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Oxidative addition reactions of $Rh(SbPh_3)_3(CO)X$ (X = Cl, Br) with organic phenyl-substituted propargyl compounds. Rhodium(III) phenylpropargyl products and their conversion to rhodiacyclic complexes

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Abstract

Reactions of $Rh(SbPh_3)_3(CO)X$ (X = Cl (**1**), Br (**2**)) with $PhC{\equiv}CCH_2Y$ (Y = OTs, Cl, Br) in CH_2Cl_2 at ambient temperature lead to formation of the oxidative addition products $Rh(SbPh_3)_2(CO)X(Y)(\eta^1\text{-}CH_2C{\equiv}CPh)$ (X = Cl, Y = OTs (**3**), Cl (**4**), Br (**5**); X = Br, Y = OTs (**6**), Br (**7**)). Complexes **3** and **6** each react with pyridine at room temperature to afford the rhodiacyclopent-3-ene-2-ones $Rh(SbPh_3)_2(py)X(\eta^2\text{-}C(O)C(Ph){=}C(OTs)CH_2)$ (X = Cl (**8**), Br (**9**)). Treatment with AgOTs converts **8** to $Rh(SbPh_3)_2(py)(OTs)(\eta^2\text{-}C(O)C(Ph){=}C(OTs)CH_2)$ (**10**). Addition of AgOTf (or $AgBF_4$) and then immediately an excess of $PhC{\equiv}CCH_2Br$ to a CH_2Cl_2 solution of **1** at ambient temperature affords an orange solid that is formulated tentatively as $[Rh(SbPh_3)_2(CO)Cl(\eta^3\text{-}CH_2CCPh)]OTf$ (or $-BF_4$) (**11a** and **11b**). All new complexes were characterized by a combination of elemental analysis, FAB mass spectrometry, IR and NMR (^1H and $^{13}C\{^1H\}$) spectroscopy and conductance measurements.

Keywords: Oxidative addition; Rhodium complexes; Propargyl complexes; Rhodiacyclic complexes

1. Introduction

Oxidative addition reactions of propargyl halides and tosylates to various d^8 and d^{10} metal centers afford η^1-allenyl and η^1-propargyl complexes [1–7]. We have recently reported [8] that reactions of $Rh(SbPh_3)_3(CO)X$ (X = Cl (**1**), Br (**2**)) with $HC{\equiv}CCH_2Y$ (Y = OTs, OBs, Cl, Br; OTs = p-$MeC_6H_4SO_3$, OBs = $PhSO_3$) lead to formation of η^1-allenyl complexes, $Rh(SbPh_3)_2(CO)X(Y)(\eta^1\text{-}CH{=}C{=}CH_2)$, when Y = OTs or OBs, and of rhodiacyclopent-3-ene-2-one complexes, $Rh(SbPh_3)_3(X \text{ or } Y)(\eta^2\text{-}C(O)CH{=}C(Y \text{ or } X)CH_2)$, when Y = Cl or Br. In this paper we present a complementary study on reactions of **1** and **2** with various phenyl-substituted propargyl compounds $PhC{\equiv}CCH_2Y$ (Y = OTs, Cl, Br) which invariably yield rhodium(III) η^1-propargyl complexes, $Rh(SbPh_3)_2(CO)X(Y)(\eta^1\text{-}CH_2C{\equiv}CPh)$. Some products were converted to the rhodiacyclic complexes $Rh(SbPh_3)_2(py)X(\eta^2\text{-}C(O)C(Ph){=}C(Y)CH_2)$ and to a cationic complex that we formulate tentatively as an η^3-allenyl/propargyl, $[Rh(SbPh_3)_2(CO)Cl(\eta^3\text{-}CH_2\text{-}CCPh)]^+$. Our preliminary communication [8a] has addressed aspects of this chemistry.

2. Experimental

2.1. General procedures and measurements

Reactions and manipulations of air-sensitive compounds were carried out under an atmosphere of argon by the use of standard procedures [9]. Solvents were

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dried [10], distilled under argon and degassed before use. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. IR, NMR (^{1}H and ^{13}C{^{1}H}) and FAB mass spectra were obtained as previously described [8b]. Conductance measurements on approximately 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 procured from various commercial sources and used as received, except as noted below. Procedures used in the literature were employed to synthesize the organic propargyl compounds PhC≡CCH_2Cl [11], PhC≡CCH_2Br [12] and PhC≡CCH_2OTs [12]. The complex $Rh(SbPh_3)_3(CO)Cl$ (**1**) [13–17] was prepared by the method of Vallarino [18], but without recrystallization, which causes loss of $SbPh_3$ and formation of $Rh(SbPh_3)_2(CO)Cl$ [17]. The analogous bromide $Rh(SbPh_3)_3(CO)Br$ (**2**) was obtained from **1** and LiBr as reported earlier [8b]. It was characterized by comparison of its spectroscopic properties with those published for **2** [17].

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 $PhC{\equiv}CCH_2OTs$

A stirred solution of **1** (0.88 g, 0.72 mmol) in 15 ml of CH_2Cl_2 was treated with PhC≡CCH_2OTs (0.29 g, 1.0 mmol) in 3 ml of CH_2Cl_2 at room temperature. The color of the resultant solution changed from red to pale yellow in 1 h as stirring continued for 1.5 h. The volume was then reduced to approximately 3 ml, and a solid was precipitated by the addition of 20 ml of hexane. The yellow $Rh(SbPh_3)_2(CO)Cl(OTs)(\eta^1$-$CH_2C{\equiv}CPh)$ (**3**) was collected on a filter frit, washed with hexane (2 × 15 ml) and dried under vacuum for 3 days. Yield, 0.71 g (85%). IR ($CDCl_3$, cm^{-1}): ν(CO) 2071. ^{1}H NMR ($CDCl_3$): δ = 7.81–6.71 (m, 39H, Ph, C_6H_4), 3.09 (d, $^2J_{RhH}$ = 3.4 Hz, 2H, CH_2), 2.29 (s, 3H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 183.18 (d, $^1J_{RhC}$ = 64.6 Hz, CO), 139.82–123.70 (m, Ph, C_6H_4), 99.73 (s, ≡*C*Ph), 88.93 (s, $CH_2C{\equiv}$), 21.23 (s, Me), −5.74 (d, $^1J_{RhC}$ = 17.9 Hz, CH_2). FAB MS; *m*/*z*: 987.0 ($M^+ + 2 - OTs$), 959.0 ($M^+ + 2 - OTs - CO$), 844.1 ($M^+ + 2 - OTs - CO - C_9H_7$). *Anal.* Found: C, 54.80; H, 4.06. Calc. for $C_{53}H_{44}ClO_4RhSSb_2$: C, 54.93; H, 3.83%.

2.3.2. Reaction of **1** with $PhC{\equiv}CCH_2Cl$

Reaction between **1** (1.0 g, 0.82 mmol) and PhC≡CCH_2Cl (0.800 ml, 1.15 g, 7.66 mmol) and subsequent work-up were conducted similarly to those for **1** and PhC≡CCH_2OTs. Yield of $Rh(SbPh_3)_2(CO)Cl_2(\eta^1$-$CH_2C{\equiv}CPh)$ (**4**), a yellow solid, was 0.75 g (90%). IR ($CHCl_3$, cm^{-1}): ν(CO) 2061. ^{1}H NMR ($CDCl_3$): δ = 7.82–6.95 (m, 35H, Ph), 2.83 (d, $^2J_{RhH}$ = 3.2 Hz, 2H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 183.51 (d, $^1J_{RhC}$ = 63.7 Hz, CO), 138.00–127.48 (m, Ph), 100.86 (s, ≡*C*Ph), 86.22 (s, $CH_2C{\equiv}$), −2.85 (d, $^1J_{RhC}$ = 17.8 Hz, CH_2). FAB MS; *m*/*z*: 987.1 ($M^+ + 2 - Cl$), 871.8 ($M^+ + 2 - Cl - C_9H_7$), 843.8 ($M^+ + 2 - Cl - C_9H_7 - CO$). *Anal.* Found: C, 52.36; H, 3.54. Calc. for $C_{46}H_{37}Cl_2ORhSb_2$: C, 54.00; H, 3.65%.

2.3.3. Reaction of **1** with $PhC{\equiv}CCH_2Br$

By a similar procedure, **1** (0.20 g, 0.16 mmol) and PhC≡CCH_2Br (0.100 ml, 0.156 g, 0.800 mmol) afforded $Rh(SbPh_3)_2(CO)Cl(Br)(\eta^1$-$CH_2C{\equiv}CPh)$ (**5**) as a yellow solid in 89% yield (0.155 g). IR ($CHCl_3$, cm^{-1}): ν(CO) 2060. ^{1}H NMR ($CDCl_3$): δ = 7.84–6.95 (m, 35H, Ph), 2.90 (d, $^2J_{RhH}$ = 3.50 Hz, 2H, CH_2), 2.82 (d, $^2J_{RhH}$ = 3.15 Hz, CH_2, minor product). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 183.66 (d, $^1J_{RhC}$ = 64 Hz, CO), 183.50 (d, $^1J_{RhC}$ = 62 Hz, CO, minor product), 136.52–124.26 (m, Ph), 101.35 (s, ≡*C*Ph, minor product), 100.76 (s, ≡*C*Ph), 86.91 (s, $CH_2C{\equiv}$, minor product), 86.81 (s, $CH_2C{\equiv}$), 0.18 (d, $^1J_{RhC}$ = 18.42 Hz, CH_2, minor product), −2.6 (d, $^1J_{RhC}$ = 18.42 Hz, CH_2). Λ_m = 0.27 Ω^{-1} cm^2 mol^{-1}. *Anal.* Found: C, 51.58; H, 3.70. Calc. for $C_{46}H_{37}BrClORhSb_2$: C, 51.75; H, 3.49%.

2.3.4. Reaction of **2** with $PhC{\equiv}CCH_2OTs$

Reaction of **2** (0.42 g, 0.33 mmol) with PhC≡CCH_2OTs (0.11 g, 0.38 mmol), conducted similarly to the preceding reactions, gave $Rh(SbPh_3)_2(CO)Br(OTs)(\eta^1$-$CH_2C{\equiv}CPh)$ (**6**) as a yellow solid in 80% yield (0.32 g). IR ($CDCl_3$, cm^{-1}): ν(CO) 2073. ^{1}H NMR ($CDCl_3$): δ = 7.85–6.70 (m, 39H, Ph, C_6H_4), 3.11 (d, $^2J_{RhH}$ = 3.55 Hz, 2H, CH_2), 2.30 (s, Me).

2.3.5. Reaction of **2** with $PhC{\equiv}CCH_2Br$

By a similar procedure, $Rh(SbPh_3)_2(CO)Br_2(\eta^1$-$CH_2C{\equiv}CPh)$ (**7**) was obtained as a yellow solid in 90% yield (0.16 g) from **2** (0.203 g, 0.160 mmol) and PhC≡CCH_2Br (0.100 ml, 0.156 g, 0.800 mmol). IR ($CDCl_3$, cm^{-1}): ν(CO) 2060. ^{1}H NMR ($CDCl_3$): δ = 7.88–6.92 (m, 35H, Ph), 2.89 (d, $^2J_{RhH}$ = 3.37 Hz, 2H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 183.40 (d, $^1J_{RhC}$ = 63.72 Hz, CO), 139.60–124.26 (m, Ph), 101.41 (s, ≡*C*Ph), 86.75 (s, $CH_2C{\equiv}$), −2.66 (d, $^1J_{RhC}$ = 17.42 Hz, CH_2).

2.4. Reactions of rhodium(III) η^1-propargyl complexes with pyridine

2.4.1. Reaction of $Rh(SbPh_3)_2(CO)Cl(OTs)(\eta^1$-$CH_2C{\equiv}CPh)$ (**3**) with pyridine

Pyridine (0.110 ml, 0.107 g, 1.37 mmol) was added to a stirred solution of **3** (0.27 g, 0.23 mmol) in 10 ml of

CH_2Cl_2 at room temperature. The color of the solution changed from yellow to pale red in a few minutes. The mixture was stirred for 1 h, and solvent was removed under vacuum to leave an oily solid which was washed with hexane (2 × 5 ml). The hexane wash containing excess pyridine was removed by decantation to leave an orange solid, $Rh(SbPh_3)_2(py)Cl(\eta^2\text{-}C(O)C(Ph)=C(OTs)CH_2)$ (**8**) which was dried under vacuum for 3 days. Yield, 0.28 g (97%). IR ($CDCl_3$, cm^{-1}): ν(C=O) 1626. ^1H NMR ($CDCl_3$): $\delta = 9.06–8.76$, 8.42–6.46 (dd, m, 44H, py, Ph, C_6H_4), 3.69 (d, $^2J_{HH} = 18.10$ Hz, 1H of CH_2), 3.26 (d, $^2J_{HH} = 18.10$ Hz, 1H of CH_2), 2.24 (s, 3H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 232.84$ (d, $^1J_{RhC} = 30.75$ Hz, C=O), 166.41 (s, =*C*OTs), 153.92–151.33 (2s, py), 149.79 (s, =*C*Ph), 147.54–123.86 (m, Ph, C_6H_4, py), 24.08 (d, $^1J_{RhC} = 25.41$ Hz, CH_2), 21.31 (s, Me). *Anal*. Found: C, 56.59; H, 4.34. Calc. for $C_{58}H_{49}ClNO_4RhSSb_2$: C, 56.27; H, 3.99%.

2.4.2. Reaction of $Rh(SbPh_3)_2(CO)Br(OTs)$-(η^1-$CH_2C{\equiv}CPh$) (6) with pyridine

By a similar procedure, $Rh(SbPh_3)_2(py)Br(\eta^2\text{-}C(O)C(Ph)=C(OTs)CH_2)$ (**9**) was obtained as an orange solid from **6** (0.29 g, 0.24 mmol) and pyridine (0.20 ml, 0.19 g, 2.4 mmol). Yield, 0.30 g (97%). IR ($CDCl_3$, cm^{-1}): ν(C=O) 1625. ^1H NMR ($CDCl_3$): $\delta = 9.08–8.85$, 8.61–6.55 (dd, m, 44H, py, Ph, C_6H_4), 3.81 (d, $^2J_{HH} = 17.66$ Hz, 1H of CH_2), 3.28 (d, $^2J_{HH} = 17.66$ Hz, 1H of CH_2), 2.31 (s, 3H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 232.79$ (d, $^1J_{RhC} = 30.63$ Hz, C=O), 167.12 (s, =*C*OTs), 154.65–152.01 (2s, py), 149.74 (s, =*C*Ph), 147.42–124.60 (m, Ph, C_6H_4, py), 24.55 (d, $^1J_{RhC} = 25.29$ Hz, CH_2), 21.29 (s, Me).

2.5. Reaction of $Rh(SbPh_3)_2(py)Cl(\eta^2\text{-}C(O)C(Ph)=C(OTs)CH_2)$ (8) with silver tosylate

Silver tosylate (0.069 g, 0.24 mmol) was added to a stirred solution of **8** (0.30 g, 0.24 mmol) in 10 ml of CH_2Cl_2 at room temperature. Stirring was continued for 2 h, and the mixture was filtered to remove silver chloride. Solvent was evaporated from the filtrate, and the remaining orange solid $Rh(SbPh_3)_2(py)(OTs)(\eta^2\text{-}C(O)C(Ph)=C(OTs)CH_2)$ (**10**) was dried under vacuum for 3 days. Yield, 0.32 g (97%). IR ($CDCl_3$, cm^{-1}): ν(C=O) 1637. ^1H NMR ($CDCl_3$): $\delta = 8.97–8.73$, 8.47–6.79 (dd, m, 48H, py, Ph, C_6H_4), 4.53 (dd, $^2J_{HH} = 18.29$ Hz, $^2J_{RhH} = 2.38$ Hz, 1H of CH_2), 3.44 (dd, $^2J_{HH} = 18.29$ Hz, $^2J_{RhH} = 2.76$ Hz, 1H of CH_2), 2.32 (s, 6H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 227.60$ (d, $^1J_{RhC} = 30.63$ Hz, C=O), 167.21 (s, =*C*OTs), 152.68–151.60 (2s, py), 146.22 (d, $^2J_{RhC} = 5.98$ Hz, =*C*Ph), 147.31–124.58 (m, Ph, C_6H_4, py), 25.88 (d, $^1J_{RhC} = 26.10$ Hz, CH_2), 21.03 (s, Me).

2.6. Reaction of $Rh(SbPh_3)_3(CO)Cl$ (1) with silver(I) salts and $PhC{\equiv}CCH_2Br$

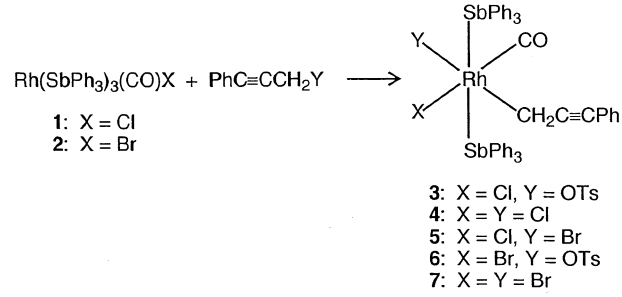
A stirred solution of **1** (0.20 g, 0.16 mmol) in 10 ml of CH_2Cl_2 at room temperature was treated first with AgOTf (0.042 g, 0.16 mmol) and then immediately with $PhC{\equiv}CCH_2Br$ (0.100 ml, 0.156 g, 0.800 mmol). The mixture was stirred for 1 h and filtered to remove a pale yellow solid, shown to be AgBr by oxidation to Br_2 with H_2O_2/HNO_3 in the presence of 1,2-dichloroethane. The filtrate was evaporated to dryness, and the residue was dissolved in approximately 2 ml of toluene. Addition of hexane (20 ml) with stirring induced precipitation of a pale orange solid, which was collected on a filter frit and washed with 10 ml of hexane. The solid was recrystallized from toluene–hexane and dried under vacuum for a few days. Yield, 0.14 g (75% of proposed **11a**). IR ($CDCl_3$, cm^{-1}): ν(CO) 2068. ^1H NMR ($CDCl_3$): $\delta = 7.85–6.89$ (m, 35H, Ph), 4.43 (s, 2H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 183.37$ (d, $^1J_{RhC} = 63.73$ Hz, CO), 139.94–121.79 (m, Ph), 101.25 (s, *C*Ph), 87.92 (s, CH_2C), 80.70 (s, CH_2). FAB MS; m/z: 987.1 ($M^+ + 2$) (for M^+=[$Rh(SbPh_3)_2(CO)Cl(\eta^3\text{-}CH_2CCPh)]^+$). $\Lambda_m = 21.55\ \Omega^{-1}\ cm^2\ mol^{-1}$. Satisfactory elemental analysis for $[Rh(SbPh_3)_2(CO)Cl(\eta^3\text{-}CH_2CCPh)]OTf$ (**11a**) could not be obtained.

A similar reaction of **1**, $AgBF_4$ and $PhC{\equiv}CCH_2Br$ yielded the corresponding BF_4^- salt, **11b**. Its IR ν(CO) and ^1H and $^{13}C\{^1H\}$ NMR spectra were essentially identical with those of **11a**. FAB MS; m/z: 987.1 ($M^+ + 2$) (for M^+=[$Rh(SbPh_3)_2(CO)Cl(\eta^3\text{-}CH_2CCPh)]^+$). $\Lambda_m = 21.70\ \Omega^{-1}\ cm^2\ mol^{-1}$.

3. Results and discussion

3.1. Rhodium(III) η^1-propargyl complexes

Reactions of $Rh(SbPh_3)_3(CO)X$ (X = Cl (**1**), Br (**2**)) with $PhC{\equiv}CCH_2Y$ (Y = OTs, Cl, Br) in CH_2Cl_2 at room temperature give complexes **3**–**7** as yellow solids in 80–90% yield (Eq. (1)).



(1)

These products have been characterized as rhodium(III) η^1-propargyl complexes by a combination of IR and NMR (^{1}H and ^{13}C{^{1}H}) spectroscopy, FAB mass spectrometry, conductance measurements and elemental analysis. Because of the near identical spectroscopic properties of **3**–**7** (cf. Section 2.3), elemental analysis determination was not considered necessary for all complexes. The molar conductivity value $\Lambda_m = 0.75$ Ω^{-1} cm^2 mol^{-1} for **5** in CH_2Cl_2 supports a nonionic, six-coordinate formulation. Solutions of 1:1 electrolytes of comparable concentration in CH_2Cl_2 give substantially higher molar conductivities (10.3–23.8 Ω^{-1} cm^2 mol^{-1} [19,20].

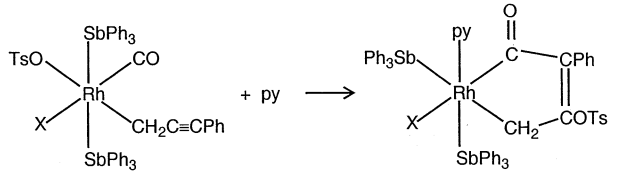
The IR spectra of **3**–**7** show one ν(CO) band at 2073–2060 cm^{-1}, with the tosylate complexes **3** and **6** absorbing at the highest energy, 2071 and 2073 cm^{-1}, respectively, as expected. The presence of the η^1-$CH_2C{\equiv}CPh$ ligand is evidenced by the appearance of a ^{1}H resonance of the CH_2 group at δ 3.11–2.83 with a small coupling constant, $^2J_{RhH} = 3.15$–3.55 Hz. The observed chemical shift is in the range appropriate for metal η^1-propargyl complexes [4,21,22], and the $^2J_{RhH}$ is that expected for a $RhCH_2$ fragment [23,24]. The ^{13}C{^{1}H} NMR spectra also support the phenylpropargyl formulation, with the ≡*C*Ph signals occurring at δ 101.41–99.73, $CH_2C{\equiv}$ signals at δ 88.93–86.22 and CH_2 signals at δ −2.6 to −5.74 with $^1J_{RhC} = 17.4$–18.4 Hz. The magnitude of the $^1J_{RhC}$ of $RhCH_2$ compares very well with that reported for $Rh(SbPh_3)_2(CO)Cl(OTs)(\eta^1\text{-}CH_2C{\equiv}CMe)$ [8b] and $Rh(SbPh_3)_2(CO)Cl(Br)(\eta^1\text{-}CH_2CH{=}CH_2)$ [25]. The ^{13}C{^{1}H} NMR spectra also show a signal of the CO ligand at δ 183.66–183.16 with $^1J_{RhC} = 63.7$–64.4 Hz. Both of these values are similar to those obtained for $Rh(SbPh_3)_2(CO)Cl(OTs)(\eta^1\text{-}CH_2C{\equiv}CMe)$ [8b], $Rh(SbPh_3)_2(CO)Cl(Br)(\eta^1\text{-}CH_2CH{=}CH_2)$ [25] and related six-coordinate rhodium(III) η^1-allenyl complexes [8].

The foregoing spectroscopic data suggest formation of only a single product for each of **3**, **4**, **6** and **7**. For **5**, the occurrence of duplicate ^{1}H and ^{13}C{^{1}H} NMR resonances in the spectra (cf. Section 2.3.3) indicates that another, minor, species, probably an isomer of the main product, is present as well. No attempt was made to separate the two complexes. The proposed ligand stereochemistry of **3**–**7** is based on the assumed *trans* oxidative addition of $PhC{\equiv}CCH_2$ and Y to a square planar Rh center, formed by dissociation of one $SbPh_3$ ligand from five-coordinate **1** or **2**. This proposal is supported by the recently elucidated structure of the iridium(III) η^1-allenyl complex $Ir(PPh_3)_2(CO)(NHSO_2Ph)Cl(\eta^1\text{-}CH{=}C{=}CH_2)$ [26] which has been related stereochemically to the product of the reaction between *trans*-$Ir(PPh_3)_2(CO)Cl$ and $HC{\equiv}CCH_2Br$ [3,6,26].

In contrast to reactions of metal complexes with $HC{\equiv}CCH_2Y$ which generally afford η^1-allenyls $MCH{=}C{=}CH_2$ [1–3,6,7], reactions of metal complexes with phenyl-substituted propargyls, $PhC{\equiv}CCH_2Y$, yield η^1-propargyls $MCH_2C{\equiv}CPh$ [1,4,21,22]. An exception to the latter behavior is provided by the oxidative addition reaction of $Pd(PPh_3)_4$ with $PhC{\equiv}CCH_2Br$ which gives an equilibrium mixture of *trans*-$Pd(PPh_3)_2Br(\eta^1\text{-}CH_2C{\equiv}CPh)$ and *trans*-$Pd(PPh_3)_2Br(\eta^1\text{-}C(Ph){=}C{=}CH_2)$ [27]. Related examples of η^1-propargyl–η^1-allenyl tautomer chemistry include isomerization of *trans*-$Pt(PPh_3)_2X(\eta^1\text{-}CH_2C{\equiv}CPh)$ to *trans*-$Pt(PPh_3)_2X(\eta^1\text{-}C(Ph){=}C{=}CH_2)$ (X = Cl, Br, I) [7a] and preparation of each $Cp(CO)_2Ru(\eta^1\text{-}CH_2C{\equiv}CPh)$ and $Cp(CO)_2Ru(\eta^1\text{-}C(Ph){=}C{=}CH_2)$ by the use of different synthetic routes [22,28]. In the present case, heating **4** in THF at 60°C for 2 h effected no conversion to a corresponding η^1-allenyl complex.

3.2. Rhodiacyclopent-3-ene-2-one complexes

Treatment of **3** and **6** with pyridine in CH_2Cl_2 at room temperature affords complexes **8** and **9**, respectively, as orange solids in 97% yield (Eq. (2)).

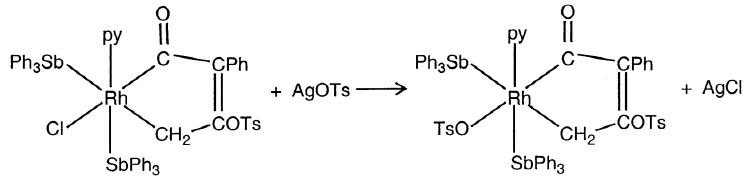


3: X = Cl
6: X = Br

8: X = Cl
9: X = Br

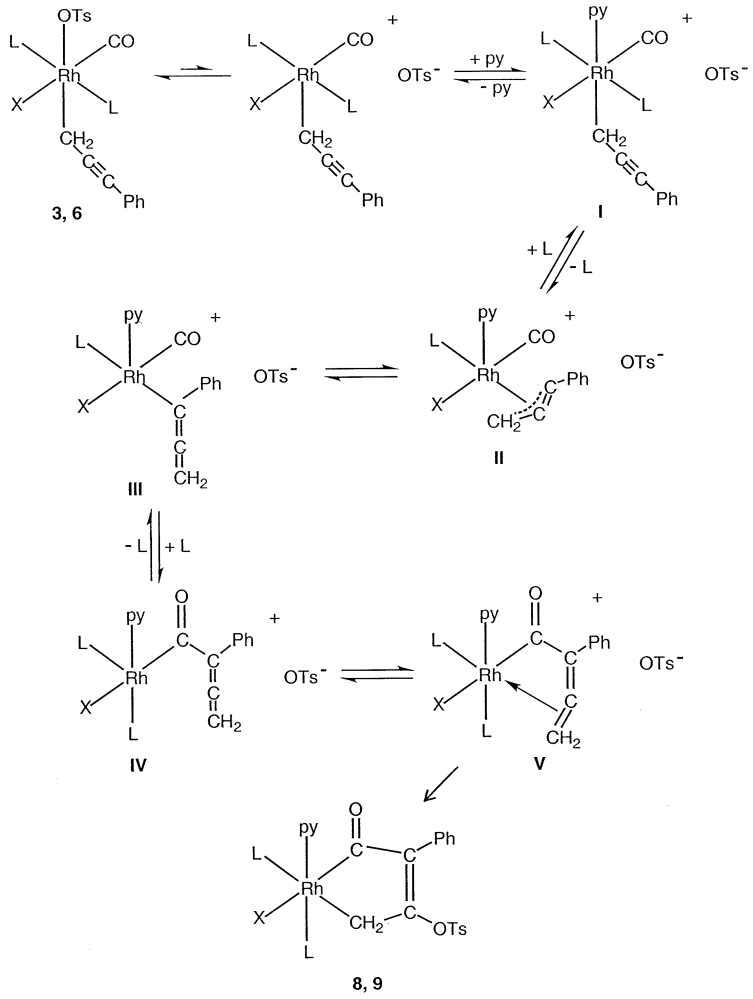
(2)

The structurally analogous **10** was obtained by replacement of bromide in **9** with tosylate from AgOTs (Eq. (3)).



8 **10**

(3)



Scheme 1. X = Cl, Br; L = $SbPh_3$.

The IR and $^{13}C\{^1H\}$ NMR spectra of **8**–**10** closely match those of the rhodiacyclic complexes $Rh(SbPh_3)_3$-(X or Y)(η^2-C(O)CH=C(Y or X)CH_2), obtained from $Rh(SbPh_3)_3(CO)X$ and $HC{\equiv}CCH_2Y$, and, especially, those of the pyridine substitution product $Rh(SbPh_3)_2$-(py)Cl(η^2-C(O)CH=C(Cl)CH_2) [8b]. Three of those complexes have been characterized by X-ray diffraction techniques [8]. In the IR spectra of **8**–**10** the ν(C=O) band of the rhodiacyclopent-3-ene-2-one ring is observed at 1637–1625 cm^{-1}, and in the $^{13}C\{^1H\}$ NMR spectra the signal of this C=O occurs at δ 232.84–227.60 with substantial coupling to ^{103}Rh ($^1J_{RhC}$ = 30.6–30.8 Hz). Other important $^{13}C\{^1H\}$ resonances are those at δ 167.21–166.41 (CH_2C(OTs)=), 149.79–146.22 (=CPh) and 25.88–24.08 (CH_2), the latter a doublet with $^1J_{RhC}$ = 26.1–25.3 Hz. The magnitude of this coupling constant indicates Rh–CH_2 bonding [8b,25,29,30]. The very similar chemical shifts for the ring CH_2C= suggest that this carbon is bonded to the same group, viz., OTs, in **8**–**10**.[2] A similar criterion was used to assign the location of X and Y (Rh or ring CH_2C=) in the rhodiacyclics derived from $Rh(SbPh_3)_3$-(CO)X and $HC{\equiv}CCH_2Y$ [8b].

The CH_2 protons of **8**–**10** are inequivalent in their NMR spectra and appear as an AB pattern with δ 4.53–3.69 and 3.44–3.26 and $^2J_{HH}$ = 17.7–18.3 Hz, as reported previously for $Rh(SbPh_3)_2$(py)Cl(η^2-C(O)CH=C(Cl)CH_2) [8b]. In the spectrum of **10**, additional small coupling to ^{103}Rh is discernible ($^2J_{RhH}$ = 2.38 and 2.76 Hz). The inequivalence of the CH_2 protons is likely due to the presence of a chiral Rh center, which would result from the two $SbPh_3$ ligands assuming *cis* positions.

[2] However, an alternative, zwitterionic rhodiacyclopent-3-ene-2-one structure of the same composition as **8**–**10**, in which pyridine is bonded to the ring CH_2C= and tosylate is bonded to the rhodium center, cannot be ruled out on the basis of the spectroscopic data.

The formation of complexes **8** and **9** may be rationalized by an adaptation of the mechanism proposed for the reactions of **1** and **2** with $HC{\equiv}CCH_2Y$ leading to rhodiacyclic products [8b]. This modified mechanism is shown in Scheme 1. Briefly, it starts with replacement of ligated tosylate with pyridine, and then dissociation of one stibine and tautomerization of η^1-propargyl to η^1-allenyl (overall **3**, **6** to **III**). This is followed by migration of $C(Ph){=}C{=}CH_2$ ligand of **III** to CO to yield **IV**, which undergoes coordination of the allenyl $C_\beta{=}C_\gamma$ to rhodium with formation of **V**. Addition of tosylate to ligated C=C of **V** completes the cycloaddition process.

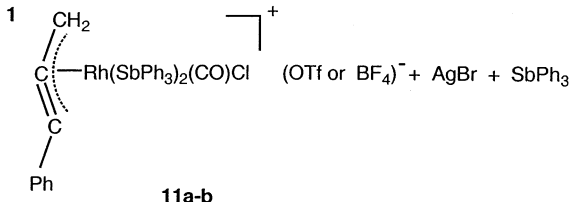
A couple of comments are warranted. First, the rhodium(III) η^1-propargyl complexes that react cleanly with pyridine to afford rhodiacyclic products are those that contain coordinated tosylate. In contrast, complexes **4** and **5**, each without ligated tosylate, gave mixtures of uncharacterized rhodium products when treated with pyridine under similar conditions. Higher molar conductivity values of the tosylato rhodium complexes compared to the analogous halogeno rhodium complexes [8] suggest that tosylate may promote cycloaddition by undergoing more extensive dissociation in CH_2Cl_2 solution. Second, the mechanism proposed in Scheme 1 requires rearrangement of $CH_2C{\equiv}CPh$ to $C(Ph){=}C{=}CH_2$, which is generally thought to proceed via an η^3-allenyl/propargyl intermediate (**II** in Scheme 1) [4,7a]. Interestingly, such a short-lived cationic intermediate would appear to be identical in composition with the isolable products of likely formula $[Rh(SbPh_3)_2(CO)Cl(\eta^3\text{-}CH_2CCPh)]^+(OTf \text{ or } BF_4^-)$ (**11a** and **11b**), considered in the next section. However, it should be noted that the proposed intermediate **II**, unlike **11a** and **11b**, is present in the chemical environment of free $SbPh_3$, pyridine and tosylate, which allows it to react further eventually to yield **8** or **9**.

3.3. Rhodium(III) η^3-allenyl/propargyl complexes

Addition of AgOTf and then an excess of $PhC{\equiv}CCH_2Br$ to a CH_2Cl_2 solution of **1** at room temperature affords after work-up a red solid, which appears to be $[Rh(SbPh_3)_2(CO)Cl(\eta^3\text{-}CH_2CCPh)]OTf$ (**11a**) on the basis of its IR and ^1H and $^{13}C\{^1H\}$ NMR spectra, molar conductivity in solution and FAB mass spectrum (Eq. (4)). The pale yellow precipitate formed in the course of this reaction was characterized as AgBr. The corresponding BF_4^- salt of the rhodium complex (**11b**) was obtained by use of $AgBF_4$ in place of AgOTf. The isolated cationic complex may be analogous to the η^3-allyls $[Rh(SbPh_3)_2(CO)X(\eta^3\text{-}CH_2CHCH_2)]^+$ prepared by treatment of $Rh(SbPh_3)_2(CO)Cl$ first with $CH_2{=}CHCH_2X$ (X = Cl, Br) and then with $AgClO_4$ or of $Rh(SbPh_3)_2(CO)Cl(X)(\eta^1\text{-}CH_2CH{=}CH_2)$ (X = Br) with $AgClO_4$ [25]. In our study, use of phenylpropargyl bromide in the reaction is important, as phenylpropargyl chloride gives a mixture of uncharacterized rhodium products. Reaction of **5** with AgOTf resulted in precipitation of AgCl, but the solid isolated from the filtrate also could not be characterized. Thus, abstraction of halide by silver(I) occurs from $PhC{\equiv}CCH_2X$ rather than from rhodium, and is favored by X = Br.

$$Rh(SbPh_3)_3(CO)Cl + PhC{\equiv}CCH_2Br + AgOTf \text{ or } AgBF_4 \longrightarrow$$

1



11a-b

(4)

The presence of a η^3-CH_2CCPh ligand in **11a** is evidenced by the appearance of a ^1H NMR signal at δ 4.43 and of $^{13}C\{^1H\}$ NMR signals at δ 101.25 (*C*Ph), 87.92 (CH_2*C*) and 80.70 (CH_2), all with no discernible coupling to ^{103}Rh. With the exception of the CH_2 resonance, which occurs at a lower field than that observed for various metal η^3-allenyl/propargyl complexes, these resonances are in line with the proposed ligand formulation [31,32]. The $^{13}C\{^1H\}$ NMR spectrum also shows a signal at δ 183.37 as a doublet with $^1J_{RhC} = 63.73$ Hz, which is assigned to a CO ligand. A strong IR ν(CO) absorption at 2068 cm^{-1} confirms the presence of CO. The corresponding spectroscopic properties of **11b** are very similar to those of **11a**. The ionic nature of **11a** and **11b** is indicated by their molar conductivity values of 21.55 and 21.70 $\Omega^{-1}\,cm^2\,mol^{-1}$, respectively, in CH_2Cl_2 solution, which are normal for 1:1 electrolytes [19,20]. The FAB mass spectra agree with the formulation of the cationic complex; unfortunately, satisfactory chemical analyses could not be obtained. Attempts to grow crystals suitable for X-ray diffraction analysis proved unsuccessful. Therefore, the proposed structure of **11** is to be considered somewhat tentative at this time.

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