ELSEVIER

Journal of Organometallic Chemistry 630 (2001) 44–56

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Reactions of $Rh(SbPh_3)_3(CO)X$ (X = Cl, Br) with organic propargyl compounds. Synthesis, structure and reactivity of rhodiacyclopent-3-ene-2-one complexes

Asgar Kayan [1], Judith C. Gallucci [2], Andrew Wojcicki *

Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, OH 43210-1185, USA

Received 3 January 2001; received in revised form 8 March 2001; accepted 8 March 2001

Abstract

The five-coordinate rhodium(I) stibine complexes $Rh(SbPh_3)_3(CO)X$ (X = Cl (**1**), Br (**2**)) react with $HC{\equiv}CCH_2Y$ (Y = Cl, Br, OTs, OBs) in CH_2Cl_2 at ambient temperature to afford the η^1-allenyl $Rh(SbPh_3)_2(CO)X(Y)(\eta^1\text{-}CH{=}C{=}CH_2)$ (X = Cl, Y = OTs (**3a**), OBs (**3b**); X = Y = Br (**3c**)) and the rhodiacyclopent-3-ene-2-one $Rh(SbPh_3)_3Cl(\eta^2\text{-}C(O)CH{=}C(Cl)CH_2)$ (**5a**) and $Rh(SbPh_3)_3Br(\eta^2\text{-}C(O)CH{=}C(X \text{ or } Y)CH_2)$ (X or Y = Cl (**5b**), Br (**5c**)) products. The corresponding reactions of $Rh(SbPh_3)_3(CO)X$ with $MeC{\equiv}CCH_2Y$ yield the η^1-propargyl $Rh(SbPh_3)_2(CO)Cl(OTs)(\eta^1\text{-}CH_2C{\equiv}CMe)$ (**4**) and the rhodiacyclic $Rh(SbPh_3)_3(X \text{ or } Y)(\eta^2\text{-}C(O)C(Me){=}C(Y \text{ or } X)CH_2)$ (**6**) complexes. The rhodiacycles **5a** and **5c** were converted to the η^1-allenyls $Rh(SbPh_3)_2(CO)Cl_2(\eta^1\text{-}CH{=}C{=}CH_2)$ (**3d**) and **3c**, respectively, upon heating at 60 °C in THF, with the relative rates being **5c** > **5a**. Treatment of **5a** and **5b** with one equivalent of AgOTf or AgOTs results in replacement of the halide bonded to Rh and formation of $Rh(SbPh_3)_3(OTf)(\eta^2\text{-}C(O)CH{=}C(Cl)CH_2)$ (**5d**) and $Rh(SbPh_3)_3(OTs)(\eta^2\text{-}C(O)CH{=}C(Cl)CH_2)$ (**5e**), respectively. The structure of **5d** (as **5d**·$0.5C_7H_8$) was determined by single-crystal X-ray diffraction analysis. Addition of two equivalents of AgOTf to **5a** and **5b**, or of one equivalent of AgOTf to **5d**, leads to the replacement of the remaining halide to afford the η^1-allenyl $Rh(SbPh_3)_2(CO)(OTf)_2(\eta^1\text{-}CH{=}C{=}CH_2)$ (**3e**). The reverse of the **5a** to **3e** conversion can be effected with chloride and $SbPh_3$; however, without added $SbPh_3$, the reaction affords the substitution product **3d** instead. Addition of excess pyridine or PPh_3 to **5a** yields the substitution products $Rh(SbPh_3)_2(py)Cl(\eta^2\text{-}C(O)CH{=}C(Cl)CH_2)$ (**9**) and five-coordinate, 16-electron $Rh(PPh_3)_2Cl(\eta^2\text{-}C(O)CH{=}C(Cl)CH_2)$ (**7**), respectively. A mechanism is proposed for the conversion of **1** and **2** to **5** and for the transformations between **5** and **3**.

Keywords: Rhodium complexes; η^1-Allenyl; η^1-Propargyl; Rhodiacyclopent-3-ene-2-one; Cycloaddition; X-ray structure

1. Introduction

Propargyl halides and tosylates react with transition metal carbonyl anions to afford metal η^1-propargyl and η^1-allenyl complexes [1–3]. They also undergo oxidative addition to various d^8 and d^{10} metal centers, especially those in phosphine complexes, to provide another general synthetic route to organometallic propargyls and allenyls [4–8]. The latter methodology has been successfully employed in the preparation of appropriate platinum(II), palladium(II), iridium(III) [4–7] and, to a lesser extent, rhodium(III) [8] complexes.

In order to further explore this chemistry of rhodium, we undertook a study of reactions of rhodium(I) complexes with propargyl halides and tosylates. Since the only reported preparative reactions of rhodium(I) with organic propargyls had utilized phosphine complexes as starting materials [8], we decided to expand the range of ligands to include stibines. Metal stibine complexes have not been much investigated in oxidative addition reactions, even though they are readily available for rhodium(I) [9]. For example, both $Rh(SbR_3)_2(CO)X$ and $Rh(SbR_3)_3(CO)X$ (X = Cl, Br; R = aryl) have been reported [10–15], with the latter

* Corresponding author. Tel.: +1-614-2924750; fax: +1-614-2921685.

E-mail address: wojcicki.1@osu.edu (A. Wojcicki).

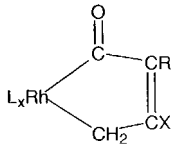
[1] Present address: Kocaeli Universitesi, Fen.-Ed. Fak., Kimya Bolumu, 41300 Izmit, Turkey.

[2] To whom inquiries concerning the crystallographic studies should be addressed.

0022-328X/01/$ - see front matter
PII: S0022-328X(01)00879-8

undergoing conversion to the former on repeated crystallization [15]. Square-planar $Rh(SbPh_3)_2(CO)Cl$ was successfully used by Chin [16] in the synthesis of rhodium(III) allyl complexes.

In this paper, we report on reactions of $Rh(SbPh_3)_3(CO)X$ (X = Cl (**1**), Br (**2**)) with propargyl halides and tosylates. Whereas reactions of **1** and **2** with the tosylates generally give the expected rhodium(III) η^1-allenyl and η^1-propargyl complexes, those with propargyl halides surprisingly afford rhodiacyclopent-3-ene-2-one products (**I**). Some η^1-allenyl and rhodiacyclic complexes were found to interconvert under appropriate experimental conditions. Part of this investigation was the subject of a preliminary communication [17].



I

2. Experimental

2.1. General procedures and measurements

All reactions and manipulations of air-sensitive compounds were carried out under an atmosphere of argon by using standard procedures [18]. Solvents were dried, distilled under argon and degassed before use. Hexane, benzene, THF and Et_2O were distilled from Na/K alloy and benzophenone, and CH_2Cl_2 from P_4O_{10}. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded on a Bruker AM-250, AC-300 and AC-200 spectrometers. IR spectra were obtained on a Perkin–Elmer 1600 Fourier transform spectrometer. Mass spectra (FAB) were recorded on a Kratos VG70-250S spectrometer by Mr David C. Chang. Conductance measurements on ca. 1 mM solutions of rhodium complexes in CH_2Cl_2 were carried out at room temperature with a YSI Model 35 conductivity apparatus.

2.2. Materials

Reagents were obtained from various commercial sources and used as received, except as noted below. Procedures reported in the literature were used to synthesize the organic propargyl compounds $RC{\equiv}CCH_2OTs$ (Ts = p-$MeC_6H_4SO_2$; R = H, Me) [19], $HC{\equiv}CCH_2OBs$ (Bs = $PhSO_2$) [19] and $MeC{\equiv}CCH_2Cl$ [4]. The complex $Rh(SbPh_3)_3(CO)Cl$ (**1**) [11–15] was prepared by the method of Vallarino [10], but without recrystallization, which causes loss of $SbPh_3$ and formation of $Rh(SbPh_3)_2(CO)Cl$ [15]. The analogous bromide $Rh(SbPh_3)_3(CO)Br$ (**2**) was obtained by reaction of **1** (1.2 g, 0.98 mmol) with LiBr (0.096 g, 1.1 mmol) in 30 ml of acetone at reflux temperature for 45 min, cooling to r.t. and removal of the solvent. Extraction of the solid residue with 40 ml of C_6H_6, filtration of the mixture to remove LiCl and excess LiBr, and evaporation to dryness of the filtrate yielded a red solid, which was dried under reduced pressure for 2 days. The product was characterized by comparison of its spectroscopic properties with those reported in the literature for **2** [15].

2.3. Reactions of $Rh(SbPh_3)_3(CO)X$ (X = Cl (**1**), Br (**2**)) with organic propargyl compounds

2.3.1. Reaction of **1** with $HC{\equiv}CCH_2OTs$

A stirred red solution of **1** (0.31 g, 0.25 mmol) in 15 ml of CH_2Cl_2 at r.t. was treated with solid $HC{\equiv}CCH_2OTs$ (0.22 g, 1.1 mmol). The solution immediately changed color to pale yellow and was stirred for an additional 30 min. The volume was then reduced to ca. 2 ml, and 25 ml of hexane was added to precipitate a yellow solid, $Rh(SbPh_3)_2(CO)Cl(OTs)(\eta^1$-$CH{=}C{=}CH_2)$ (**3a**). The product was collected by filtration, washed with hexane (2 × 10 ml) and dried in vacuo for 2 days. Yield: 0.22 g (80%). IR ($CHCl_3$, cm^{-1}): ν(CO) 2073. ^{1}H-NMR ($CDCl_3$): δ 8.0–6.9 (m, 34H, Ph, C_6H_4), 5.71 (q, 1H, $^4J_{HH} = {}^2J_{RhH} = 6.0$ Hz, CH), 4.17 (dd, 2H, $^4J_{HH} = 6.0$ Hz, $^4J_{RhH} = 1.3$ Hz, CH_2), 2.31 (s, 3H, Me). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 206.0 (s, =C=), 182.6 (d, $^1J_{RhC} = 62.6$ Hz, CO), 140.1–126.0 (m, Ph, C_6H_4), 72.1 (s, CH_2), 67.6 (d, $^1J_{RhC} = 24.4$ Hz, CH), 21.3 (s, Me). Anal. Found: C, 52.19; H, 3.76. Calc. for $C_{47}H_{40}ClO_4RhSSb_2$: C, 52.14; H, 3.72%.

2.3.2. Reaction of **1** with $HC{\equiv}CCH_2OBs$

Reaction between **1** (0.20 g, 0.16 mmol) and $HC{\equiv}CCH_2OBs$ (0.12 g, 0.61 mmol) was conducted similarly to that described above. Yield of $Rh(SbPh_3)_2(CO)Cl(OBs)(\eta^1$-$CH = C = CH_2)$ (**3b**), a yellow solid: 0.146 g (84%). IR ($CHCl_3$, cm^{-1}): ν(CO) 2078. ^{1}H-NMR ($CDCl_3$): δ 7.8–7.1 (m, 35H, Ph), 5.72 (q, 1H, $^4J_{HH} = {}^2J_{RhH} = 6.0$ Hz, CH), 4.19 (dd, 2H, $^4J_{HH} = 6.0$ Hz, $^4J_{RhH} = 1.3$ Hz, CH_2). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 206.0 (s, =C=), 182.7 (d, $^1J_{RhC} = 62.2$ Hz, CO), 141.5–126.6 (m, Ph), 72.3 (s, CH_2), 67.6 (d, $^1J_{RhC} = 24.4$ Hz, CH). FAB MS; m/z 1064 ($M^+ - 2$), 910 ($M^+ + 2 -$ OBs), 883 ($M^+ + 2 -$ OBs $-$ CO). $\Lambda_m = 1.01$ Ω^{-1} cm^2 mol^{-1}. Anal. Found: C, 51.50; H, 3.80. Calc. for $C_{46}H_{38}ClO_4RhSSb_2$: C, 51.70; H, 3.58%.

2.3.3. Reaction of **1** with $MeC{\equiv}CCH_2OTs$

Reaction between **1** (0.42 g, 0.34 mmol) and $MeC{\equiv}CCH_2OTs$ (0.10 g, 0.45 mmol) in CH_2Cl_2 (15 ml)

was carried out similarly to the preceding reactions. After 90 min of stirring at r.t., the reaction solution was filtered through Celite, and the filtrate was concentrated to ca. 1.5 ml. Addition of 20 ml of hexane to the filtrate afforded a yellow solid, which was washed with hexane (2 × 10 ml) and dried in vacuo. Yield: 0.29 g. The solid was shown by NMR spectroscopy to be a mixture of three products: $Rh(SbPh_3)_2(CO)Cl(OTs)(\eta^1\text{-}CH_2\text{-}C{\equiv}CMe)$ (**4**), $Rh(SbPh_3)_3Cl(\eta^2\text{-}C(O)C(Me){=}(OTs)CH_2)$ (**6a**) and $Rh(SbPh_3)_3(OTs)(\eta^2\text{-}C(O)C(Me){=}C(Cl)CH_2)$ (**6b**), in ca. 1:1:1 ratio, respectively. IR ($CHCl_3$, cm^{-1}): ν(CO) 2069 (**4**). ^{1}H-NMR (CD_2Cl_2): δ 7.8–6.8 (m, Ph, C_6H_4), 4.09 (br s, CH_2, **6b**), 3.45 (br s, CH_2, **6a**), 2.84 (m, CH_2, **4**), 2.46 (s, OTs *Me*, **6b**), 2.38 (s, OTs *Me*, **6a**), 2.30 (s, OTs *Me*, **4**), 1.48 (s, =C*Me*, **6b**), 1.11 (s, =C*Me*, **6a**), 1.04 (t, $^5J_{HH} = 2.7$ Hz, ≡C*Me*, **4**). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 227.8 (d, $^1J_{RhC} = 21.4$ Hz, C=O, **6a**), 220.5 (d, $^1J_{RhC} = 24.5$ Hz, C=O, **6b**), 183.4 (d, $^1J_{RhC} = 67.1$ Hz, CO, **4**), 173.8 (s, =*C*OTs, **6a**), 165.1 (s, =CCl, **6b**), 144.5 (s, =*C*Me, **6b**), 144.1 (s, =*C*Me, **6a**), 141.8–126.5 (m, Ph, C_6H_4), 89.6 (s, ≡*C*Me, **4**), 87.3 (s, ≡*C*CH_2, **4**), 29.8 (d, $^1J_{RhC} = 19.6$ Hz, CH_2, **6b**), 21.7 (s, OTs *Me*, **6a,b**), 21.4 (s, OTs *Me*, **4**), 20.4 (d, $^1J_{RhC} = 19.8$ Hz, CH_2, **6a**), 11.2 (s, =C*Me*, **6b**), 10.8 (s, =C*Me*, **6a**), 3.8 (s, ≡C*Me*, **4**), −5.4 (d, $^1J_{RhC} = 19.8$ Hz (CH_2, **4**). FAB MS; *m*/*z*: 925 ($M^+ + 2 - OTs$) (**4**).

2.3.4. Reaction of **1** with $HC{\equiv}CCH_2Cl$

A solution of **1** (0.20 g, 0.16 mmol) in 10 ml of CH_2Cl_2 was treated with $HC{\equiv}CCH_2Cl$ (0.101 g, 1.35 mmol), and the mixture was stirred at r.t. for 1 h. Work-up was as described for the initial reaction in this section. Yield of $Rh(SbPh_3)_3Cl(\eta^2\text{-}C(O)CH{=}C(Cl)CH_2)$ (**5a**), a green solid: 0.166 g (78%). IR ($CHCl_3$, cm^{-1}): ν(C=O) 1596. ^{1}H-NMR ($CDCl_3$): δ 7.4–6.9 (m, 45H, Ph), 5.64 (s, 1H, CH), 3.71 (s, 2H, CH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 230.0 (d, $^1J_{RhC} = 23.1$ Hz, C=O), 170.2 (s, =CCl), 140.4 (s, CH), 136.7–128.3 (m, Ph), 32.4 (d, $^1J_{RhC} = 21.4$ Hz, CH_2). FAB MS: *m*/*z*: 911 ($M^+ + 2 - Cl - SbPh_3$). $\Lambda_m = 0.07$ $\Omega^{-1}\,cm^2\,mol^{-1}$. Anal. Found: C, 53.58; H, 3.92. Calc. for $C_{58}H_{48}Cl_2ORhSb_3$: C, 53.58; H, 3.72%.

2.3.5. Reaction of **1** with $HC{\equiv}CCH_2Br$

A similarly conducted reaction between **1** (0.22 g, 0.18 mmol) and $HC{\equiv}CCH_2Br$ (0.160 g, 1.35 mmol) yielded 0.183 g (76%) of yellow $Rh(SbPh_3)_3Br(\eta^2\text{-}C(O)CH{=}C(Cl)CH_2)$ (**5b**) after work-up. IR ($CHCl_3$, cm^{-1}): ν(C=O) 1599. ^{1}H-NMR ($CDCl_3$): δ 7.4–6.9 (m, 45H, Ph), 5.65 (s, 1H, CH), 3.68 (s, 2H, CH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 230.4 (d, $^1J_{RhC} = 23.2$ Hz, C=O), 170.8 (s, =CCl), 140.6 (s, CH), 136.7–128.3 (m, Ph), 32.3 (d, $^1J_{RhC} = 21.5$ Hz, CH_2). FAB MS; *m*/*z*: 911 ($M^+ + 2 - Br - SbPh_3$). $\Lambda_m = 0.068$ $\Omega^{-1}\,cm^2\,mol^{-1}$. Anal. Found: C, 51.94; H, 3.49. Calc. for $C_{58}H_{48}BrClORhSb_3$: C, 51.81; H, 3.60%.

2.3.6. Reaction of **2** with $HC{\equiv}CCH_2Cl$

This reaction was conducted analogously to the immediately preceding one. The IR and NMR spectra of the product were identical with those of **5b** obtained from **1** and $HC{\equiv}CCH_2Br$.

2.3.7. Reaction of **2** with $HC{\equiv}CCH_2Br$

Propargyl bromide (0.240 g, 2.03 mmol) was added to a solution of **2** (0.31 g, 0.24 mmol) in 10 ml of CH_2Cl_2 at r.t. The resulting solution was stirred for 1 h and then treated the same as for the other reactions. Yield: 0.25 g of a yellow solid, which was shown spectroscopically to be a ca. 1:1 mixture of $Rh(SbPh_3)_3Br(\eta^2\text{-}C(O)CH{=}C(Br)CH_2)$ (**5c**) and $Rh(SbPh_3)_2(CO)Br_2(\eta^1\text{-}CH{=}C{=}CH_2)$ (**3c**). IR ($CHCl_3$, cm^{-1}): ν(CO) 2066 (**3c**), ν(C=O) 1596 (**5c**). ^{1}H-NMR ($CDCl_3$): δ 7.9–6.6 (m, Ph), 5.75 (d, $^3J_{RhH} = 0.8$ Hz, CH, **5c**), 5.65 (q, $^4J_{HH} = {}^2J_{RhH} = 5.9$ Hz, CH, **3c**), 3.91 (dd, $^4J_{HH} = 5.9$ Hz, $^4J_{RhH} = 1.3$ Hz, CH_2, **3c**), 3.88 (d, $^2J_{RhH} = 1.2$ Hz, CH_2, **5c**). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 231.1 (d, $^1J_{RhC} = 23.6$ Hz, C=O, **5c**), 206.2 (s, =C=, **3c**), 182.8 (d, $^1J_{RhC} = 62.4$ Hz, CO, **5c**), 161.3 (s, =CBr), 144.5 (d, $^2J_{RhC} = 5.2$ Hz, CH, **5c**), 137.1–128.3 (m, Ph), 71.6 (d, $^1J_{RhC} = 24.0$ Hz, CH, **3c**), 69.0 (s, CH_2, **3c**), 35.7 (d, $^1J_{RhC} = 21.6$ Hz, CH_2, **5c**).

2.3.8. Reaction of **1** with $MeC{\equiv}CCH_2Cl$

Reaction of **1** (1.0 g, 0.82 mmol) with $MeC{\equiv}CCH_2Cl$ (0.41 g, 4.6 mmol) was carried out similarly to the preceding reactions and utilized the same work-up. Yield, 1.0 g (93%) of a beige solid, $Rh(SbPh_3)_3Cl(\eta^2\text{-}C(O)C(Me){=}C(Cl)CH_2)$ (**6c**). IR (Nujol, cm^{-1}): ν(C=O) 1600. ^{1}H-NMR ($CDCl_3$): δ 7.4–6.9 (m, 45H, Ph), 3.78 (br s, 2H, CH_2), 1.31 (br s, 3H, Me). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 163.4 (s, =CCl), 146.4 (s, *C*Me), 136.7–128.2 (m, Ph), 30.4 (d, $^1J_{RhC} = 22.9$ Hz, CH_2), 12.9 (s, Me) (C=O signal was not observed because of low solubility of **6c**). FAB MS; *m*/*z*: 925 ($M^+ + 2 - Cl - SbPh_3$). Anal. Found: C, 54.07; H, 4.02. Calc. for $C_{59}H_{50}Cl_2ORhSb_3$: C, 53.93; H, 3.84%.

2.3.9. Reaction of **2** with $MeC{\equiv}CCH_2OTs$

Reaction of **2** (0.365 g, 0.287 mmol) with $MeC{\equiv}CCH_2OTs$ (0.10 g, 0.45 mmol), conducted similarly to the other reactions, yielded 0.275 g (64%) of $Rh(SbPh_3)_3Br(\eta^2\text{-}C(O)C(Me){=}C(OTs)CH_2)$ (**6d**) as a pale orange solid. ^{1}H-NMR ($CDCl_3$): δ 7.8–6.9 (m, 49H, Ph, C_6H_4), 3.49 (d, $^2J_{RhH} = 1.9$ Hz, 2H, CH_2), 2.37 (s, 3H, OTs *Me*), 1.28 (s, 3H, =C*Me*). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 228.1 (d, $^1J_{RhC} = 25.0$ Hz, C=O), 174.2 (s, =*C*OTs), 144.1 (s,=*C*Me), 140.6–127.3 (m, Ph, C_6H_4), 21.6 (s, OTs *Me*), 20.3 (d, $^1J_{RhC} = 21.7$ Hz, CH_2), 10.8 (s, =C*Me*).

2.4. Thermolysis of rhodiacyclic complexes **5**

2.4.1. Thermolysis of $Rh(SbPh_3)_3Br(\eta^2\text{-}C(O)CH{=}C(Br)CH_2)$ (**5c**)

A mixture of **5c** and $Rh(SbPh_3)_2(CO)Br_2(\eta^1\text{-}CH{=}C{=}CH_2)$ (**3c**) (0.250 g), obtained from **2** and $HC{\equiv}CCH_2Br$ (vide supra), was dissolved in 10 ml of THF, and the resulting solution was stirred at 60 °C for 1 h. After cooling to r.t. and concentration of the solution to ca. 2 ml, hexane (20 ml) was added to induce the precipitation of an orange solid. The solid was washed with 10 ml of hexane and dried in vacuo for 2 days. The IR and ^{1}H-NMR spectra showed the presence of pure **3c**.

2.4.2. Thermolysis of $Rh(SbPh_3)_3Cl(\eta^2\text{-}C(O)CH{=}C(Cl)CH_2)$ (**5a**)

A solution of **5a** (0.22 g, 0.17 mmol) in 15 ml of THF was maintained at 60 °C with stirring for 16 h. The work-up was identical with that in the immediately preceding experiment and resulted in the isolation of a yellow solid. A ^{1}H-NMR spectrum of this solid showed ca. 3:1 mixture of **5a** and $Rh(SbPh_3)_2(CO)Cl_2(\eta^1\text{-}CH{=}C{=}CH_2)$ (**3d**). The solid was then extracted with a mixture of methanol (2 ml) and Et_2O (3 ml), and a green residue (pure **5a**) was removed by filtration. The filtrate was evaporated to dryness to leave a yellow solid, **3d**. Yield: 0.048 g (30%). IR (CD_2Cl_2, cm^{-1}): ν(CO) 2066. ^{1}H-NMR (CD_2Cl_2): δ 7.7–7.0 (m, 30H, Ph), 5.49 (q, 1H, $^4J_{HH} = {}^2J_{RhH} = 5.9$ Hz, CH), 3.95 (dd, 2H, $^4J_{HH} = 5.9$ Hz, $^4J_{RhH} = 1.2$ Hz, CH_2).

2.5. Reactions of rhodiacyclic complexes **5** with silver(I) salts

2.5.1. Reaction of $Rh(SbPh_3)_3Cl(\eta^2\text{-}C(O)CH{=}C(Cl)CH_2)$ (**5a**) with silver triflate

Silver triflate (AgOTf, $Tf = CF_3SO_2$; 0.037 g, 0.14 mmol, one equivalent) was added to a solution of **5a** (0.18 g, 0.14 mmol) in 10 ml of CH_2Cl_2, and the mixture was stirred at r.t. for 75 min. AgCl was filtered off, the filtrate was concentrated to ca. 5 ml, and 5 ml of hexane was added with stirring. The resulting mixture was filtered again, and the filtrate was evaporated to dryness. Crystallization of the residue from CH_2Cl_2–hexane afforded a green solid (0.19 g, 97% yield), $Rh(SbPh_3)_3(OTf)(\eta^2\text{-}C(O)CH{=}C(Cl)CH_2)$ (**5d**), which was dried in vacuo for 2 days. IR ($CHCl_3$, cm^{-1}): ν(C=O) 1613. ^{1}H-NMR ($CDCl_3$): δ 7.3–6.9 (m, 45H, Ph), 5.82 (s, 1H, CH), 3.93 (s, 2H, CH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 217.7 (d, $^1J_{RhC} = 22.7$ Hz, C=O), 172.3 (s, =CCl), 137.6 (s, CH), 136.6–128.2 (m, Ph), 32.1 (d, $^1J_{RhC} = 22.4$ Hz, CH_2). $\Lambda_m = 5.13$ Ω^{-1} cm^2 mol^{-1}. Anal. Found: C, 50.62; H, 3.70. Calc. for $C_{59}H_{48}ClF_3O_4RhSSb_3$: C, 50.13; H, 3.42%.

2.5.2. Reaction of $Rh(SbPh_3)_3Br(\eta^2\text{-}C(O)CH{=}C(Cl)CH_2)$ (**5b**) with silver triflate

Reaction between **5b** (0.15 g, 0.11 mmol) and AgOTf (0.029 g, 0.11 mmol, one equivalent) was conducted very similarly to that between **5a** and AgOTf. The precipitated AgBr was qualitatively analyzed for bromide by treatment with nitric acid, 1,2-dichloroethane and 3% H_2O_2 to afford bromine in the organic layer. The product $Rh(SbPh_3)_3(OTf)(\eta^2\text{-}C(O)CH{=}C(Cl)CH_2)$ (**5d**) was isolated in 95% yield (0.15 g) and characterized by comparison of its spectroscopic properties with those of the **5d** obtained from the immediately preceding reaction.

2.5.3. Reaction of $Rh(SbPh_3)_3(OTf)(\eta^2\text{-}C(O)CH{=}C(Cl)CH_2)$ (**5d**) with silver triflate

A solution containing **5d** (0.297 g, 0.210 mmol) and AgOTf (0.055 g, 0.21 mmol, one equivalent) in 10 ml of CH_2Cl_2 was stirred at r.t. for 75 min, filtered, concentrated and treated with 20 ml of hexane. The precipitated green solid was filtered off, washed with hexane (10 ml) and dried in vacuo. Yield of $Rh(SbPh_3)_2(CO)(OTf)_2(\eta^1\text{-}CH{=}C{=}CH_2)$ (**3e**), 0.212 g (86%). IR ($CHCl_3$, cm^{-1}): ν(CO) 2080, ν(C=C=C) 2012. ^{1}H-NMR ($CDCl_3$): δ 7.8–6.9 (m, 30H, Ph), 5.70 (q, 1H, $^4J_{HH} = {}^2J_{RhH} = 5.8$ Hz, CH), 4.38 (d, 2H, $^4J_{HH} = 5.8$ Hz, CH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 207.2 (s, =C=), 179.5 (d, $^1J_{RhC} = 68.5$ Hz, CO), 136.7–126.0 (m, Ph), 76.9 (s, CH_2), 71.4 (d, $^1J_{RhC} = 24.6$ Hz, CH).

3e was also obtained, in comparable yield, directly from either $Rh(SbPh_3)_3Cl(\eta^2\text{-}C(O)CH{=}C(Cl)CH_2)$ (**5a**) or $Rh(SbPh_3)_3Br(\eta^2\text{-}C(O)CH{=}C(Cl)CH_2)$ (**5b**) by reaction with two equivalents of AgOTf in CH_2Cl_2 at r.t. The experimental procedures were very similar to those of the two immediately preceding reactions.

2.5.4. Reaction of $Rh(SbPh_3)_3Br(\eta^2\text{-}C(O)CH{=}C(Cl)CH_2)$ (**5b**) with silver tosylate

Silver tosylate (0.028 g, 0.10 mmol, one equivalent) was added to a solution of **5b** (0.135 g, 0.10 mmol) in 10 ml of CH_2Cl_2, and the mixture was stirred at r.t. for 90 min. The solution was then filtered to remove AgBr, which was qualitatively analyzed for bromide by oxidation to bromine with H_2O_2–HNO_3 in the presence of 1,2-dichloroethane (vide supra). The filtrate was concentrated to ca. 5 ml, and 5 ml of hexane was added. After another filtration, the solvent was evaporated from the filtrate, and the solid residue was dried in vacuo. Yield of pale green $Rh(SbPh_3)_3(OTs)(\eta^2\text{-}C(O)CH{=}C(Cl)CH_2)$ (**5e**): 0.14 g (97%). IR ($CHCl_3$, cm^{-1}): ν(C=O) 1607. ^{1}H-NMR ($CDCl_3$): δ 7.8–6.7 (m, 49H, Ph, C_6H_4), 5.82 (s, 1H, CH), 4.13 (s, 2H, CH_2), 2.44 (s, 3H, Me). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 222.7 (d, $^1J_{RhC} = 22.2$ Hz, C=O), 172.5 (s, =CCl), 139.5 (s, CH), 141.7–126.6 (m, Ph, C_6H_4), 31.9 (d, $^1J_{RhC} = 21.3$ Hz, CH_2), 21.4 (s, Me). $\Lambda_m = 0.61$ Ω^{-1} cm^2 mol^{-1}. Anal.

Found: C, 54.96; H, 3.99. Calc. for $C_{65}H_{55}ClO_4RhSSb_3$: C, 54.37; H, 3.86%.

2.6. Reactions of rhodium complexes **3** and **5** with chloride salts

2.6.1. Reaction of $Rh(SbPh_3)_2(CO)(OTf)_2$-(η^1-CH=C=CH_2) (**3e**) with [(n-Bu)$_4$N]Cl

A solution of **3e** (0.20 g, 0.17 mmol) and [(*n*-Bu)$_4$N]Cl (0.096 g, 0.34 mmol, two equivalents) in 10 ml of CH_2Cl_2 was stirred at r.t. for 4 h. The solvent was then evaporated, and the solid residue was extracted with cold methanol (3 × 3 ml). The extracts containing [(*n*-Bu)$_4$N]OTf were separated from the solid by decantation and discarded. The remaining solid was dissolved in 3 ml of Et_2O, and the solution was filtered. The filtrate was evaporated to dryness under reduced pressure to leave a yellow solid (0.064 g, 40% yield), which was dried in vacuo. Its IR and ^{1}H-NMR spectra were identical with those of the $Rh(SbPh_3)_2(CO)Cl_2(\eta^1$-CH=C=$CH_2$) (**3d**) obtained by thermolysis of $Rh(SbPh_3)_3Cl(\eta^2$-C(O)CH=C(Cl)CH_2) (**5a**).

2.6.2. Reaction of $Rh(SbPh_3)_2(CO)(OTf)_2$-(η^1-CH=C=CH_2) (**3e**) with [(n-Bu)$_4$N]Cl and $SbPh_3$

A solution containing **3e** (0.20 g, 0.17 mmol), [(*n*-Bu)$_4$N]Cl (0.096 g, 0.34 mmol, two equivalents) and $SbPh_3$ (0.060 g, 0.17 mmol) in 10 ml of CH_2Cl_2 was stirred at r.t. for 4 h and then evaporated to dryness. The residue was extracted with MeOH (3 × 3 ml), and the mixture was filtered. The extracts were discarded, and the remaining solid was recrystallized from CH_2Cl_2–hexane and dried in vacuo. Yield: 0.15 g (68%) of $Rh(SbPh_3)_3Cl(\eta^2$-C(O)CH=C(Cl)CH_2) (**5a**). The product was characterized by the comparison of its spectroscopic properties with those of an authentic **5a**.

2.6.3. Reaction of $Rh(SbPh_3)_3(OTf)(\eta^2$-C(O)-CH=C(Cl)CH_2) (**5d**) with [(n-Bu)$_4$N]Cl

Reaction between **5d** (0.235 g, 0.166 mmol) and [(*n*-Bu)$_4$N]Cl (0.047 g, 0.17 mmol, one equivalent) was conducted similarly to the immediately preceding reaction. The solid product was recrystallized from CH_2Cl_2–hexane to afford 0.098 g (45% yield) of $Rh(SbPh_3)_3Cl(\eta^2$-C(O)CH=C(Cl)CH_2) (**5a**), which was characterized by comparison of its IR and ^{1}H-NMR spectra with those of the **5a** obtained from **1** and propargyl chloride.

2.6.4. Reaction of $Rh(SbPh_3)_3Br(\eta^2$-C(O)C(Me)=C(OTs)CH_2) (**6d**) with [(n-Bu)$_4$N]Cl

A solution of **6d** (0.163 g, 0.109 mmol) and [(*n*-Bu)$_4$N]Cl (0.031 g, 0.11 mmol, one equivalent) in 10 ml of CH_2Cl_2 was stirred at r.t. for 4 h. It was then filtered, the filtrate was concentrated to ca. 1.5 ml, and a pale orange solid was precipitated with 10 ml of MeOH. The solid was filtered off, washed with 5 ml of hexane and dried in vacuo. Yield, 0.10 g (68%) of $Rh(SbPh_3)_3Br(\eta^2$-C(O)C(Me)=C(Cl)CH_2) (**6e**). IR ($CHCl_3$, cm^{-1}): ν(C=O) 1586. ^{1}H-NMR ($CDCl_3$): δ 7.5–6.9 (m, 45H, Ph), 3.77 (s, 2H, CH_2), 1.32 (s, 3H, Me). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 228.9 (d, $^1J_{RhC}$ = 26.4 Hz, C=O), 163.9 (s, =CCl), 146.5 (s, =*C*Me), 136.9–128.2 (m, Ph), 30.3 (d, $^1J_{RhC}$ = 21.1 Hz, CH_2), 12.9 (s, Me).

2.7. Reactions of rhodiacyclic complexes **5** and **6** with triphenylphosphine

2.7.1. Reaction of $Rh(SbPh_3)_3Cl(\eta^2$-C(O)CH=C(Cl)CH_2) (**5a**) with PPh_3

A solution of **5a** (0.42 g, 0.32 mmol) and PPh_3 (0.25 g, 0.96 mmol) in 15 ml of CH_2Cl_2 was stirred at r.t. for 3 h and then concentrated to 3 ml under reduced pressure. Addition of 20 ml of hexane induced the precipitation of a green solid, $Rh(PPh_3)_2Cl(\eta^2$-C(O)CH=C(Cl)CH_2) (**7**), which was collected on a filter frit, washed with hexane (2 × 15 ml) and dried in vacuo. Yield: 0.18 g (75%). IR ($CHCl_3$, cm^{-1}): ν(C=O) 1648. ^{1}H-NMR ($CDCl_3$): δ 7.5–7.2 (m, 30H, Ph), 4.84 (s, 1H, CH), 2.64 (m, 2H, CH_2). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 29.56 (d, $^1J_{RhP}$ = 123.8 Hz). FAB MS; *m*/*z*: 729 ($M^+ - Cl$), 701 ($M^+ - Cl - CO$), 662 ($M^+ - Cl - C_4H_3O$), 627 ($M^+ - 2Cl - C_4H_3O$). Anal. Found: C, 62.58; H, 4.50. Calc. for $C_{40}H_{33}Cl_2OP_2Rh$: C, 62.76; H, 4.35%.

2.7.2. Reaction of $Rh(SbPh_3)_3Cl(\eta^2$-C(O)C(Me)=C(Cl)CH_2) (**6c**) with PPh_3

The procedure employed was very similar to that for the immediately preceding reaction. By using 0.20 g (0.15 mmol) of **6c** and 0.11 g (0.42 mmol) of PPh_3, 0.087 g (73% yield) of a beige solid, $Rh(PPh_3)_2Cl(\eta^2$-C(O)C(Me)=C(Cl)CH_2) (**8**), was obtained after recrystallization from CH_2Cl_2–hexane. IR ($CHCl_3$, cm^{-1}): ν(C=O) 1631. ^{1}H-NMR ($CDCl_3$): δ 7.7–7.3 (m, 30H, Ph), 2.81 (br s, 2H, CH_2), 0.85 (s, 3H, Me). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 29.12 (d, $^1J_{RhP}$ = 124.2 Hz). FAB MS; *m*/*z*: 743 ($M^+ - Cl$), 662 ($M^+ - Cl - C_5H_5O$), 627 ($M^+ - 2Cl - C_5H_5O$).

2.8. Reaction of $Rh(SbPh_3)_3Cl(\eta^2$-C(O)CH=C(Cl)CH_2) (**5a**) with pyridine

Pyridine (0.073 g, 0.93 mmol) was added to a solution of **5a** (0.20 g, 0.15 mmol) in 10 ml of CH_2Cl_2, and the resulting solution was stirred at r.t. for 30 min and then concentrated to ca. 1.5 ml under reduced pressure. Addition of hexane (20 ml) induced the precipitation of a light green solid, which was collected on a filter frit and washed with hexane (2 × 5 ml). After recrystallization from CH_2Cl_2–hexane, the product was dried in vacuo. Yield: 0.12 g, (76%) of $Rh(SbPh_3)_2(py)Cl(\eta^2$-C(O)CH=C(Cl)$CH_2$) (**9**). IR ($CHCl_3$, cm^{-1}): ν(C=O)

1606. ^{1}H-NMR ($CDCl_3$): δ 9.1–8.9, 7.7–7.0 (dd, m, 35H, py, Ph), 5.69 (s, 1H, CH), 3.56 (d, $^2J_{HH} = 17.4$ Hz, 1H of CH_2), 2.77 (d, $^2J_{HH} = 17.4$ Hz, 1H of CH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 234.4 (d, $^1J_{RhC} = 26.6$ Hz, C=O), 170.2 (s, =CCl), 153.9–151.7 (2s, py), 137.6–124.1 (m, Ph, py), 28.1 (d, $^1J_{RhC} = 24.2$ Hz, CH_2) (CH signal was not identified). FAB MS; m/z: 911 ($M^+ + 2 - Cl - py$). Anal. Found: C, 51.98; H, 4.02. Calc. for $C_{45}H_{38}Cl_2NORhSb_2$: C, 52.67; H, 3.73%.

2.9. Crystallographic analysis of $Rh(SbPh_3)_3(OTf)(\eta^2\text{-}C(O)CH{=}C(Cl)CH_2)\cdot 0.5C_7H_8$ (**5d**·0.5C_7H_8)

Crystals of **5d**·0.5C_7H_8 were grown by slow diffusion of hexane into a solution of **5d** in toluene. The crystal used for data collection was a rectangular rod in shape. Examination of the diffraction pattern on a Rigaku AFC5S diffractometer indicated a monoclinic crystal system. Based on the systematic absences, $0k0$, $k \neq 2n$, and $h0l$, $h + l \neq 2n$, the space group was uniquely determined as $P2_1/n$. Unit cell constants were obtained by a least-squares fit of the setting angles for 25 reflections in the 2θ range 21–30° with Mo–Kα radiation ($\lambda(K\alpha_1) =$ 0.70930 Å). Six standard reflections were measured during data collection and showed a non-uniform decrease in intensity, especially above 2θ of 45°. Data reduction was done with the TEXSAN package [20]. No decay correction was applied to the data. An empirical ψ scan absorption correction [21] was applied to the data with transmission factors of 0.899–1.0. The data set was truncated at 45° in 2θ because of two factors: the non-uniform decay of the standards mentioned above and the fact that reflections in the 45–50° shell were very weak.

The structure was solved by starting with the direct methods procedure in SHELXS-86 [22] and then using several cycles of structure factor/Fourier calculations to elucidate the whole molecule. Full-matrix least-squares refinements based on F^2 were performed in SHELXL-93 [23]. There is also a molecule of toluene in the asymmetric unit, which appears to be disordered. The phenyl ring portion of the toluene was modeled as a rigid group and the occupancy factor for this molecule was set to 0.5. The Rh complex was refined anisotropically and the toluene molecule was refined isotropically. The hydrogen atoms were included in the model at calculated positions with C–H = 0.98 Å and fixed. The final refinement cycle was based on the 6923 intensities with $I > 0$ and 666 variables and resulted in agreement factors of $R_1 = 0.053$ and $wR_2 = 0.140$ for the 4989 reflections with $I > 2\sigma(I)$. The final difference electron density map contains maximum and minimum peak heights of 0.96 and -0.75 e Å^{-3}. Neutral atom scattering factors were used and include terms for anomalous dispersion [24]. A summary of the crystal data and the details of the intensity data collection and refinement are provided in Table 1.

Table 1
Crystal data and structure refinement parameters for **5d**·0.5C_7H_8

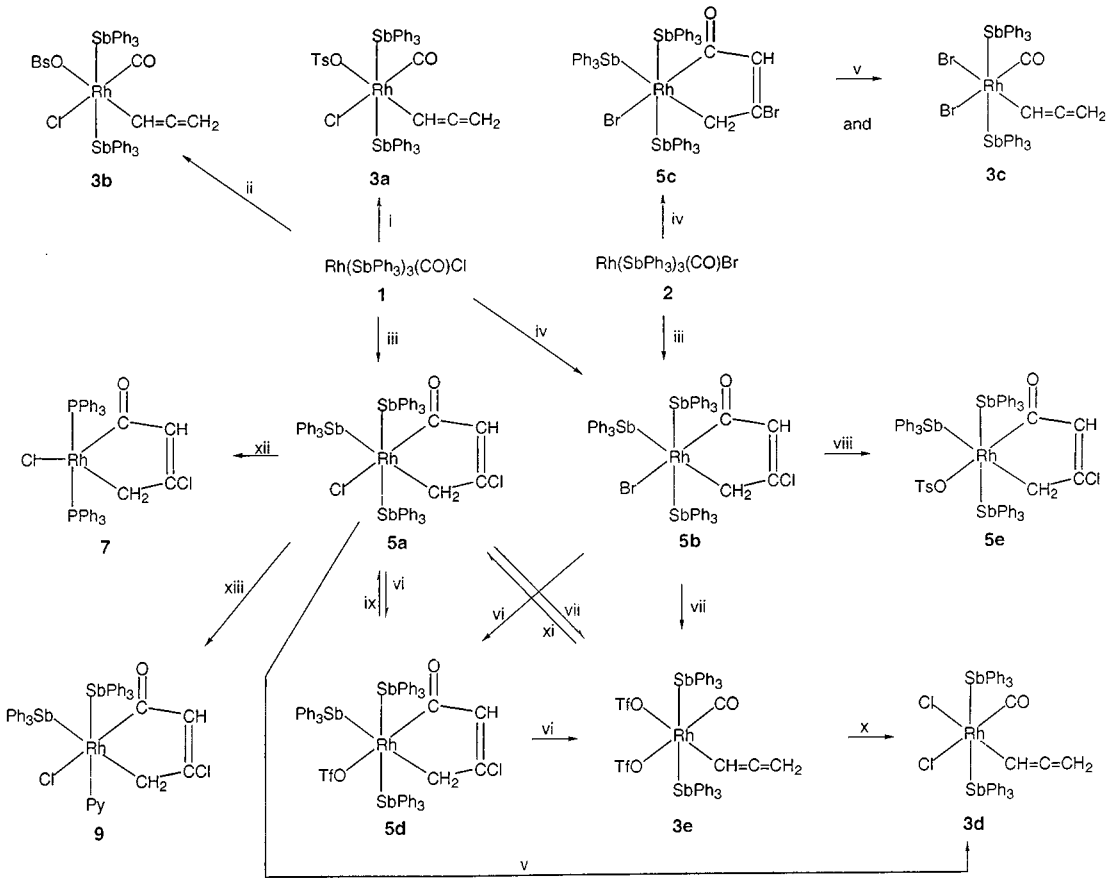
Empirical formula	$C_{59}H_{48}ClF_3O_4RhSSb_3\cdot 0.5C_7H_8$
Formula weight	1459.71
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	17.518(4)
b (Å)	16.588(4)
c (Å)	21.962(4)
β (°)	99.47(2)
V (Å^3)	6295(2)
Z	4
D_{calc} (g cm^{-3})	1.540
Crystal size (mm)	0.19 × 0.19 × 0.31
Absorption coefficient (mm^{-1})	1.658
Data collection range in θ (°)	2.04–22.50
Index ranges	$0 \leq h \leq 18$, $0 \leq k \leq 17$, $-23 \leq l \leq 23$
Reflections collected	8948
Independent reflections (R_{int})	8619 [$R_{int} = 0.054$]
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	6923/0/666
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.053$, $wR_2 = 0.140$
R indices (all data)	$R_1 = 0.085$, $wR_2 = 0.152$
Goodness-of-fit on F^2	1.032
Largest difference peak and hole (e Å^{-3})	0.956 and -0.753

3. Results and discussion

3.1. Reaction chemistry

Reactions of the five-coordinate rhodium(I) complexes $Rh(SbPh_3)_3(CO)X$ (X = Cl (**1**), Br (**2**)) with organic propargyl compounds HC≡CCH_2Y as well as the chemistry of the resultant products are set out in Scheme 1. The corresponding reaction chemistry starting with **1** or **2** and organic methylpropargyl compounds MeC≡CCH_2Y is presented in Scheme 2.

Treatment of **1** in CH_2Cl_2 at room temperature with an excess of HC≡CCH_2OTs or HC≡CCH_2OBs affords the rhodium(III) η^1-allenyl complexes $Rh(SbPh_3)_2(CO)Cl(OTs)(\eta^1\text{-}CH{=}C{=}CH_2)$ (**3a**) and $Rh(SbPh_3)_2(CO)Cl(OBs)(\eta^1\text{-}CH{=}C{=}CH_2)$ (**3b**), respectively, as yellow solids in 80–84% yield. This behavior parallels that generally observed for reactions of metal complexes with the unsubstituted propargyl compounds which yield η^1-allenyl oxidative addition products [1,4,6–8,25]. In contrast to the foregoing, reaction of **1** with an excess of HC≡CCH_2Cl or HC≡CCH_2Br under comparable conditions surprisingly leads to the formation of the rhodiacyclopent-3-ene-2-one complexes $Rh(SbPh_3)_3Cl(\eta^2\text{-}C(O)CH{=}C(Cl)CH_2)$ (**5a**) and Rh



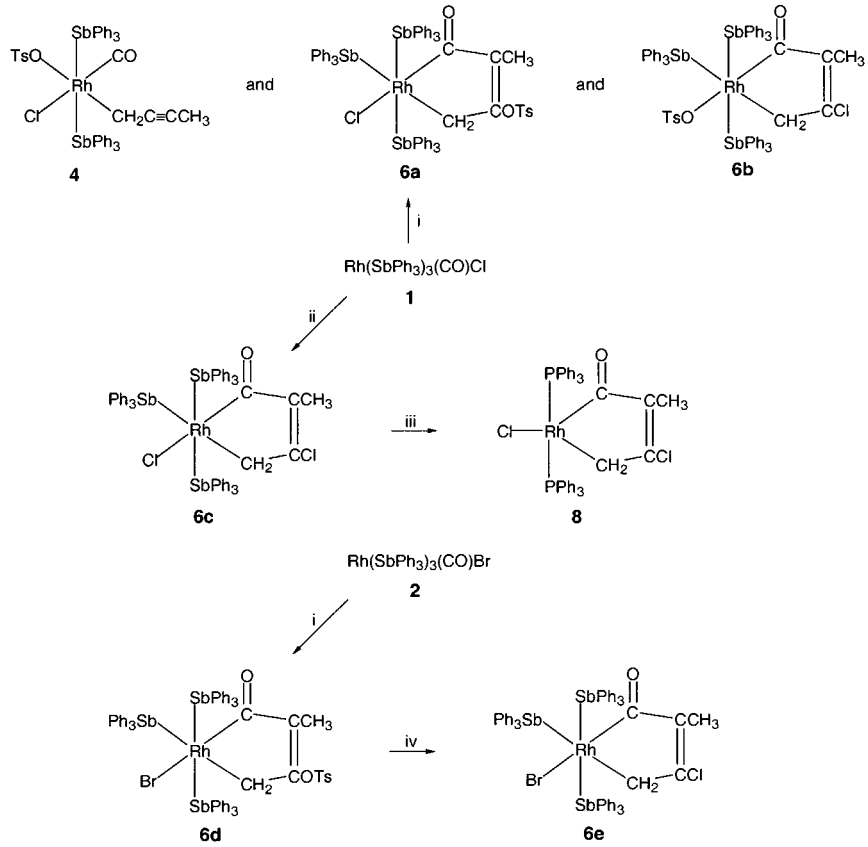
Scheme 1. (i) $HC{\equiv}CCH_2OTs$; (ii) $HC{\equiv}CCH_2OBs$; (iii) $HC{\equiv}CCH_2Cl$; (iv) $HC{\equiv}CCH_2Br$; (v) thermolysis at 60 °C; (vi) one equivalent AgOTf; (vii) two equivalents AgOTf; (viii) one equivalent AgOTs; (ix) one equivalent $[(n\text{-}Bu)_4N]Cl$; (x) two equivalents $[(n\text{-}Bu)_4N]Cl$; (xi) two equivalents $[(n\text{-}Bu)_4N]Cl$, $SbPh_3$; (xii) PPh_3; (xiii) pyridine.

$(SbPh_3)_3Br(\eta^2\text{-}C(O)CH{=}C(Cl)CH_2)$ (**5b**) as green and yellow solids, respectively, in ca. 75% yield. A similar oxidative addition reaction of **2** with $HC{\equiv}CCH_2Cl$ also affords **5b** in comparable yield. However, reaction of **2** with $HC{\equiv}CCH_2Br$ generates a mixture (ca. 1:1) of the rhodiacyclopent-3-ene-2-one complex $Rh(SbPh_3)_3Br(\eta^2\text{-}C(O)CH{=}C(Br)CH_2)$ (**5c**) and the η^1-allenyl $Rh(SbPh_3)_2(CO)Br_2(\eta^1\text{-}CH{=}C{=}CH_2)$ (**3c**). Several metallacyclopent-3-ene-2-one complexes, including those of rhodium(III), have been reported; however, they were all obtained by methods very different from those for **5a**–**5c** [26–31].

The new rhodiacyclics **5a** and **5b** undergo a number of substitution reactions at rhodium. Thus, coordinated chloride or bromide can be replaced with triflate or tosylate by use of the soluble salts AgOTf or AgOTs. In this manner, each of **5a** and **5b** was converted to $Rh(SbPh_3)_3(OTf)(\eta^2\text{-}C(O)CH{=}C(Cl)CH_2)$ (**5d**), and **5b** was transformed to $Rh(SbPh_3)_3(OTs)(\eta^2\text{-}C(O)CH{=}C(Cl)CH_2)$ (**5e**), with one equivalent of AgOTf and AgOTs, respectively. The two products were isolated in high (86–97%) yield. The substitution reaction was shown to be reversible by conversion of **5d** back to **5a** with one equivalent of $[(n\text{-}Bu)_4N]Cl$ in CH_2Cl_2.

The rhodiacyclic complex **5a** also undergoes substitution of $SbPh_3$ by pyridine or PPh_3. Accordingly, reaction of **5a** with an excess of pyridine in CH_2Cl_2 at room temperature affords 76% $Rh(SbPh_3)_2(py)Cl(\eta^2\text{-}C(O)CH{=}C(Cl)CH_2)$ (**9**) in which one of the *trans* $SbPh_3$ ligands of **5a** was replaced with pyridine. In contrast, reaction of **5a** with a threefold excess of PPh_3 in CH_2Cl_2 at ambient temperature yields a five-coordinate, 16-electron rhodiacyclic complex, $Rh(PPh_3)_2Cl(\eta^2\text{-}C(O)CH{=}C(Cl)CH_2)$ (**7**), which contains two *trans* phosphines. Related rhodiacyclopent-3-ene-2-one complexes of the general formula $Rh(PPh_3)_2Cl(\eta^2\text{-}C(O)C(R){=}C(R')CH_2)$ were synthesized by Liebeskind and co-workers [29,30] by the application of other methodologies.

Thermolysis of rhodiacyclic complexes **5** results in the formation of the corresponding η^1-allenyls **3**. When a ca. 1:1 mixture of **3c** and **5c**, obtained from **2** and $HC{\equiv}CCH_2Br$ (vide supra), was heated in THF solution at 60 °C for 1 h, all of **5c** converted to **3c**. A similar treatment of **5a** for 16 h afforded a 30% conversion to the η^1-allenyl $Rh(SbPh_3)_2(CO)Cl_2(\eta^1\text{-}CH{=}C{=}CH_2)$ (**3d**), with the rest of the rhodiacyclopent-3-ene-2-one complex remaining unchanged.



Scheme 2. (i) $MeC{\equiv}CCH_2OTs$; (ii) $MeC{\equiv}CCH_2Cl$; (iii) PPh_3, (iv) $[(n\text{-}Bu)_4N]Cl$.

Conversion of **5** to **3** has also been effected by use of AgOTf. Accordingly, reaction of **5a** or **5b** with two equivalents of AgOTf, or of **5d** with one equivalent of AgOTf, all in CH_2Cl_2 solution at ambient temperature, results in a loss of one $SbPh_3$ ligand, replacement of all halide with triflate, and rearrangement to the six-coordinate η^1-allenyl complex $Rh(SbPh_3)_2(CO)(OTf)_2(\eta^1\text{-}CH{=}C{=}CH_2)$ (**3e**), which was isolated as a green solid in 85–90% yield. Stirring a solution of **3e** and two equivalents of $[(n\text{-}Bu)_4N]Cl$ in THF at room temperature afforded complete substitution of triflate by chloride to give **3d**, which is also accessible directly from **5a** by thermolysis (vide supra). The reverse of the thermolysis reaction of **5**, viz., transformation of the η^1-allenyl complexes **3** to the rhodiacycles **5**, was accomplished in 68% yield for **3e** to **5a** by treatment with two equivalents of $[(n\text{-}Bu)_4N]Cl$ and one equivalent of $SbPh_3$ in CH_2Cl_2 solution at room temperature for 4 h.

Reactions of **1** and **2** with methylpropargyl chloride and tosylate ($MeC{\equiv}CCH_2Y$) are similar to those with the corresponding unsubstituted propargyl compounds $HC{\equiv}CCH_2Y$; nevertheless, some differences have been noted. Thus, treatment of **1** with an excess of $MeC{\equiv}CCH_2OTs$ in CH_2Cl_2 at room temperature affords a mixture of the η^1-propargyl $Rh(SbPh_3)_2(CO)Cl(OTs)(\eta^1\text{-}CH_2C{\equiv}CMe)$ (**4**) and what appear to be two regioisomers of rhodiacyclopent-3-ene-2-one that differ in the location of Cl and OTs—$Rh(SbPh_3)_3Cl(\eta^2\text{-}C(O)C(Me){=}C(OTs)CH_2)$ (**6a**) and $Rh(SbPh_3)_3(OTs)(\eta^2\text{-}C(O)C(Me){=}C(Cl)CH_2)$ (**6b**)—in an approximate 1:1:1 ratio. Crystallization of this mixture from CH_2Cl_2–hexane increases the relative amount of **4**. The formation of the η^1-propargyl **4** rather than a corresponding rhodium(III) η^1-allenyl conforms to the generally observed outcome of reactions of metal complexes with organic propargyl compounds upon alkyl or aryl substitution at the latter's carbon [2,32,33]. In contrast to the aforementioned reaction, the bromide complex **2** and $MeC{\equiv}CCH_2OTs$ afford under comparable conditions only the rhodiacycle $Rh(SbPh_3)_3Br(\eta^2\text{-}C(O)C(Me){=}C(OTs)CH_2)$ (**6d**), where tosylate is a substituent on the ring and bromide remains bonded to rhodium. Treatment of **6d** with $[(n\text{-}Bu)_4N]Cl$ gives $Rh(SbPh_3)_3Br(\eta^2\text{-}C(O)C(Me){=}C(Cl)CH_2)$ (**6e**) by replacement of OTs with Cl.

Reaction of **1** with $MeC{\equiv}CCH_2Cl$, like that of **1** with $HC{\equiv}CCH_2Cl$, yields a rhodiacyclic product, now $Rh(SbPh_3)_3Cl(\eta^2\text{-}C(O)C(Me){=}C(Cl)CH_2)$ (**6c**). Complex **6c** reacts with a ca. threefold excess of PPh_3 to form five-coordinate $Rh(PPh_3)_2Cl(\eta^2\text{-}C(O)C(Me){=}C(Cl)CH_2)$ (**8**), in which two PPh_3 ligands replace three $SbPh_3$

ligands in **6c**. Product **8** appears to be structurally analogous to **7**.

3.2. Characterization of products

All new complexes were characterized by a combination of IR and NMR (^{1}H-, ^{13}C{^{1}H}- and ^{31}P{^{1}H}-) spectroscopy, FAB mass spectrometry, conductance measurements and elemental analysis. The structures of **5a**, **5b** (as **5b**·0.5CH_2Cl_2) and **5d** (as **5d**·0.5C_7H_8) were elucidated by X-ray diffraction techniques.

For complexes **3**, the presence of an η^1-CH=C=CH_2 ligand is evidenced in the ^{1}H-NMR spectrum by the appearance of a quartet at δ 5.72–5.56 ($^4J_{HH} \sim {}^2J_{RhH} = 5.8–6.0$ Hz) for the CH proton and of a doublet of doublets at δ 4.38–3.91 ($^4J_{HH} = 5.8–6.0$ Hz, $^4J_{RhH} = 1.2–1.3$ Hz) for the CH_2 protons. The positions of these signals and the values of $^4J_{HH}$ are in good agreement with the corresponding data reported for a number of transition metal η^1-allenyl complexes [2,4,25,34–36]. Further support for this ligand formulation is furnished by the ^{13}C{^{1}H}-NMR spectra, which show resonances at δ 207.2–206.0 (=C=), 76.9–69.0 (CH_2) and 71.6–67.6 (CH, $^1J_{RhC} = 24.0–24.6$ Hz), all consistent with the η^1-allenyl assignment [2,25,34–36]. The ^{13}C{^{1}H}-NMR spectra also show a signal at δ 182.8–179.5 as a doublet with $^1J_{RhC} = 62.2–68.5$ Hz, which is assigned to a CO ligand. The presence of CO is confirmed by a strong IR ν(CO) absorption at 2080–2065 cm^{-1}. The proposed ligand stereochemistry of **3** is based on the assumed *trans* oxidative addition of HC=C=CH_2 and X to a square planar Rh center, formed by dissociation of one $SbPh_3$ ligand from five-coordinate **1** or **2**. A recent structure determination of a six-coordinate iridium(III) η^1-allenyl complex, $Ir(PPh_3)_2(CO)(NHSO_2Ph)Cl(\eta^1$-CH=C=$CH_2)$ [36], supports this assignment. Molar conductivity measurements on complex **3b** show it to be essentially unionized in CH_2Cl_2 solution ($\Lambda_m = 1.01\ \Omega^{-1}\ cm^2\ mol^{-1}$). Comparable Λ_m values were obtained for structurally similar iridium(III) phosphine η^1-allenyl complexes [37]. In contrast, CH_2Cl_2 solutions of 1:1 electrolytes give substantially higher molar conductivities, 10.30–26.8 $\Omega^{-1}\ cm^2\ mol^{-1}$ [37,38].

The ^{1}H- and ^{13}C{^{1}H}-NMR spectra of **4** allow assignment of an η^1-propargyl structure to the hydrocarbyl ligand. Thus, the CH_2 proton signal occurs as an unresolved multiplet at δ 2.82, whereas the Me signal is observed at δ 1.04 as a triplet with a $^5J_{HH} = 2.7$ Hz. These data are characteristic of those for $MCH_2C{\equiv}CMe$ complexes [25,32,33]. The ^{13}C{^{1}H} resonances at δ 89.6, 87.3, 3.8 and −5.4 for the C_3H_2Me ligand further support this formulation. The conspicuous absence of a signal associated with =C= at ca. δ 205 [2,25,34–36] rules out an alternative η^1-allenyl tautomeric formulation, and the high-field CH_2 signal (δ −5.4, $^1J_{RhC} =$ 19.5 Hz) strongly supports the propargyl structure. The arrangement of ligands in **4** is assigned from the same considerations as for complexes **3**.

All rhodiacyclic complexes **5**–**9** show one IR absorption at 1648–1586 cm^{-1}, but no terminal ν(CO) bands. With the aid of structure determinations of **5a**, **5b** and **5d** (vide infra), this absorption is assigned to ν(C=O) of the rhodiacyclopent-3-ene-2-one ring. In the ^{13}C{^{1}H}-NMR spectrum, the resonance of this C=O occurs at δ 234.4–217.7 with coupling to ^{103}Rh ($^1J_{RhC} = 21–27$ Hz).

Complexes **5** reveal ^{1}H-NMR signals of ring CH at δ 5.82–5.64 and CH_2 at δ 4.13–3.68, the latter with the generally unresolved coupling to ^{103}Rh. In the ^{13}C{^{1}H}-NMR spectra, the corresponding signals appear at δ 144.5–137.6 (CH) and δ 35.7–28.1 ($^1J_{RhC} = 20–24$ Hz, CH_2). The ^{13}C chemical shift of the rhodiacyclic =CX is dependent on X and, for **5**, occurs in the range δ 172.5–170.2 when X = Cl and at δ 161.3 when X = Br. With the exception of **5d**, complexes **5** are non-electrolytes in CH_2Cl_2 solution, in which they show molar conductivity values of less than 1 $\Omega^{-1}\ cm^2\ mol^{-1}$. For **5d**, a Λ_m of 5.13 $\Omega^{-1}\ cm^2\ mol^{-1}$ indicates considerable dissociation of triflate in solution [37,38].

Rhodiacyclic complexes **6**, derived from methylpropargyl organics and $Rh(SbPh_3)_3(CO)X$, show proton CH_2 and carbon-13 =*C*Me and CH_2 chemical shifts that are similar to those of **5**, as well as comparable $^1J_{RhC}$ for the CH_2. Their ^{13}C chemical shift of the ring =CX is also dependent on X, being observed at δ 165.1–163.4 for X = Cl and δ 174.2–173.8 for X = OTs. This difference is the basis for the assignment of structure to the presumably isomeric **6a** and **6b** as well as to **6d**.

The ^{1}H-NMR spectral features associated with the rhodiacyclic ring of the triphenylphosphine-containing complexes **7** and **8** are similar to those of **5** and **6**, and their ^{31}P{^{1}H}-NMR spectra consist of a doublet at δ 29.5–29.1 with $^1J_{RhP} = 124$ Hz to indicate that the PPh_3 ligands are *trans*. These data as well as elemental analysis and FAB mass spectra implicate five-coordinate formulations that are analogous to those reported earlier [29–31].

Replacement of one $SbPh_3$ ligand in **5a** with pyridine affords **9**, which shows ^{1}H- and ^{13}C{^{1}H}-NMR spectra similar to those of its parent complex with additional signals of pyridine. However, the CH_2 protons of **9**, unlike those of **5**–**8**, are inequivalent and appear in the spectrum as an AB pattern with δ 3.56 and 2.77 and $^2J_{HH} = 17.4$ Hz. This inequivalence is attributed to the presence of a chiral Rh center that resulted from pyridine entering a position *trans* to $SbPh_3$.

The structures of three rhodiacyclic complexes **5**—**5a**, **5b** and **5d**—were elucidated by X-ray diffraction analysis. That of **5a** was communicated earlier [17]; for further details see information in Section 5. Crystallo-

graphic analysis of **5b** (as **5b**·0.5CH_2Cl_2) established its molecular structure as depicted in Scheme 1, with Rh–Br and C–Cl bonding; however, the metrical parameters are of insufficient accuracy for comparison and discussion. The structure of **5d** (as **5d**·0.5C_7H_8) represents the most accurate of the three structures and is considered here in some detail. An ORTEP drawing of **5d** is shown in Fig. 1, and selected bond distances and angles are given in Table 2.

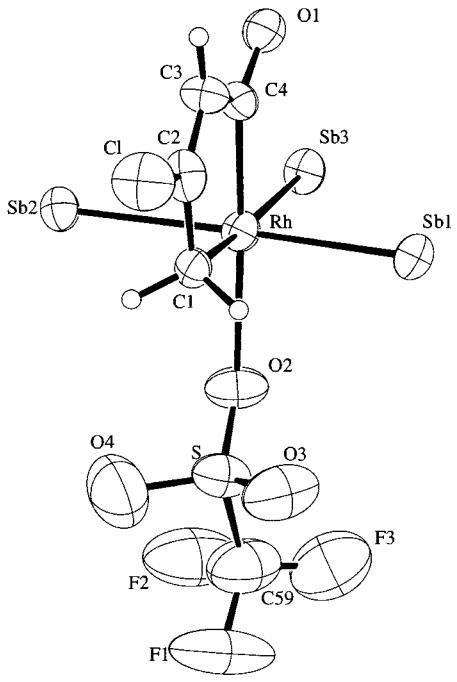


Fig. 1. ORTEP plot of **5d** in **5d**·0.5C_7H_8. The non-hydrogen atoms are drawn at the 30% probability level. For clarity the phenyl groups are omitted.

Table 2
Selected bond lengths (Å) and bond angles (°) for **5d**·0.5C_7H_8

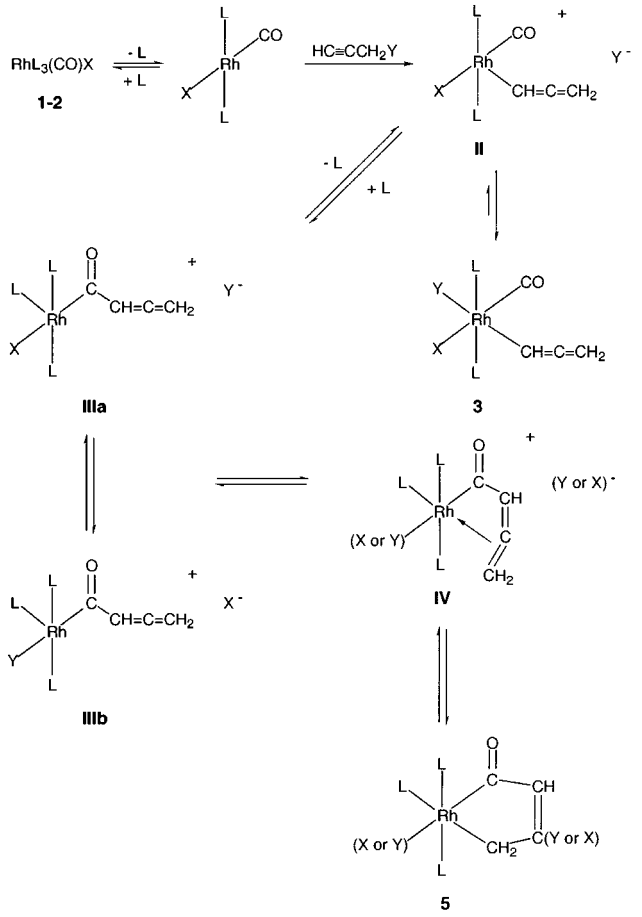
Bond lengths			
Rh–C(1)	2.099(9)	C(1)–C(2)	1.49(2)
Rh–C(4)	1.962(11)	C(2)–C(3)	1.291(14)
Rh–O(2)	2.310(8)	C(3)–C(4)	1.47(2)
Rh–Sb(1)	2.602(1)	Cl–C(2)	1.753(11)
Rh–Sb(2)	2.612(1)	O(1)–C(4)	1.226(11)
Rh–Sb(3)	2.695(1)		
Bond angles			
C(1)–Rh–C(4)	83.2(4)	Sb(1)–Rh–Sb(2)	172.29(4)
C(1)–Rh–O(2)	92.7(4)	Sb(1)–Rh–Sb(3)	93.56(4)
C(1)–Rh–Sb(1)	85.7(3)	Sb(2)–Rh–Sb(3)	94.03(3)
C(1)–Rh–Sb(2)	86.6(3)	C(2)–C(1)–Rh	105.7(7)
C(1)–Rh–Sb(3)	176.0(3)	C(3)–C(4)–Rh	114.4(8)
C(4)–Rh–O(2)	175.7(4)	O(1)–C(4)–Rh	123.5(8)
C(4)–Rh–Sb(1)	90.2(3)	C(1)–C(2)–C(3)	122.1(10)
C(4)–Rh–Sb(2)	88.1(3)	C(2)–C(3)–C(4)	114.5(10)
C(4)–Rh–Sb(3)	92.9(4)	C(3)–C(4)–O(1)	122.0(10)
O(2)–Rh–Sb(1)	90.5(2)	C(1)–C(2)–Cl	117.2(9)
O(2)–Rh–Sb(2)	90.7(2)	C(3)–C(2)–Cl	120.6(10)
O(2)–Rh–Sb(3)	91.2(2)		

The coordination environment around the Rh center is approximately octahedral, with the three $SbPh_3$ ligands adopting a meridional configuration. The inequivalent $SbPh_3$ is located *trans* to the CH_2 carbon of the η^2-C(O)CH=C(Cl)CH_2 ligand, and the triflate is positioned *trans* to the C(O) carbon. This general stereochemistry—$SbPh_3$ ligands arranged meridionally and the CH_2 *trans* to $SbPh_3$—was also found in **5a** [17] and **5b**.

The rhodiacyclic ring is essentially planar, with the deviations from the least-squares plane being Rh 0.008(1), C(1) −0.005(10), C(2) −0.002(11), C(3) −0.011(11) and C(4) −0.012(11) Å. The Rh–C bond distances Rh–C(1) = 2.099(9) and Rh–C(4) = 1.962(11) Å may be compared with the corresponding distances of 2.064(9) and 1.973(6) Å in $Rh(PPh_3)_2Cl(\eta^2$-C(O)CH=C(C(O)Ph)CH_2) [30] and of 2.089(6) and 2.012(5) Å in $Cp(PPh_3)Rh(\eta^2$-C(O)C(Et)=C(Et)CH_2) [29]. The bite angle of η^2-C(O)CH=C(Cl)CH_2, C(1)–Rh–C(4), measures 83.2(4)° and is somewhat larger than that of the appropriate analogous ligand in $Rh(PPh_3)_2Cl(\eta^2$-C(O)CH=C(C(O)Ph)CH_2) (80.6(3)° [30]) and $Cp(PPh_3)Rh(\eta^2$-C(O)C(Et)=C(Et)CH_2) (80.6(2)° [29]). The C–C bond distances within the rhodiacyclic ring (C(1)–C(2) = 1.49(2), C(2)–C(3) = 1.291(14) and C(3)–C(4) = 1.47(2) Å) are all in the range expected for this structure and compare quite well with the corresponding distances in similar compounds [29,30].

Of the three Rh–Sb bond distances, those for the *trans* $SbPh_3$ ligands are essentially equal (Rh–Sb(1) = 2.602(1), Rh–Sb(2) = 2.612(1) Å) whereas that for the remaining $SbPh_3$ (*trans* to CH_2) is longer (Rh–Sb(3) = 2.695(1) Å). This difference may result from steric effects associated with the size of $SbPh_3$, since ligand–ligand repulsion would be most pronounced for the stibine *cis* to each of the other two stibenes. Indeed, the bond angles Sb(1)–Rh–Sb(2) = 172.29(4), Sb(1)–Rh–Sb(3) = 93.56(4) and Sb(2)–Rh–Sb(3) = 94.03(3)° reflect distortions that are consistent with repulsion between large $SbPh_3$ ligands in *cis* positions. Furthermore, Rh–Sb bond lengths in octahedral rhodium(III) complexes containing only *trans* $SbPh_3$ ligands are shorter than those in **5d**: 2.588(1) Å in *trans*-$Rh(SbPh_3)_2(NCMe)(Ph)Cl_2$ [39] and 2.551(2) and 2.588(2) Å in *trans*-$Rh(SbPh_3)_2(DPD)Ph_2$·$2C_6H_6$ (DPD = 1,3-diphenyl-1,3-propandionate) [40].

The triflate is bonded to rhodium with Rh–O = 2.310(8) Å. This bond length may be compared with other Rh–OTf distances of 2.37(1) Å in [$Rh_2(\eta^1$-$OCMe_2)(\mu$-CO)(CO)(OTf)(dppm)$_2$](OTf)·0.5C_6H_6 (dppm = 1,2-bis(diphenylphosphino)methane) [41] and 2.323(6) and 2.332(6) Å in [{Rh(μ-Pz)(Me)(CNBu-t)$_2$}$_2$(μ-OTf)](OTf) (Pz = pyrazolate) [42].



Scheme 3. $L = Sb(C_6H_5)_3$.

3.3. Mechanistic aspects

A possible mechanism of formation of complexes **3** and **5** from $Rh(SbPh_3)_3(CO)X$ (X = Cl (**1**), Br (**2**)) and $HC{\equiv}CCH_2Y$ (Y = Cl, Br, OTs, OBs) is presented in Scheme 3. Salient features of this mechanism are:

(a) Complexes **1** and **2** undergo dissociation of $SbPh_3$ to afford square-planar $Rh(SbPh_3)_2(CO)X$ in solution [15].

(b) Oxidative addition of $HC{\equiv}CCH_2Y$ to the rhodium center in $Rh(SbPh_3)_2(CO)X$ generates transient $[Rh(SbPh_3)_2(CO)X(\eta^1\text{-}CH{=}C{=}CH_2)]^+Y^-$ (**II**). Such an ionic process has been proposed on the basis of kinetic studies of oxidative addition of alkyl halides, especially MeI, to iridium(I) in various $Ir(PR_3)_2(CO)X$ complexes [43,44]. Furthermore, cationic intermediates have been isolated or detected in oxidative addition of alkyl and acyl halides to rhodium(I), iridium(I), palladium(II) and platinum(II) complexes [45]. In the present case, the addition of $HC{\equiv}CCH_2Y$ proceeds by attack of Rh at the CH carbon (S_N2' mechanism) to yield $RhCH{=}C{=}CH_2$. Again, ample precedent exists for such a behavior of organic propargyl halides and tosylates toward metal complexes [1,4,6–8,25].

(c) Addition of $Y^- = OTs^-$ or OBs^- to rhodium in **II** produces six-coordinate η^1-allenyl complexes **3**. Alternatively, the η^1-allenyl ligand of **II** can migrate onto coordinated CO. Reactions of four-coordinate rhodium(I) carbonyl complexes with MeI are known [46] to yield methylrhodium(III) and acetylrhodium(III) products. The migratory insertion of **II** may be promoted by an external ligand—Y^- or $SbPh_3$—to give intermediate **III**. We favor $SbPh_3$ to be the assisting ligand, since this would yield a cationic product, which is expected to be more reactive than an electrically neutral product to the addition of nucleophile to coordinated $C(O)CH{=}C{=}CH_2$ (vide infra).

(d) Intermediate **III** undergoes coordination of the allenyl $C_\beta = C_\gamma$ to rhodium to form **IV**, which then adds external X^- or Y^- to give the rhodiacyclic product **5**. Alternatively, but less likely,[3] ligation occurs through the allenyl $C_\alpha = C_\beta$. The latter type of η^3 coordination of $C(O)C(R){=}C{=}CH_2$ to one metal has been documented crystallographically for a binuclear FeRu complex [47]. Addition of nucleophile to C_β of ligated allene is a known reaction [48].

(e) The proposed equilibrium between **IIIa** and **IIIb** which results from exchange of X and Y readily accounts for the formation of **5b** alone from the reaction of either **1** with $HC{\equiv}CCH_2Br$ or **2** with $HC{\equiv}CCH_2Cl$. (However, this aspect of reactivity can also be explained by the addition of either ionic Y^- or ligated X to the $C(O)CH{=}C{=}CH_2$ in **IV** originating from **IIIa**.)

The stereochemistry at rhodium of the foregoing transformations is consistent with the elucidated structures of **5a**, **5b** and **5d**. Thus, the migratory insertion of CO (i.e. conversion of **II** to **III**) and coordination of $C_\beta = C_\gamma$, both required to proceed with cis stereochemistry at metal, lead to the correct isomeric structure of the rhodiacyclic product.

A number of reactions in Scheme 1 may be rationalized on the basis of the relative ease of substitution and rearrangement of β-halo and β-sulfonato enones [49] and of the comparative leaving ability of these substituent groups. For example, the formation of **3a** and **3b** from **1** and $HC{\equiv}CCH_2OTs$ and $HC{\equiv}CCH_2OBs$, respectively, may be attributed to the excellent leaving properties of the organic sulfonates compared to chloride. This would disfavor formation of the rhodiacyclic structures **5** and instead produce the η^1-allenyls **3**.

The conversion reactions of **5** to **3** may be explained similarly. Thus, thermolysis of **5** proceeds more readily for **5c** than for **5a**, consistent with Br^- being a better

[3] Molecular modeling indicates that $C_\beta = C_\gamma$ is more likely to coordinate to the metal than $C_\alpha = C_\beta$. We thank an anonymous reviewer for providing us with this result.

leaving group than Cl^-. Likewise, substitution of the rhodiacyclic ring Cl in **5a**, **5b** or **5d** with OTf leads to the formation of the η^1-allenyl complex **3e**. Presumably the reaction is driven by the excellent leaving group properties of triflate.

The reverse reaction, i.e. conversion of **3** to **5**, was effected for **3** with Cl^- in the presence of $SbPh_3$ to give **5a**. Without added $SbPh_3$, there is only ligand substitution of chloride for triflate to yield η^1-allenyl **3d**. The formation of **5a** may occur by intermediacy of **II**, which would then proceed to the rhodiacyclic product by the mechanism in Scheme 3.

The reactions of methylpropargyl organics with **1** and **2**, set out in Scheme 2, likely take place by a similar pathway. Here, however, initial interaction of $MeC{\equiv}CCH_2Y$ with the rhodium(I) center may afford either an η^1-allenyl or a propargyl complex [2,32,33] analogous to **II** in Scheme 3, or a mixture of both. This would account for the formation of **4** as well as of **6a** and **6b** from **1** and $MeC{\equiv}CCH_2OTs$.

4. Conclusions

We have shown in this study that the five-coordinate rhodium(I) stibine complexes $Rh(SbPh_3)_3(CO)X$ (X = Cl (**1**), Br (**2**)) undergo new and unusual reactions with the electrophilic propargyl compounds $RC{\equiv}CCH_2Y$ (R = H, Me; Y = Cl, Br, OTs, OBs). Generally, the products are rhodiacyclopent-3-ene-2-one complexes (**5**, **6**), although η^1-allenyl (**3**) and propargyl (**4**) complexes have also been obtained. The nature of the product depends on whether the propargyl substituent R is H or Me and on the leaving group properties of X or Y. Rhodiacyclic complexes **5** can be converted to η^1-allenyl complexes **3** by thermolysis or replacement of β-halogen of the enone fragment in the ring with the excellent leaving group triflate. The reverse reaction, **3** to **5**, was effected by use of $SbPh_3$ together with chloride to replace coordinated triflate. Results of this study suggest that five-coordinate triphenylstibine-containing complexes of rhodium(I) may possess unusual chemical reactivity with potential applications in synthesis.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 118727, 141260, and 154326 for compounds **5a**, **5b**·$0.5CH_2Cl_2$ and **5d**·$0.5C_7H_8$, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This study was supported in part by the National Science Foundation and The Ohio State University.

References

[1] (a) A. Wojcicki, C.E. Shuchart, Coord. Chem. Rev. 65 (1990) 219;
(b) S. Doherty, J.F. Corrigan, A.J. Carty, E. Sappa, Adv. Organomet. Chem. 37 (1995) 39;
(c) J.-T. Chen, Coord. Chem. Rev. 192 (1999) 1143.
[2] C.E. Shuchart, R.R. Willis, A. Wojcicki, J. Organomet. Chem. 424 (1992) 185.
[3] A.L. Hurley, M.E. Welker, C.S. Day, Organometallics 17 (1998) 2832.
[4] J.P. Collman, J.N. Cawse, J.W. Kang, Inorg. Chem. 8 (1969) 2574.
[5] P.W. Blosser, D.G. Schimpff, J.C. Gallucci, A. Wojcicki, Organometallics 12 (1993) 1993.
[6] J.M.A. Wouters, R.A. Klein, C.J. Elsevier, L. Häming, C.H. Stam, Organometallics 13 (1994) 4586.
[7] R.-H. Hsu, J.-T. Chen, G.-H. Lee, Y. Wang, Organometallics 16 (1997) 1159.
[8] (a) D.M. Roundhill, P.B. Tripathy, B.W. Rense, Inorg. Chem. 10 (1971) 727;
(b) A.E. Crease, B.D. Gupta, M.D. Johnson, S. Moorhouse, J. Chem. Soc. Dalton Trans. (1978) 1821.
[9] (a) P.R. Sharp, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 8, Pergamon Press, Oxford, 1995 (chap. 2);
(b) R.P. Hughes, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 5, Pergamon Press, Oxford, 1982 (chap. 35).
[10] L. Vallarino, J. Chem. Soc. (1957) 2287.
[11] W. Hieber, H. Heusinger, O. Vohler, Chem. Ber. 90 (1957) 2425.
[12] R. Ugo, F. Bonati, S. Cenini, Inorg. Chim. Acta 3 (1969) 220.
[13] D.F. Steele, T.A. Stephenson, J. Chem. Soc. (1972) 2162.
[14] P.E. Garrou, G.E. Hartwell, J. Organomet. Chem. 69 (1974) 445.
[15] K. Goswami, M.M. Singh, J. Indian Chem. Soc. 56 (1979) 477.
[16] C.S. Chin, S.Y. Shin, C. Lee, J. Chem. Soc. Dalton Trans. (1992) 1323.
[17] A. Kayan, J. Gallucci, A. Wojcicki, Inorg. Chem. Commun. 1 (1998) 446.
[18] D.F. Shriver, M.A. Drezdzon, The Manipulation of Air-Sensitive Compounds, 2nd ed., Wiley, New York, 1986.
[19] L. Brandsma, H.D. Verkruijsse, Synthesis of Acetylenes, Allenes and Cumulenes, Elsevier, New York, 1981 (pp. 221–224).
[20] TEXSAN, 1995. Crystal Structure Analysis Package, Version 1.7-2, Molecular Structure Co., The Woodlands, TX.
[21] A.C.T. North, D.C. Phillips, F.S. Mathews, Acta Crystallogr. Sect. A 24 (1968) 351.
[22] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467 (SHELXS-86).
[23] G.M. Sheldrick, 1993. SHELXL-93, Program for the Refinement of Crystal Structures, University of Göttingen, Germany.
[24] A.J.C. Wilson (Ed.), International Tables for X-Ray Crystallography, vol. C, Kluwer Academic, Dordrecht, 1992.
[25] A.J. Canty, H. Jin, J.D. Penny, J. Organomet. Chem. 573 (1999) 30.
[26] F.A. Cotton, J.M. Troup, W.E. Billups, L.P. Lin, C.V. Smith, J. Organomet. Chem. 102 (1975) 345.
[27] J.R. Bleeke, T. Haile, M.Y. Chiang, Organometallics 10 (1991) 19.

[28] T. Mitsudo, H. Watanabe, T. Sasaki, Y. Takegami, Y. Watanabe, K. Kafuki, K. Nakatsu, Organometallics 8 (1989) 368.
[29] M.A. Huffman, L.S. Liebeskind, W.T. Pennington Jr., Organometallics 9 (1990) 2194.
[30] M.A. Huffman, L.S. Liebeskind, W.T. Pennington, Organometallics 11 (1992) 255.
[31] R.P. Hughes, P.R. Rose, A.L. Rheingold, Organometallics 12 (1993) 3109.
[32] J.-L. Roustan, P. Cadiot, C.R. Acad. Sci. Ser. C 268 (1969) 734.
[33] J.E. Thomasson, P.W. Robinson, D.A. Ross, A. Wojcicki, Inorg. Chem. 10 (1971) 2130.
[34] R.-S. Keng, Y.-C. Lin, Organometallics 9 (1990) 289.
[35] J. Pu, T.S. Peng, A.M. Arif, J.A. Gladysz, Organometallics 11 (1992) 3232.
[36] J.-T. Chen, Y.-K. Chen, J.-B. Chu, G.-H. Lee, Y. Wang, Organometallics 16 (1997) 1476.
[37] R.-H. Hsu, J.-T. Chen, G.-H. Lee, Y. Wang, Organometallics 16 (1997) 1159.
[38] P. Uguagliati, G. Deganello, L. Busetto, U. Belluco, Inorg. Chem. 8 (1969) 1625.
[39] R. Cini, G. Giorgi, E. Periccioli, Acta Crystallogr. Sect. C 47 (1991) 716.
[40] G.J. Lamprecht, J.G. Leipoldt, C.P. van Biljon, Inorg. Chim. Acta 88 (1984) 55.
[41] F. Shafiq, R. Eisenberg, J. Organomet. Chem. 472 (1994) 337.
[42] C. Tejel, M.A. Ciriano, A.J. Edwards, F.J. Lahos, L.A. Oro, Organometallics 16 (1997) 45.
[43] P.B. Chock, J. Halpern, J. Am. Chem. Soc. 88 (1966) 3511.
[44] R. Ugo, A. Pasini, A. Fusi, S. Cenini, J. Am. Chem. Soc. 94 (1972) 7364.
[45] (a) A.J. Oliver, W.A.G. Graham, Inorg. Chem. 9 (1970) 243;
(b) A.J. Hart-Davis, W.A.G. Graham, Inorg. Chem. 9 (1970) 2658;
(c) P.K. Byers, A.J. Canty, B.W. Skelton, P.R. Traill, A.A. Watson, A.H. White, Organometallics 11 (1992) 3085;
(d) M. Crespo, R.J. Puddephatt, Organometallics 6 (1987) 2548.
[46] (a) J.C. Douek, G. Wilkinson, J. Chem. Soc. A (1969) 2604;
(b) S. Fraks, F.R. Hartley, J.R. Chipperfield, Inorg. Chem. 20 (1981) 3238;
(c) A.M. Trzeciak, J.J. Ziółkowski, Inorg. Chim. Acta 115 (1986) L43;
(d) G. Tresoldi, S. Sergi, S.L. Schiavo, P. Piraino, J. Organomet. Chem. 322 (1987) 369;
(e) J.V. Heras, E. Pinilla, P. Ovejero, J. Organomet. Chem. 332 (1987) 213;
(f) D.K. Dutta, M.M. Singh, J. Indian Chem. Soc. 65 (1988) 235;
(g) E. Lindner, H. Norz, Chem. Ber. 123 (1990) 459.
[47] C.E. Shuchart, A. Wojcicki, M. Calligaris, P. Faleschini, G. Nardin, Organometallics 13 (1994) 1999.
[48] F.P. Pruchnik, Organometallic Chemistry of the Transition Elements, Plenum Press, New York, 1990, pp. 420–421.
[49] (a) E. Piers, I. Nagakura, J. Org. Chem. 40 (1975) 2694;
(b) E. Piers, C.K. Lau, I. Nagakura, Tetrahedron Lett. (1976) 3233;
(c) J.L. Coke, H.J. Williams, S. Natarajan, J. Org. Chem. 42 (1977) 2380;
(d) E. Piers, I Nagakura, H.E. Morton, J. Org. Chem. 43 (1978) 3630.