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Reactivity of $[Cp^*Rh(\eta^6\text{-}C_6H_3NH_2\text{-}2,6\text{-}i\text{-}Pr_2)](OTf)_2$ toward phosphines and alkynes

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Abstract

The cationic aniline complex $[Cp^*Rh(\eta^6\text{-}2,6\text{-}(Me_2CH)_2C_6H_3NH_2)](OTf)_2$ (**1**) was prepared from either $[Cp^*Rh(\eta^2\text{-}NO_3)(\eta^1\text{-}OTf)]$ or $[Cp^*Rh(OH_2)_3](OTf)_2$ and 2,6-diisopropylaniline. Complex **1** underwent substitution with phosphines or phosphites, indicating the labile character of the η^6-aniline ligand. Complex **1** mediated cycloaddition reactions of several alkynes in refluxing ethanol: the [2 + 2] dimerization for Ph—C≡C—Ph and the [2 + 2 + 1] trimerization for Ph—C≡C—H and $CH_3C_6H_4$—C≡C—H. The unexpected cyclobutadiene complex $[Cp^*Rh(\eta^4\text{-}C_4(C(O)CH_3)_2H(SiMe_3))]$ was obtained from complex **1** and Me_3Si—C≡C—C≡C—$SiMe_3$ and structurally characterized by X-ray diffraction.

Keywords: Rhodium aniline complex; Phosphine; Alkynes; [2 + 2 + 1] Cycloaddition

1. Introduction

Various transition-metal complexes mediate the [2 + 2 + 2] cyclotrimerization of alkynes [1–10]. By contrast, there have been only a limited number of reports on the formal [2 + 2 + 1] cyclotrimerization of alkynes to give five-membered rings [11–22]. Very recently, we reported the reactivity of $[Cp^*Rh(\eta^2\text{-}NO_3)(OTf)]$ toward terminal aryl alkynes (H—C≡C—Ph and H—C≡C—$C_6H_4CH_3$) in alcohol (EtOH and *n*-BuOH) [11]. These reactions produced five-membered cycloadducts, substituted Cp ligands, by the [2 + 2 + 1] cyclotrimerization of those aryl alkynes.

Cationic mixed-sandwich complexes such as $[Cp^*Rh(\eta^6\text{-arene})]^{2+}$ have been attracted because of their oxidizing properties [23–26]. In particular, the aryl ligand in those complexes is typically electrophilic and subject to nucleophilic addition and substitution reactions [27–29], primarily because the cationic metal strongly withdraws electron density from two cyclic ligands. When we treated $[Cp^*Rh(\eta^6\text{-}C_6H_3NH_2\text{-}2,6\text{-}i\text{-}Pr_2)](OTf)_2$ (**1**), a cationic mixed-sandwich Rh complexes, with mild nucleophiles such as phosphines and phosphites, we obtained the corresponding substitution products $[Cp^*Rh(PR_3)_3](OTf)_2$ (**2a–e**), instead of nucleophilic addition products. This indicates the labile character of the arene ligand in complex **1**, and therefore we decided to compare its reactivity toward alkynes with that found for $[Cp^*Rh(\eta^2\text{-}NO_3)(OTf)]$, whose reactivity was proposed to come from the labile ligands (NO_3^- and OTf^-). Herein, we report the reactivity of complex **1** toward phosphines (PMe_3, PEt_3, PPh_3), phosphites ($P(OMe)_3$, $P(OEt)_3$), an internal alkyne (Ph—C≡C—Ph), terminal alkynes (H—C≡C—Ph and H—C≡C—C_6H_4-CH_3), and a diyne ($(Me_3Si$—C≡C—C≡C—$SiMe_3)$), together with some crystal structures of products.

2. Experimental

All reactions were performed under argon. The starting complex $[Cp^*Rh(\eta^6\text{-}C_6H_3NH_2\text{-}2,6\text{-}i\text{-}Pr_2)](OTf)_2$ (**1**) was prepared from either $[Cp^*Rh(\eta^2\text{-}NO_3)(\eta^1\text{-}OTf)]$ [30] or $[Cp^*Rh(OH_2)_3](OTf)_2$ [31]. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded with a Bruker AMX

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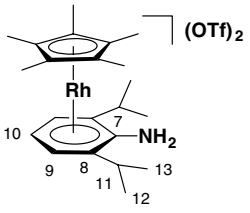
500 MHz spectrometer at CCRF (Cooperative Center for Research Facilities) in the Sungkyunkwan University. IR spectra were recorded with a Nicolet Avatar 320 FTIR spectrophotometer. Elemental analyses were performed by the Korea Basic Science Institute.

2.1. Preparation of $[Cp^*Rh(\eta^6\text{-}2,6\text{-}(Me_2CH)_2C_6H_3NH_2)](OTf)_2$ (**1**)

2.1.1. Method 1: preparation from $[Cp^*Rh(\eta^2\text{-}NO_3)(\eta^1\text{-}OTf)]$

At room temperature, 2,6-diisopropylaniline (0.124 ml, 0.66 mmol) was added to an orange solution of $[Cp^*Rh(\eta^2\text{-}NO_3)(\eta^1\text{-}OTf)]$ (0.100 g, 0.22 mmol) in THF (30 ml). The mixture was stirred for 3 h. The solvent was removed under vacuum to give a yellow powder, which was washed with diethyl ether (3×10 ml) and then dried under vacuum. This product was recrystallized from acetone–hexane to give complex **1** (84 mg, 0.115 mmol, 53%).

^{1}H NMR (acetone-d_6): δ 7.30 (d, 2H, $J = 6.5$ Hz, H(9) in Ph), 7.28 (br, 2H, NH_2), 6.98 (t, 1H, $J = 6.5$ Hz, H(10) in Ph), 3.36 (m, 2H, CHMe$_2$), 2.23 (s, 15H, Cp*), 1.50 (d, 6H, $J = 6.5$ Hz, CH(CH_3)$_2$), 1.36 (d, 6H, $J = 7.0$ Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (acetone-d_6): δ 132.5 (s, C(7) in Ph), 112.7 (d, $J_{Rh-C} = 4.5$ Hz, C(8) in Ph), 108.8 (d, $J_{Rh-C} = 7.8$ Hz,C_5Me$_5$), 100.4 (d, $J_{Rh-C} = 5.0$ Hz, C(9) in Ph), 94.9 (d, $J_{Rh-C} = 6.7$ Hz, C(10) in Ph), 26.8 (s, CHMe$_2$), 20.2 (s, CH(CH$_3$)$_2$), 19.3 (s, CH(CH$_3$)$_2$), 9.42 (s, C$_5$(CH$_3$)$_5$). IR (KBr): 3346 (N–H), 3227 (N–H), 3097, 2978, 1659, 1537, 1470, 1377, 1275, 1156, 1073, 1032, 636 cm^{-1}. M.p.: 269–271 °C (decomp). Anal. Calc. for $C_{24}H_{34}F_6NO_6RhS_2$: C, 40.40; H, 4.80; N, 1.96; S, 8.99. Found: C, 40.56; H, 4.95; N, 1.93; S, 8.52%.



2.1.2. Method 2: preparation from $[Cp^*Rh(OH_2)_3](OTf)_2$

At room temperature, 2,6-diisopropylaniline (0.50 ml, 2.60 mmol) was added to $[Cp^*Rh(OH_2)_3](OTf)_2$ (0.508 g, 0.86 mmol) in THF (30 ml). The mixture was stirred for 3 h. The product was recrystallized from acetone–hexane to give complex **1** (557 mg, 0.781 mmol, 91%).

2.2. Preparation of $[Cp^*Rh(PR_3)_3](OTf)_2$ (R = Me (**2a**), R = Et (**2b**), R = Ph (**2c**); R = OMe (**2d**), R = OEt (**2e**))

Trimethylphosphine (0.25 ml, 0.25 mmol) was added to a yellow solution of **1** (51 mg, 0.071 mmol) in 30 ml of acetone. After 4 h stirring at room temperature, the solvent was removed under vacuum. The residue was washed with diethyl ether ($20 \text{ ml} \times 2$), and then dried under vacuum to give an orange solid of $[Cp^*Rh(PMe_3)_3](OTf)_2$ (**2a**, 36 mg, 0.047 mmol, 66%). This product was recrystallized from acetone–hexane.

^{1}H NMR (acetone-d_6): δ 2.20 (s, 15H, Cp*), 1.98 (m, 27H, PMe$_3$). ^{13}C{^{1}H} NMR (acetone-d_6): δ 109.8 (m, C_5(CH$_3$)$_5$), 18.8 (m, P(CH$_3$)$_3$), 10.9 (s, C$_5$(CH$_3$)$_5$). ^{31}P{^{1}H} NMR (acetone-d_6): δ 0.52 (d, $J_{Rh-P} = 122.2$ Hz). IR (KBr): 2925, 1631, 1430, 1271, 1147, 1032, 945, 636 cm^{-1}. M.p.: 246–248 °C (decomp). Anal. Calc. for $C_{21}H_{42}O_6F_6P_3S_2Rh$: C, 32.99; H, 5.54; S, 8.39. Found: C, 32.99; H, 5.64; S, 8.47%.

Complex **2b** was prepared similarly to complex **2a**. Yield: 45%. ^{1}H NMR (acetone-d_6): δ 2.45 (m, 18H, P(CH_2CH$_3$)$_3$), 2.17 (s, 15H, Cp*), 1.76 (m, 27H, P(CH$_2$$CH_3$)$_3$). ^{13}C{^{1}H} NMR (acetone-d_6): δ 103.5 (m, C_5(CH$_3$)$_5$), 18.9 (m, P(CH$_2$CH$_3$)$_3$), 12.3 (m, P(CH$_2$$CH_3$)$_3$), 10.6 (s, C$_5$($CH_3$)$_5$). ^{31}P{^{1}H} NMR (acetone-d_6): δ 40.5 (d, $J_{Rh-P} = 134.2$ Hz). IR (KBr): 2973, 2049, 1635, 1462, 1420, 1384, 1268, 1154, 1031, 760, 721, 636 cm^{-1}. Anal. Calc. for $C_{30}H_{60}O_6F_6P_3S_2Rh$: C, 40.45; H, 6.79; S, 7.20. Found: C, 40.56; H, 6.32; S, 6.41%.

Complex **2c** was similarly prepared, but the solution was refluxed to enhance the yield and to complete the reaction. Yield: 57%. ^{1}H NMR ($CDCl_3$): δ 7.24–7.86 (m, 45H, PPh$_3$), 1.19 (q, 15H, $J_{H-P} = 3.5$ Hz, Cp*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 125.1–143.3 (m, PPh$_3$), 104.5 (m, C_5(CH$_3$)$_5$), 10.2 (s, C$_5$(CH$_3$)$_5$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 48.5 (d, $J_{Rh-P} = 146.7$ Hz). IR (KBr): 3057, 2965, 2924, 1659, 1636, 1588, 148, 1437, 1381, 1267, 1224, 1154, 1118, 1092, 1030, 747, 723, 696, 638, 541, 520 cm^{-1}. M.p.: 114–116 °C (decomp). Anal. Calc. for $C_{66}H_{60}O_6F_6P_3S_2Rh$: C, 59.91; H, 4.57; S, 4.85. Found: C, 58.93; H, 4.31; S, 4.56%.

Complex **2d** was prepared similarly to **2a**. Yield: 49%. ^{1}H NMR (acetone-d_6): δ 4.16 (m, OMe), 1.93 (q, $J_{H-P} = 2.5$ Hz, C$_5$Me$_5$). ^{13}C{^{1}H} NMR (acetone-d_6): δ 111.5 (m, C_5Me$_5$), 57.1 (m, OMe), 9.42 (s, C$_5$(CH$_3$)$_5$). ^{31}P{^{1}H} NMR (acetone-d_6): δ 119.5 (d, $J_{Rh-P} = 195.3$ Hz). IR (KBr): 2978, 2931, 1659, 1447, 1275, 1154, 1030, 805, 638 cm^{-1}. M.p.: 194–196 °C (decomp). Anal. Calc. for $C_{21}H_{42}O_{15}F_6P_3S_2Rh$: C, 27.76; H, 4.66; S, 7.06. Found: C, 27.74; H, 4.65; S, 7.25%.

Complex **2e** was also prepared similarly to **2a**. Yield: 51%. ^{1}H NMR (acetone-d_6): δ 4.50 (m, 18H, P(OCH_2CH$_3$)$_3$), 2.09 (s, 15H, C$_5$Me$_5$), 1.50 (t, 27H, $J_{H-P} = 7$ Hz, P(OCH$_2$CH_3)$_3$). ^{13}C{^{1}H} NMR (acetone-d_6): δ 110.6 (m, C_5(CH$_3$)$_5$), 67.0 (m, P(OCH$_2$CH$_3$)$_3$), 15.5 (m, P(OCH$_2$$CH_3$)$_3$), 9.42 (s, C$_5$($CH_3$)$_5$); ^{31}P{^{1}H} NMR (acetone-d_6): δ 114.4 (d, $J_{P-Rh} = 219.8$ Hz). IR (KBr): 2986, 1661, 1473, 1389, 1274, 1151, 1030, 963, 784, 636, 569 cm^{-1}. M.p.: 170–172 °C (decomp). Anal. Calc. for $C_{30}H_{60}O_{15}F_6P_3S_2Rh$: C, 34.82; H, 5.84; S, 6.20. Found: C, 35.63; H, 5.41; S, 6.69%.

2.3. Preparation of [$Cp^*Rh(\eta^4$-$C_4Ph_4)$] (3)

A solution of **1** (52 mg, 0.073 mmol) and diphenylacetylene (55 mg, 0.31 mmol) in ethanol (40 ml) was refluxed for 20 h. After cooling at room temperature, the solution was filtered, and the resulting yellow precipitates were washed with ethanol (10 ml × 2) and diethyl either (10 ml × 2), and then dried under vacuum. This product was recrystallized from CH_2Cl_2–hexane. The resulting complex was identified by comparing its NMR spectra, melting point, and X-ray diffraction data with the literature data [33].

Yield: 69%, 30 mg, 0.050 mmol. ^{1}H NMR ($CDCl_3$): δ 1.54 (s, 15H, $C_5(CH_3)_5$), 7.26–7.12 (m, 20H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 9.34 (s, $C_5(CH_3)_5$), 93.9 (d, $J_{Rh-C} = 6.7$ Hz, $C_5(CH_3)_5$). IR (KBr): 3058, 2965, 1635, 1597, 1498, 1065, 1025, 779, 743, 699, 559 cm^{-1}. M.p.: 273–275 °C (decomp).

2.4. Preparation of [$Cp^*Rh(\eta^5$-$C_5H_2Ar_2$–$CH(Ar)OEt)$-(OTf) (Ar = Ph (**4a**), p-tolyl (**4b**))

A solution of **1** (49 mg, 0.069 mmol) and phenylacetylene (0.030 ml, 0.27 mmol) in ethanol (40 ml) was refluxed for 15 h, and then the solvent was removed under vacuum. The residue was washed with diethyl either (10 ml × 2) and hexane (10 ml × 2), and then dried under vacuum to give an orange solid of **4a**. This product was recrystallized from CH_2Cl_2–hexane.

Yield: 79%, 40 mg, 0.054 mmol. ^{1}H NMR ($CDCl_3$): δ 7.24–7.71 (m, 15H, Ph), 6.29 (d, $^4J_{H-H} = 1.5$ Hz, 1H, Cp), 6.08 (d, $^4J_{H-H} = 1.5$ Hz, 1H, Cp), 5.47 (s, 1H, C*H*(Ph)OEt), 3.37 (dq, $^2J_{H-H} = 3.0$ Hz, $^3J_{H-H} = 7.0$ Hz, 2H, OCH_2CH_3), 1.67 (s, 15H, $C_5(CH_3)_5$), 1.11 (dt, $^2J_{H-H} = 3.0$ Hz, $^3J_{H-H} = 7.0$ Hz, 3H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 126.45–139.32 (m, Ph), 106.98 (d, $^1J_{Rh-C} = 7.3$ Hz, $C_5(CH_3)_5$), 106.26 (d, $^1J_{Rh-C} = 6.0$ Hz, Cp *C*Ph), 103.15 (d, $^1J_{Rh-C} = 6.7$ Hz, Cp *C*Ph), 101.43 (d, $^1J_{Rh-C} = 7.8$ Hz, Cp *C*C), 84.91 (d, $^1J_{Rh-C} = 7.3$ Hz, Cp *C*H), 84.40 (d, $^1J_{Rh-C} = 7.3$ Hz, Cp *C*H), 77.82 (s, *C*H(Ph)OEt), 65.10 (s, OCH_2CH_3), 15.23 (s, OCH_2CH_3), 9.46 (s, $C_5(CH_3)_5$). IR (KBr): 3083, 2972, 1667, 1629, 1454, 1385, 1263, 1160, 1030, 769, 699, 638 cm^{-1}. M.p.: 126–128 °C (decomp). Anal. Calc. for $C_{37}H_{38}F_3O_4SRh$: C, 60.16; H, 5.19; S, 4.34. Found: C, 59.89; H, 5.07; S, 4.21% [11].

Complex **4b** was prepared similarly to complex **4a**. Yield: 59%. ^{1}H NMR ($CDCl_3$): δ 7.13–7.59 (m, 15H, $C_6H_4CH_3$), 6.12 (d, $^4J_{H-H} = 1.5$ Hz, 1H, Cp), 6.01 (d, $^4J_{H-H} = 1.5$ Hz, 1H, Cp), 5.38 (s, 1H, C*H*(*p*-tolyl)OEt), 3.33 (dq, $^2J_{H-H} = 3.0$ Hz, $^3J_{H-H} = 7.0$ Hz, 2H, OCH_2CH_3), 2.44 (s, 3H, $C_6H_4CH_3$), 2.37 (s, 3H, $C_6H_4CH_3$), 2.32 (s, 3H, $C_6H_4CH_3$), 1.65 (s, 15H, $C_5(CH_3)_5$), 1.09 (dt, $^2J_{H-H} = 3.0$ Hz, $^3J_{H-H} = 7.0$ Hz, 3H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 124.56–140.71 (m, $C_6H_4CH_3$), 106.33 (d, $^1J_{Rh-C} = 7.3$ Hz, $C_5(CH_3)_5$), 106.09 (d, $^1J_{Rh-C} = 6.2$ Hz, Cp *C*Ph), 103.45 (d, $^1J_{Rh-C} = 6.7$ Hz, Cp *C*Ph), 101.21 (d, $^1J_{Rh-C} = 7.8$ Hz, Cp *C*C), 84.32 (d, $^1J_{Rh-C} = 7.3$ Hz, Cp *C*H), 83.95 (d, $^1J_{Rh-C} = 6.7$ Hz, Cp *C*H), 77.64 (s, *C*H(*p*-tolyl)OEt), 64.91 (s, OCH_2CH_3), 21.61 (s, $C_6H_4CH_3$), 21.57 (s, $C_6H_4CH_3$), 21.39 (s, $C_6H_4CH_3$), 15.23 (s, OCH_2CH_3), 9.50 (s, $C_5(CH_3)_5$). IR (KBr): 3081, 2974, 1637, 1473, 1386, 1264, 1156, 1031, 826, 769, 638 cm^{-1}. Mp: 188–190 °C (decomp). Anal. Calc. for $C_{40}H_{44}F_3O_4SRh$: C, 61.54; H, 5.68; S, 4.11. Found: C, 61.65; H, 5.49; S, 4.03% [11].

2.5. Preparation of [$Cp^*Rh(\eta^4$-$C_4(C(O)CH_3)_2H$-$(SiMe_3)$)] (5)

After a deep purple solution of **1** (53 mg, 0.074 mmol) and 1,4-bis(trimethylsilyl)-1,3-butadiyne (15 mg, 0.077 mmol) in EtOH (40 ml) was refluxed with stirring for 30 h, the solvent was removed under vacuum. The residue was washed with hexane (20 ml × 3), and then dried under vacuum to give a red-orange solid of **5**. This product was crystallized from CH_2Cl_2–hexane.

Yield: 42%, 14 mg, 0.031 mmol. ^{1}H NMR ($CDCl_3$): δ 4.90 (d, 1H, $J_{Rh-H} = 1.0$ Hz, (η^4-C$_4$)*H*), 1.90 (s, 15H, $C_5(CH_3)_5$), 1.85 (s, 6H, C(O)C*H*$_3$), 0.23 (s, 9H, Si(C*H*$_3$)$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 195.4 (s, *C*(O)CH$_3$), 116.5 (s, *C*SiMe$_3$), 95.6 (d, $J_{Rh-C} = 7.3$ Hz, $C_5(CH_3)_5$), 79.8 (d, $J_{Rh-C} = 10.1$ Hz, *C*C(O)CH$_3$), 72.0 (d, 1H, $J_{Rh-C} = 11.1$ Hz, (η^4-C$_3$*C*)*H*), 25.2 (s, C(O)*C*H$_3$), 10.4 (s,

Table 1
X-ray data collection and structure refinement for **1** · H_2O, **2e**, and **5**

	1 · H_2O	**2e**	**5**
Formula	$C_{24}H_{36}F_6NO_7RhS_2$	$C_{30}H_{60}F_6O_{15}P_3RhS_2$	$C_{21}H_{31}O_2RhSi$
F_w	731.57	1034.72	446.46
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	$Cmc2_1$	$P2_1/c$	$P\bar{1}$
a (Å)	19.851(2)	12.186(2)	9.152(1)
b (Å)	9.870(1)	20.690(2)	9.178(1)
c (Å)	15.775(1)	18.774(5)	14.650(2)
α (°)			72.649(9)
β (°)		96.90(2)	73.985(9)
γ (°)			72.238(8)
V (Å^3)	3090.8(4)	4699(2)	1095.2(2)
Z	4	4	2
D_{cal} (g cm^{-3})	1.572	1.463	1.354
μ (mm^{-1})	0.765	0.635	0.845
$F(000)$	1496	2144	464
T_{min}	0.8052	0.5716	0.7849
T_{max}	0.9345	0.8695	0.9413
No. of reflns measured	9456	8588	4069
No. of reflns unique	3611	8184	3809
No. of reflns with $I > 2\sigma(I)$	3414	4405	3690
No. of params refined	217	440	235
Max in $\Delta\rho$ (e Å^{-3})	0.604	1.037	0.224
Min in $\Delta\rho$ (e Å^{-3})	−0.318	−1.024	−0.255
GOF on F^2	1.075	1.029	1.066
R_1[a]	0.0329	0.0995	0.0207
wR_2[b]	0.0874	0.2600	0.0550

[a] $R_1 = \sum\|F_o| - |F_c\|\Sigma|F_o|$.
[b] $wR_2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

$C_5(CH_3)_5$), 0.46 (s, $Si(CH_3)_3$). IR (KBr): 2957, 2910, 1659, 1461, 1381, 1213, 842, 455 cm^{-1}. M.p.: 184–186 °C (decomp). Anal. Calc. for $C_{21}H_{31}O_2SiRh$: C, 56.49; H, 7.00. Found: C, 55.44; H, 6.88%.

2.6. X-ray crystal structure determination

X-ray data were collected with either a Bruker CCD SMART diffractometer (complex $\mathbf{1} \cdot H_2O$) or a Siemens P4 diffractometer (complexes **2e** and **5**) equipped with a Mo X-ray tube. Intensity data were empirically corrected for absorption with ψ-scan data, except complex $\mathbf{1} \cdot H_2O$ for which absorption corrections were made with SADABS. All calculations were carried out with the use of SHELXTL programs [34]. All the structures were solved by direct methods. Unless otherwise stated, all non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated in ideal positions and refined in a riding mode (see Table 1).

A dark brown crystal of $\mathbf{1} \cdot H_2O$, shaped as a block of approximate dimensions $0.33 \times 0.18 \times 0.10$ mm, was used for crystal- and intensity-data collection. Unit-cell parameters and systematic absences indicated three possible space groups: *Cmc*2_1, *Cmcm*, and *Ama*2. The structure analysis converged only in *Cmc*2_1. An orange crystal of **2e** (block, $0.26 \times 0.24 \times 0.20$ mm) was used. The atoms in highly disordered triflate counterions in **2e** were refined isotropically. A yellow crystal of **5** (block, $0.54 \times 0.49 \times 0.44$ mm) was used. The hydrogen (H16) atom attached to the cyclobutadiene ring was located and refined isotropically. Selected bond lengths and angles are shown in Table 2.

3. Results and discussion

3.1. Preparation of $[Cp^*Rh(\eta^6\text{-}2,6\text{-}(Me_2CH)_2C_6H_3NH_2)](OTf)_2$ (1)

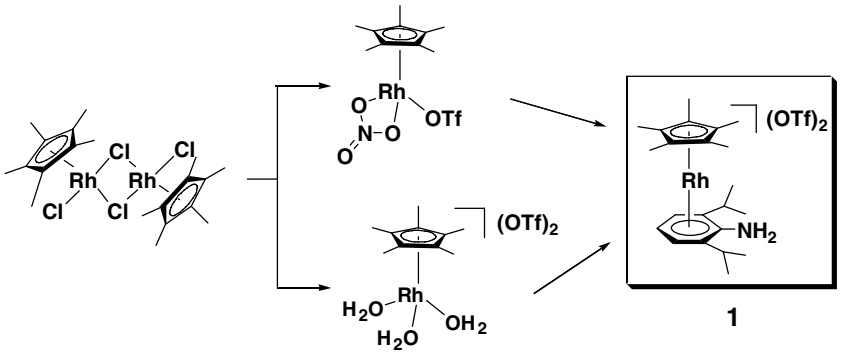
As mentioned in Section 2, the cationic Cp^*Rh–aniline complex **1** could be prepared in two ways (Scheme 1). In the first method, the commercially available $[Cp^*Rh(\mu\text{-}Cl)Cl]_2$ is converted to $[Cp^*Rh(NO_3)(OTf)]$ [30] by the two-step addition of $AgNO_3$ and AgOTf, which is subsequently treated with 2,6-diisopropylaniline to give complex **1** in 53% yield. The second method starts from $[Cp^*Rh(OH_2)_3](OTf)_2$ [31], which can be prepared from $[Cp^*Rh(\mu\text{-}Cl)Cl]_2$ in high yield just in a single step. The reaction involving $[Cp^*Rh(OH_2)_3](OTf)_2$ produced complex **1** in 91% yield. A series of dicationic Cp^*Rh–arene and Cp^*Rh–aniline complexes $[Cp^*Rh(X)]Y_2$ (X = aniline or arene; Y = BF_4 or PF_6), which closely resemble complex **1**, have been reported [31,32].

Complex **1** is stable both in solution and in the solid state, and has been fully characterized by NMR (^1H and $^{13}C\{^1H\}$), IR, elemental analysis, and X-ray diffraction. The N–H bonds in the aniline ligand appear at 3346 and 3227 cm^{-1} in the IR spectrum. The ^1H NMR of complex **1** displays two doublets at δ 1.50 and 1.36 ppm, which correspond to two distinct methyl protons. This observation is due to the presence of the diastereotopic methyl protons in the isopropyl group that is bonded to the C8 (Fig. 1) on the aniline ring. This carbon can be thought of as bonding to four different groups (C7, C9, C11, and Rh), and therefore as a pseudo-chiral center. The diastereotopic nature of the germinal dimethyl groups is also reflected in the $^{13}C\{^1H\}$ NMR spectrum, which displays a pair of singlets at 19.3 and 20.2 ppm.

The structure of the cationic part of complex **1** with the atom-numbering scheme is shown in Fig. 1, which shows a molecular mirror plane passing through C4, C1, Rh1, C10, C7, and N1 atoms. The coordination sphere of Rh can be described as pseudo-octahedral if the coordination numbers of both rings (Cp^* and aniline) are taken to be three. The η^5-Cp^* and η^6-aniline rings are essentially parallel to each other with a dihedral angle of 0.4(3)°. The Rh–C_{Cp^*} (C_{Cp^*} is the centroid of the Cp^* ring) and Rh–$C_{Cp'}$ ($C_{Cp'}$ is the centroid of the aniline ring) distances are 1.796 and 1.793 Å, respectively, and the C_{Cp^*}–Rh–$C_{Cp'}$ angle is 177°.

Table 2
Selected bond lengths (Å) and bond angles (°)

Complex $\mathbf{1} \cdot H_2O$					
Rh1–C3	2.159(3)	Rh1–C1	2.173(5)	Rh1–C2	2.177(3)
Rh1–C10	2.220(4)	Rh1–C9	2.245(3)	Rh1–C8	2.323(3)
Rh1–C7	2.395(3)				
Complex **2e**					
Rh1–P2	2.273(3)	Rh1–P3	2.278(3)	Rh1–P1	2.285(3)
P2–Rh1–P3	90.6(1)	P2–Rh1–P1	94.6(1)	P3–Rh1–P1	91.9(1)
Complex **5**					
Rh1–C16	2.100(2)	Rh1–C13	2.121(2)	Rh1–C15	2.127(2)
Rh1–C14	2.132(2)	C13–C16	1.449(3)	C13–C14	1.475(3)
C14–C15	1.475(3)	C15–C16	1.447(3)	O1–C12	1.207(3)
O2–C17	1.207(3)	C11–C12	1.499(3)	C17–C18	1.508(3)
C16–C13–C12	133.0(2)	C16–C13–C14	91.3(2)	C12–C13–C14	135.7(2)
C13–C14–C15	87.6(2)	C16–C15–C14	91.4(2)	C15–C16–C13	89.7(2)
O1–C12–C13	122.1(2)	O1–C12–C11	121.5(2)	C13–C12–C11	116.4(2)
O2–C17–C15	122.1(2)	O2–C17–C18	121.7(2)	C15–C17–C18	116.2(2)



Scheme 1.

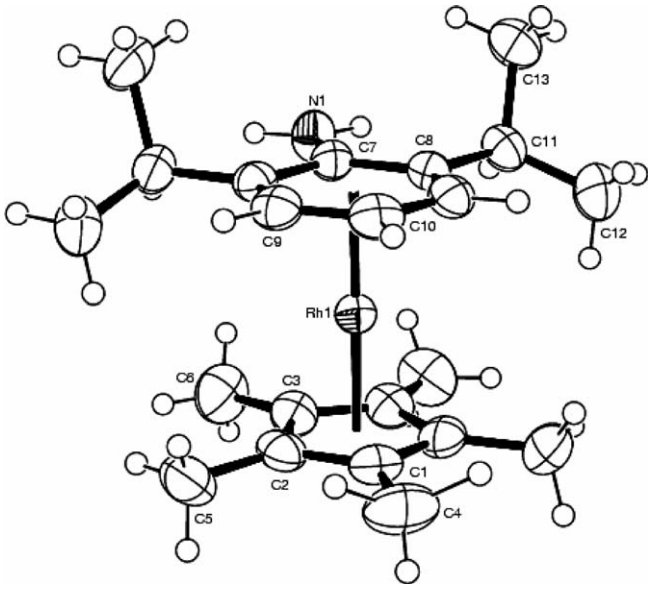
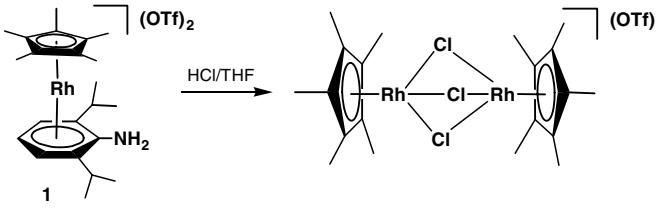


Fig. 1. ORTEP drawing of the cationic part of complex $\mathbf{1} \cdot H_2O$, showing the atom-labeling scheme and 50% probability thermal ellipsoids.

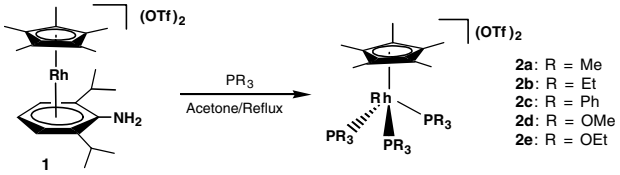
We examined whether complex **1** would return to its starting complex $[Cp^*Rh(\mu\text{-}Cl)Cl]_2$ on addition of HCl. Interestingly, treating complex **1** with HCl (1.0 M solution in diethyl ether) in THF gave $[Cp^*Rh(\mu\text{-}Cl)_3RhCp^*](OTf)$, a dinuclear complex triply bridged by three μ-Cl ligands (Eq. (1)). This product has been identified by comparing its spectral data (NMR and IR spectra), melting point, and X-ray crystal structure with those for the genuine complex in the literature [33]. This reaction gives the same product (92% isolation yield), regardless of the stoichiometric mole ratios between complex **1** and HCl (1:1, 1:2, 1:3), although the lower-ratio reaction leaves some unreacted complex **1**. These results indicate that the aniline ligand in complex **1** is labile enough to be replaced by the weak nucleophilic Cl^- ion. Closely related complexes $[Cp^*Rh(\mu\text{-}Cl)_3RhCp^*](BPh_4)$, $[Cp^*Rh(\mu\text{-}Cl)_3RhCp^*](PF_6)$, and $[Cp^*Rh(\mu\text{-}I)_3RhCp^*](BF_4)$ have been reported [35–37].



(1)

3.2. Reactivity of *1* toward phosphines and phosphites

Treatment of **1** with 3 equiv. of PR_3 (R = Me, Et, Ph, OMe, OEt) in refluxing acetone gave $[Cp^*Rh(PR_3)_3](OTf)_2$ (**2a**–**e**) in 54–66% yields (Eq. (2)). At room temperature, these reactions proceed in much lower yields. In particular, the room-temperature reaction with triphenylphosphine does not occur at all. This observation suggests that triphenylphosphine may experience steric hindrance on approaching the rhodium metal center of complex **1**, which may be explained on the basis of cone angles of phosphines (PMe_3: 118°; PEt_3: 132°; PPh_3: 145°).



(2)

Complexes **2a**–**e** were characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR, IR, and elemental analysis. In particular, complex **2e** was structurally characterized by X-ray diffraction. Whereas complexes **2b** and **2c** are somewhat air-sensitive, the other complexes are air-stable. The IR spectra of these complexes display characteristic peaks for the common OTf^- counterion at 1267–1275 (S=O), 1030–1033 (S–O), 1147–1154 (C–F), and 636–638 cm^{-1} (S–O). Complexes containing the counterion PF_6^-, $[Cp^*Rh(P(OMe)_3)_3](PF_6)_2$ and $[Cp^*Rh(P(OEt)_3)_3](PF_6)_2$, which are quite close to complexes **2d** and **2e**, were previously prepared from the acetone solvate complex $[Cp^*Rh(acetone)_3](PF_6)_2$ and the corresponding phosphites, and characterized by ^1H and $^{13}C\{^1H\}$ NMR [38].

The structure of the cationic part of complex **2e** is shown in Fig. 2. It has a three-legged piano-stool structure with three triethyl phosphite ligands being regarded as three legs. The Rh–P bond lengths range from 2.273(3) to 2.285(3) Å. The P–Rh–P bond angles are in the range of 90.6(1)–94.6(1)° with an average of 92.4°.

3.3. Reactivity of *1* with alkynes

The reactivity of complex **1** toward alkynes depends on the nature of the alkyne and the solvent used.

Complex **1** mediated the [2 + 2] cycloaddition of diphenylacetylene to generate a tetraphenylcyclobutadiene ligand. Refluxing an ethanol solution containing complex **1** and diphenylacetylene produced the Rh–cyclobutadiene complex [$Cp^*Rh(\eta^4\text{-}C_4Ph_4)$] (**3**) in 69% yield (Scheme 2). Complex **3** was identified by comparing its NMR, IR, and X-ray diffraction data with those for the genuine complex in the literature, which was originally prepared from [$Cp^*Rh(\eta^2\text{-}NO_3)(\eta^1\text{-}OTf)$] and diphenylacetylene [33]. This observation also indicates the labile character of the aniline ligand in complex **1**. Unfortunately, reactions involving other alkynes, terminal or internal, such as $CH_3(CH_2)_3{-}C{\equiv}C{-}H$, $Me_3Si{-}C{\equiv}C{-}H$, $Me_3Si{-}C{\equiv}C{-}SiMe_3$, $CH_3OCH_2{-}C{\equiv}C{-}H$, $Ph{-}C{\equiv}C{-}C{\equiv}C{-}Ph$, $Et{-}C{\equiv}C{-}Et$, and $Ph{-}C{\equiv}C{-}Me$, gave only intractable mixtures, from which the products could not be isolated.

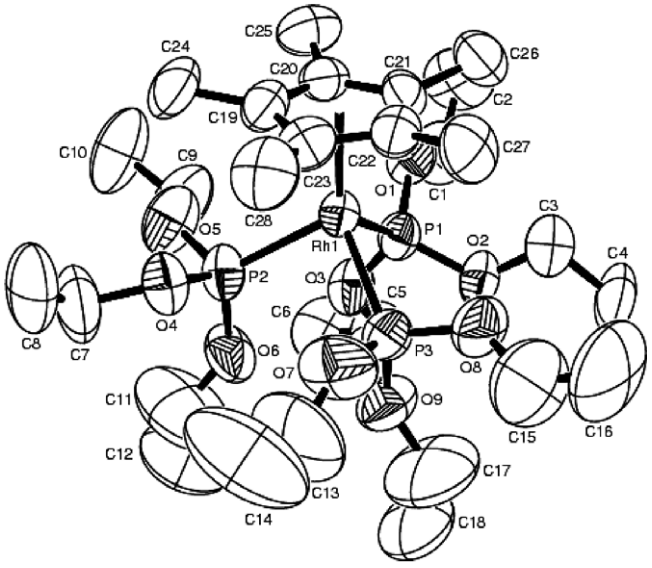
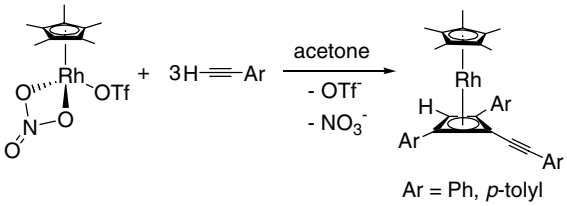


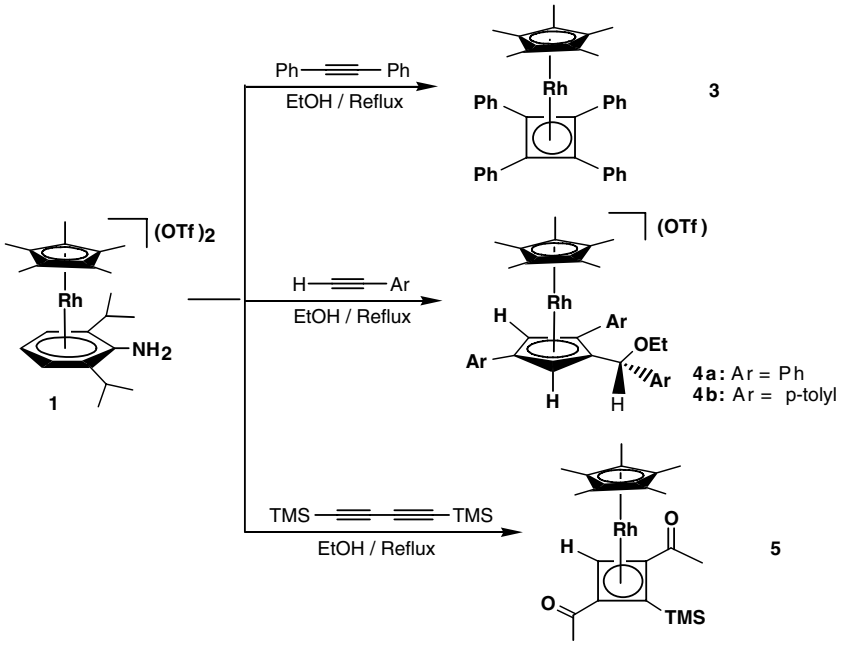
Fig. 2. ORTEP drawing of the cationic part of complex **2e**.

We recently observed a rather unusual cyclotrimerization of some terminal aryl alkynes $H{-}C{\equiv}C{-}Ar$ (Ar = Ph or *p*-tolyl) in acetone mediated by [$Cp^*Rh(\eta^2\text{-}NO_3)(OTf)$] to give ($\eta^4$-cyclobutadiene)rhodium complexes [$Cp^*Rh(\eta^4\text{-}C_4HAr_2{-}C{\equiv}CAr)$] (Eq. (3)) [33]. For a comparative study, we treated complex **1** with the same terminal alkynes, but did not observe any sign of reactivity even in refluxing acetone. It should be mentioned that Carmona's group was the first to report this type of cyclotrimerization of aryl alkynes with [Cp^*Rh(L-alaninate)Cl] [39].



(3)

Considering the lack of reactivity of complex **1** toward the terminal aryl alkynes in acetone, we decided to change the solvent from acetone to ethanol with an attempt to

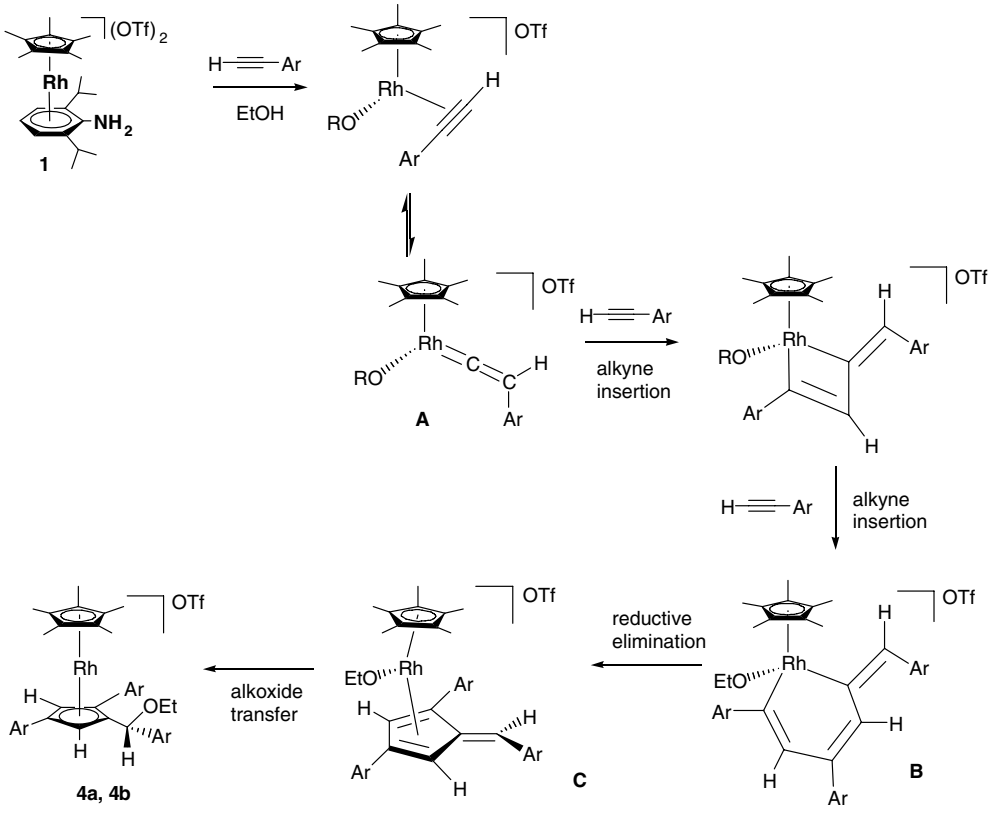


Scheme 2.

bring about different reactions. Consistent with our expectation, complex **1** did exhibit reactivity in ethanol. Refluxing a mixture of complex **1** and these alkynes (HC≡CPh and HC≡$CC_6H_4CH_3$) in ethanol produced the cationic rhodonocene-like complexes, $[Cp^*Rh(\eta^5\text{-}C_5H_2Ar_2\text{–}CH(Ar)(OEt))]^+(OTf)^-$ (Ar = Ph (**4a**), *p*-tolyl (**4b**)) (Scheme 2). The same reactivity was very recently observed in the reactions of $[Cp^*Rh(\eta^2\text{-}NO_3)(OTf)]$ with terminal aryl alkynes (HC≡CPh and HC≡$CC_6H_4CH_3$) in alcohol (EtOH and *n*-BuOH) [11]. It is worth noting that $[Cp^*Rh(\eta^2\text{-}NO_3)(OTf)]$ reacted with the terminal alkynes at room temperature, but complex **1** reacted under reflux conditions. These results indicate the lower reactivity of complex **1** compared to $[Cp^*Rh(\eta^2\text{-}NO_3)(OTf)]$ and suggest that the active species in reactions of both complexes probably be the cationic $[Cp^*Rh]^+$ moiety. In this contest, the difference in reactivity between these complexes is believed to arise basically from the difference in lability between the acting ligands (arene versus NO_3^- and triflate). This type of reactivity also appears to occur in other refluxing alcohol solvents such as methanol and isopropanol, although we failed to characterize products. Room-temperature reactions, however, do not proceed in all cases.

Although the present results do not give any detailed information about how rhodocenium cations have been formed, we do believe that our reaction proceeds according to the mechanism proposed for the reaction involving $[Cp^*Rh(\eta^2\text{-}NO_3)(OTf)]$, as shown in Scheme 3 [11]. The first step involves the formation of the rhodium–vinylidene species **A** by proton transfer of an aryl alkyne and the binding of an alkoxide with the liberation of HOTf. Two aryl alkynes then sequentially insert to give the metallacyclohexadiene intermediate **B**, which undergoes reductive elimination to give the fulvene-type species **C**. Finally, the coordinated ethoxide attacks the exocyclic carbon of the intermediate **C** to give the ultimate product. On the [2 + 2 + 1] cyclotrimerization of alkynes, two mechanisms have been proposed so far: a metallacyclopentadiene route and a metallacyclohexadiene route [13–22]. The mechanism involving the metallacyclohexadiene intermediate seems to be appropriate to our case.

Complex **1** mediated an unexpected transformation of bis(trimethylsilyl)butadiene ($Me_3Si\text{–}C{\equiv}C\text{–}C{\equiv}C\text{–}SiMe_3$). Refluxing an ethanol solution containing complex **1** and bis(trimethylsilyl)butadiene for 30 h gave $[Cp^*Rh(\eta^4\text{-}C_4(C(O)CH_3)_2H(SiMe_3))]$ (**5**) in 42% yield (Scheme 2). However, no reaction occurred in ethanol at room temperature. Furthermore, we did not see any sign of reactivity in acetone and THF regardless of various reaction conditions. The chemical formula of complex **5** indicates several facts. (1) The Rh metal was formally reduced from +3 to +1 during the reaction. (2) One dyne appears to be involved in the cyclization with the release of one trimethylsilyl group. (3) The solvent ethanol was oxidized and bound



Scheme 3.

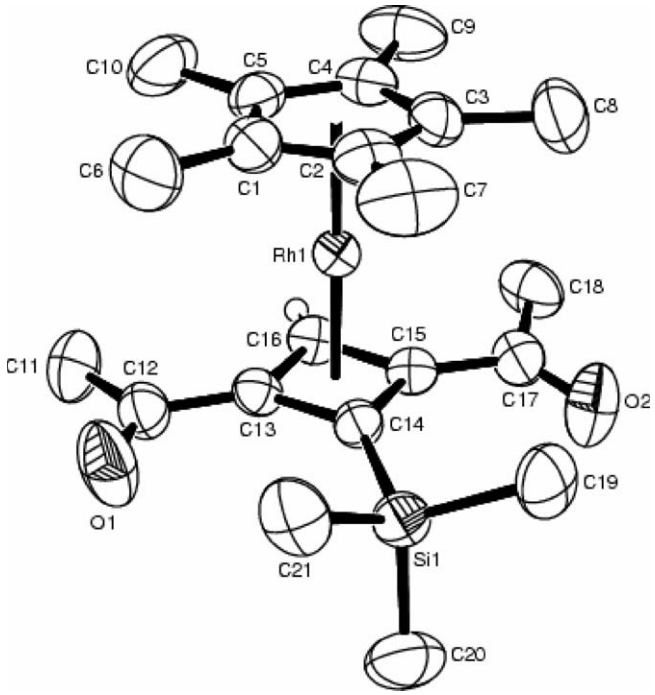


Fig. 3. ORTEP drawing of complex **5**.

to the newly formed cyclobutadiene ring in the form of an acetyl group. Despite the facts described above, we cannot provide a reasonable explanation for the formation of complex **5**.

The molecular structure of complex **5** is shown in Fig. 3. It has a two-legged piano-stool structure with a cyclobutadiene ring being regarded as two legs. The hydrogen atom attached to C16 in the cyclobutadiene ring was located and reasonably refined. Two acetyl groups are not parallel to each other, and their dihedral angle is 12.0(2)°. The Cp^* and cyclobutadiene rings are essentially planar, and their dihedral angle is 3.4(1)°. The Rh–Ct1 (Ct1 is the centroid of C1–C5; 1.836 Å) and Rh–Ct2 (Ct2 is the centroid of C13–C16; 1.851 Å) distances and the Ct1–Rh–Ct2 angle (178.27°) are very close to those in $[Cp^*Rh(\eta^4\text{-}C_4Ph_4)]$ and [33] and $[Cp^*Rh(\eta^4\text{-}C_4HPh_2\text{–}C{\equiv}C\text{–}Ph)]$ [39].

In summary, we investigated the reactivity of $[Cp^*Rh(\eta^6\text{-}C_6H_3NH_2\text{–}2,6\text{-}i\text{-}Pr_2)](OTf)_2$ toward phosphines (PMe_3, PEt_3, PPh_3), phosphites ($P(OMe)_3$, $P(OEt)_3$), an internal alkyne (Ph—C≡C—Ph), terminal alkynes (H—C≡C—Ph and H—C≡C—$C_6H_4CH_3$), and a dyne ($(Me_3Si—C{\equiv}C—C{\equiv}C—SiMe_3)$). Complex **1** underwent substitution with phosphines or phosphites. Whereas complex **1** mediated the [2 + 2] cycloaddition of diphenylacetylene to give a tetraphenylcyclobutadiene ligand, it mediated the [2 + 2 + 1] cyclotrimerization of terminal alkynes to produce rhodonocene-like complexes containing one Cp^* and one substituted-Cp, $[Cp^*Rh(\eta^5\text{-}C_5H_2Ar_2\text{–}CH(Ar)\text{-}(OEt))]^+(OTf)^-$ (Ar = Ph, *p*-tolyl). Interestingly, the corresponding reaction with 1,4-bis(trimethylsilyl)-1,3-butadiyne ($Me_3Si—C{\equiv}C—C{\equiv}C—SiMe_3$) produced an unusual complex $[Cp^*Rh(\eta^4\text{-}C_4(C(O)CH_3)_2H(SiMe_3))]$, which appears to have been formed through a complex series of reactions. Other reactivity studies are currently in progress.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center: 602168 (**1**), 602169 (**2e**), and 602170 (**5**). Copies of this information may be obtained free of charge from: The director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 336 033, email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

Acknowledgement

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