstraction: complexes **4** were also prepared by the reactions of allyl halides **2** with the filtrate obtained by removing AgCl produced in the reaction of **1** and $\mathrm{AgClO_4}$ in benzene in the presence of acetonitrile.

Reactions.—Complex **4c** reacts with alcohols, amines and triphenylphosphine to produce **1** and allyl ethers, diallylamines

Table 1 Proton NMR data for $[Rh(\sigma\text{-}CH_2CH{=}CH_2)Cl(Br)(CO)L_2]$ **3**, $[Rh(\eta^3\text{-}CH_2CHCH_2)Br(CO)L_2]ClO_4$ **4a**, $[Rh(\eta^3\text{-}CH_2CHCHMe)Br(CO)L_2]ClO_4$ **4b**, $[Rh(\eta^3\text{-}CH_2CHCH_2)Cl(CO)L_2]ClO_4$ **4c**, $[Rh(\eta^3\text{-}CH_2CHCHMe)Cl(CO)L_2]ClO_4$ **4d** = **4f**, $[Rh(\eta^3\text{-}CH_2CMeCH_2)Cl(CO)L_2]ClO_4$ **4e** and $[Rh(\eta^3\text{-}CH_2CHCHPh)Cl(CO)L_2]ClO_4$ **4g** (L = $SbPh_3$) at 270 or 300 MHz in $CDCl_3$ at 25 °C

Compound		δ					
		H_A	H_B	H_C	H_D	H_E	J/Hz
3		4.38 (d)	4.58 (d)	5.95 (m)	3.21 (d)		$J(H_AH_C)$ = 16.7, $J(H_BH_C)$ = 10.4, $J(H_CH_D)$ = 7.1
4a		3.83 (d)	5.28 (d)	6.17 (m)			$J(H_AH_C)$ = 13.7, $J(H_BH_C)$ = 7.0
4b		5.11 (m)	3.59 (d)	5.16 (d)	6.18 (m)	1.84 (d)	$J(H_AH_E)$ = 5.7, $J(H_BH_D)$ = 12.6, $J(H_CH_D)$ = 7.2
4c		3.67 (d)	5.38 (d)	6.25 (m)			$J(H_AH_C)$ = 13.1, $J(H_BH_C)$ = 7.6
4d		4.94 (m)	3.42 (d)	5.21 (d)	6.30 (m)	1.86 (d)	$J(H_AH_E)$ = 7.2, $J(H_BH_D)$ = 14.1, $J(H_CH_D)$ = 8.1
4e		3.65 (s)	5.17 (s)	2.41 (d)[a]			$J(Rh\text{-}H_C)$ = 2.0
4g		5.80 (d)	3.59 (d)	5.38 (d)	*b*	*b*	$J(H_AH_D)$ = 13.5, $J(H_BH_D)$ = 12.0, $J(H_CH_D)$ = 7.5

[a] Very small $J(Rh\text{-}H_C)$ is observed as reported in ref. 2*d*. [b] Overlapped with signals for CPh and SbPh in the region of δ 7.1–7.7.

and allylphosphonium salt [see equations (4)–(6)]. Taube and

$$\underset{\textbf{4c}}{[Rh(\eta^3\text{-}CH_2CHCH_2)Cl(CO)(SbPh_3)_2]ClO_4} + ROH \longrightarrow$$

$$\underset{\textbf{1}}{[RhCl(CO)(SbPh_3)_2]} + CH_2{=}CHCH_2OR + HClO_4 \quad (4)$$

$$\textbf{4c} + \tfrac{3}{2}NH_2R \longrightarrow$$

$$\textbf{1} + \tfrac{1}{2}NR(CH_2CH{=}CH_2)_2 + NH_2R{\cdot}HClO_4 \quad (5)$$

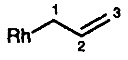
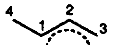
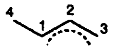
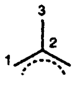
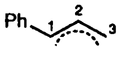
$$\textbf{4c} + PPh_3 \longrightarrow \textbf{1} + [PPh_3(CH_2CH{=}CH_2)]ClO_4 \quad (6)$$

co-workers[3a] found that an osmium(IV)–allyl complex reacts with methanol, pyridine and PPh_3 to give osmium(IV) complexes containing co-ordinated $\eta^2\text{-}H_2C{=}CHCH_2OMe$, $\eta^2\text{-}H_2C{=}CHCH_2NC_5H_5$ and $\eta^2\text{-}H_2C{=}CHCH_2PPh_3$ ligands. When a small amount of triphenylphosphine (Rh/PPh_3 = 1 : 1) was added to a solution of **4c** in benzene all the added PPh_3 was converted into the phosphonium salt and there was no sign of rhodium-bound $SbPh_3$ being replaced by PPh_3.

Attempts to prepare the dicationic complex $[Rh(\eta^3\text{-}CH_2CHCH_2)(CO)(SbPh_3)_2]^{2+}$ by reaction of **4a** (or **4c**) with $AgClO_4$ have been unsuccessful. The reaction of **4c** with $AgClO_4$ in the presence of a nitrile (MeCH=CHCN), however, seems to produce a mixture of $[Rh(\eta^3\text{-}CH_2CHCH_2)(CO)(MeCH{=}CHCN)(SbPh_3)_2][ClO_4]_2$ and other uncharacterized rhodium complex(es) (see Experimental section).

Catalytic Activities.—Stoichiometric reactions of complex **4c** with alcohols [equation (4)] led us to investigate the reactions of allylic halides with alcohols catalysed by **4**. The reaction of $PhCH{=}CHCH_2Cl$ **2g** (34 mmol) with EtOH (100 mmol) gives $PhCH{=}CHCH_2OEt$ quantitatively within 24 h at 30 °C in benzene in the presence of $[Rh(\eta^3\text{-}CH_2CHCHPh)Cl(CO)(SbPh_3)_2]ClO_4$ **4g** (0.17 mmol) and $NaClO_4$ (38 mmol), while the reaction mixture of **2g**, EtOH and $NaClO_4$ in the absence of **4g** gave only a trace amount of the ether in 24 h. It has also been found that the formation of the ether is not catalysed by $[RhCl(CO)(SbPh_3)_2]$ **1** in the absence of $NaClO_4$. The reaction mixture of **1**, **2g**, EtOH, however, in the presence of $NaClO_4$ produces a significant amount of the ether. It has been found that the reactions of **1** with allyl halides and $NaClO_4$ also produce η^3-allyl complexes **4**. The catalytic activities of **4** are more prominent for the reactions of Pr^iOH (100 mmol) with allyl halides, $MeCH{=}CHCH_2Cl$ **2d** (16 mmol) and $CH_2{=}CHCH(Me)Cl$ **2f** (16 mmol): the formation of the ether, $MeCH{=}CHCH_2OPr^i$ (which is obtained from both reaction of **2d** and **2f** with Pr^iOH) could be completed within 48 h in the presence of $[Rh(\eta^3\text{-}CH_2CHCHMe)Cl(CO)(SbPh_3)_2]ClO_4$ **4d** (0.23 mmol) and $NaClO_4$ (16 mmol) in refluxing dichloromethane while the

Table 2 Carbon-13 NMR data at 68 or 75 MHz in $CDCl_3$ at 25 °C

Compound		δ (J/Hz)				
		C^1	C^2	C^3	C^4	CO
3		23.7 (17.0)	111.1	147.7		183.9 (65.2)
4a		77.2 (4.9)	108.7 (2.5)			177.8 (56.8)
4b		103.4 *	108.4 *	71.3 (6.0)	21.2	178.9 (56.4)
4c		79.2 (5.1)	109.0 (2.1)			178.4 (56.1)
4d		106.0 *	108.5 *	73.7 *	21.1	179.0 (56.4)
4e		78.0 (5.0)	131.3 *	24.0 *		181.3 (58.4)
4g		102.5 *	108.2 *	74.2 (6.1)		178.8 (56.9)

* Poorly resolved, probably due to very small J(Rh–C).

Table 3 Infrared data (Nujol, cm^{-1})

Compound	ν(CO)	ν(CCC)
3	2034	
4a	2065	502
4b	2061	503
4c	2066	512
4d	2068	512
4e	2056	514
4g	2059	511

ether was never observed for 8 d under the same experimental conditions in the absence of the rhodium complex.

Reactions of amines with allyl halides to give diallylamines are also catalysed by complexes **4**: $PhCH_2NH_2$ (42 mmol) reacts with $CH_2{=}CHCH_2Cl$ (28 mmol) to give $PhCH_2N(CH_2CH{=}CH_2)_2$ quantitatively in the presence of $[Rh(\eta^3\text{-}CH_2CHCH_2)Cl(CO)(SbPh_3)_2]ClO_4$ **4c** (0.23 mmol) and $NaClO_4$ (30 mmol) in refluxing benzene for 5 h, whereas it took 48 h to obtain the same amount of diallyl(benzyl)amine in the absence of the rhodium complex.

Experimental

The NMR spectra were obtained on either a Bruker WH-300 or JEOL GX 270 spectrometer at 300 or 270 MHz for ^1H and 75 or 68 MHz for ^{13}C. Infrared spectra were measured on a Shimadzu IR-440, and a Varian 3700 gas chromatograph was used for analysis of products. Conductance measurements were carried out with a Wiss-Tech Werstatten Weilheim/Obb. LBR conductivity meter. Elemental analyses were performed at the Organic Chemistry Research Center, Sogang University, Korea. The complex $[RhCl(CO)(SbPh_3)_2]$ was prepared by the literature method.[5] Allyl halides were purchased from Aldrich and used without further purification.

Preparations.—$[Rh(\sigma\text{-}CH_2CH{=}CH_2)Cl(Br)(CO)(SbPh_3)_2]$ **3**. A suspension of $[RhCl(CO)(SbPh_3)_2]$ (0.2 g, 0.23 mmol) and $CH_2{=}CHCH_2Br$ **2a** (0.38 mmol) in MeOH (8.0 cm^3) was stirred under nitrogen for 1 h at 25 °C. The reaction mixture remained as a suspension during the reaction. The yellow solid obtained was filtered off, washed with cold methanol (20 cm^3) and dried in vacuum. Yield 90% based on **3** (Found: C, 48.7; H, 3.25. Calc. for $C_{40}H_{35}BrClORhSb_2$: C, 48.4; H, 3.55%).

$[Rh(\eta^3\text{-}CH_2CHCH_2)Br(CO)(SbPh_3)_2]ClO_4$ **4a**. Silver perchlorate (0.23 mmol) was added to a yellowish red benzene (10 cm^3) solution of $[RhCl(CO)(SbPh_3)_2]$ (0.2 g, 0.23 mmol) and $CH_2{=}CHCH_2Br$ (*ca.* 0.8 mmol) at 25 °C under nitrogen and the resulting yellow solution and white precipitation of AgCl was stirred for 30 min. Addition of hexane (25 cm^3) to the solution after the removal of AgCl by filtration resulted in precipitation of pale yellow microcrystals which were filtered off, washed with cold benzene (5 cm^3) and hexane (5 cm^3) and dried in vacuum. Yield 90% based on **4a** (Found: C, 45.1; H, 3.30. Calc. for $C_{40}H_{35}BrClO_5RhSb_2$: C, 45.4; H, 3.35%). Λ_M = 54 $ohm^{-1}\ cm^2\ mol^{-1}$ ([Rh] = 4.4×10^{-4} mol dm^{-3} in CH_2Cl_2 at 25 °C), *cf.* Λ_M of NBu_4ClO_4 is 48 $ohm^{-1}\ cm^2\ mol^{-1}$ in CH_2Cl_2.

Other η^3*-allyl complexes*. Complexes **4b**–**4g** were prepared in the same manner as described above for **4a**. Their elemental analyses were satisfactory and measured molar conductance values (Λ_M) were in good agreement with those of 1:1 electrolytes.

Reactions of $[Rh(\eta^3\text{-}CH_2CHCH_2)Cl(CO)(SbPh_3)_2]ClO_4$ **4c**. —*With* MeOH. Methanol (0.4 mmol) was added to a chloroform (10 cm^3) solution of complex **4c** (0.2 mmol) at 25 °C under N_2 and the resulting solution was stirred for 30 min. Addition of hexane (20 cm^3) resulted in precipitation of $[RhCl(CO)(SbPh_3)_2]$ which was identified by the IR spectrum. The other product, CH_2CHCH_2OMe in the filtrate, was analysed by GC.

With $PhCH_2NH_2$. Addition of $PhCH_2NH_2$ (0.46 mmol) to a chloroform (10 cm^3) solution of **4c** (0.2 mmol) at 25 °C immediately resulted in a white precipitate of $PhCH_2NH_2 \cdot HClO_4$ which was removed by filtration. The purple-red solid was isolated after the addition of hexane (20 cm^3) to the filtrate and identified as $[RhCl(CO)(SbPh_3)_2]$ by the IR spectrum. The GC analysis of the filtrate showed a quantitative amount of $(CH_2{=}CHCH_2)_2NCH_2Ph$.

With PPh_3. Addition of PPh_3 (0.2 mmol) to a chloroform (10 cm^3) solution of complex **4c** (0.2 mmol) immediately resulted in a white precipitate of $[PPh_3(CH_2CH{=}CH_2)]ClO_4$ which was isolated by filtration and identified by IR and ^1H NMR measurements. Hexane (20 cm^3) was added to the filtrate to yield $[RhCl(CO)(SbPh_3)_2]$ which was identified by the IR spectrum.

With $AgClO_4$ *in the presence of* $MeCH{=}CHCN$. Silver perchlorate (0.2 mmol) was added to a dichloromethane (10 cm^3) solution of complex **4c** (0.2 mmol) and $MeCH{=}CHCN$ (0.3 mmol) at 25 °C under nitrogen and the resulting solution was stirred for 30 min until a significant amount of a white precipitate of AgCl was observed. This was removed by filtration and hexane (10 cm^3) was added to the filtrate to precipitate a pale yellow solid which was filtered off and dried in vacuum. The IR spectrum (Nujol) of this yellow solid showed $\nu(CO)$ at 1991w and 2098s, $\nu(CN)$ at 2266, $\nu(C{=}C)$ at 1622 cm^{-1} and most absorptions of **4c**.

Catalytic Reactions.—$PhCH{=}CHCH_2Cl$ *and* EtOH *in the presence of* $[Rh(\eta^3\text{-}CH_2CHCHPh)Cl(CO)(SbPh_3)_2]ClO_4$ **4g** *and* $NaClO_4$. The reaction mixture of $PhCH{=}CHCH_2Cl$ (34 mmol), EtOH (100 mmol), $NaClO_4$ (38 mmol) and complex **4g** (0.17 mmol) in benzene (25 cm^3) was stirred for 24 h. The organic layer was dried with $MgSO_4$ after being extracted with water. Addition of hexane resulted in the precipitation of uncharacterized rhodium complex(es) which was separated by filtration. The GC analysis of the filtrate showed a quantitative amount of $PhCH{=}CHCH_2OEt$.

Reactions of Pr^iOH with $MeCH{=}CHCH_2Cl$ **2d** and $CH_2{=}CHCH(Me)Cl$ **2f** in the presence of $[Rh(\eta^3\text{-}CH_2CHCHMe)Cl(CO)(SbPh_3)_2]ClO_4$ **4d** and $NaClO_4$ were carried out in the same manner as described above.

$PhCH_2NH_2$ *with* $CH_2{=}CHCH_2Cl$ *in the presence of* $[Rh(\eta^3\text{-}CH_2CHCH_2)Cl(CO)(SbPh_3)_2]ClO_4$ **4c** *and* $NaClO_4$. This reaction was carried out in a similar manner.

Acknowledgements

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