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Multiple Desilylation of Silylated Cyclopentadienes Promoted by Ionic Ruthenium and Rhodium Halides

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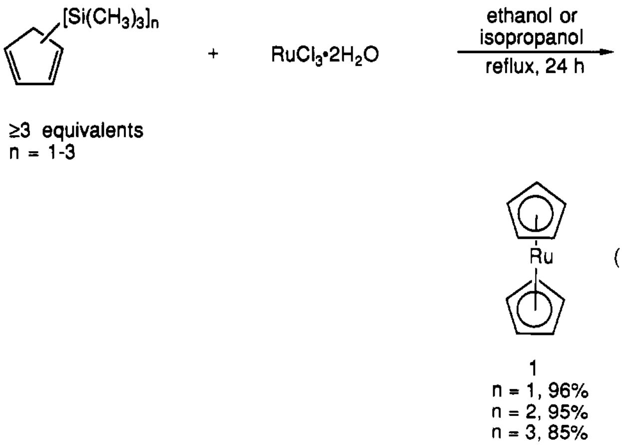
The reactivity of hydrated ruthenium trichloride and hydrated rhodium trichloride toward silylated cyclopentadienes was investigated. Treatment of ruthenium trichloride with (trimethylsilyl)cyclopentadiene, bis(trimethylsilyl)cyclopentadiene, or tris(trimethylsilyl)cyclopentadiene in alcohol solvents afforded ruthenocene in 85–96% isolated yields. GLC analysis of these reactions, as well as the reactions of benzyltriethylammonium chloride with (trimethylsilyl)cyclopentadiene, bis(trimethylsilyl)cyclopentadiene, and tris(trimethylsilyl)cyclopentadiene, revealed a novel chloride ion-induced desilylation of the silylated cyclopentadienes. These experiments demonstrated that the silylated cyclopentadienes were completely desilylated by chloride ion to afford cyclopentadiene, which then reacted with the ruthenium ion to afford ruthenocene. Treatment of hydrated rhodium trichloride with (trimethylsilyl)cyclopentadiene or cyclopentadiene monomer afforded cyclopentadienylrhodium dichloride oligomer in 93% and 82% yields, respectively. Treatment of hydrated rhodium trichloride with bis(trimethylsilyl)cyclopentadiene afforded cyclopentadienylrhodium dichloride oligomer (27%) and (trimethylsilyl)cyclopentadienylrhodium dichloride dimer (70%). The structure of (trimethylsilyl)cyclopentadienylrhodium dichloride dimer was determined, showing that this compound crystallized in the triclinic space group $P\bar{1}$ with cell dimensions a = 10.797(6) Å, b = 11.204(4) Å, c = 11.335(3) Å, α = 79.23(2)°, β = 70.28(3)°, γ = 64.75(3)°, V = 1166.0(8) Å^3, and Z = 2.

The reaction of transition metal halides with silylated and stannylated cyclopentadienes can represent an efficient approach to the synthesis of cyclopentadienyl complexes.[1,2] These transformations occur under very mild conditions and offer an attractive alternative to the use of strongly reducing cyclopentadienyl anions. In all such cleavages reported to date, the element-substituted cyclopentadiene $C_5(ER_3)_nH_{6-n}$ (n = 1–3; E = Si, Sn) reacts with a metal halide to afford a cyclopentadienyl complex which contains one less trialkylsilyl or trialkylstannyl group than was present in the starting cyclopentadiene. The trialkylsilyl halide or trialkylstannyl halide is also liberated in this process. We now report that the reaction of polysilylated cyclopentadienes with ruthenium and rhodium halides in polar solvents takes a very different course.[3] Treatment of ruthenium trichloride with (trimethylsilyl)cyclopentadiene, bis(trimethylsilyl)cyclopentadiene, and tris(trimethylsilyl)cyclopentadiene affords nearly quantitative yields of ruthenocene. The related reactions of rhodium trichloride with bis(trimethylsilyl)cyclopentadiene and tris(trimethylsilyl)cyclopentadiene are more complicated and yield mixtures of cyclopentadienyl complexes. These transformations occur through a novel chloride ion-induced desilylation process, which ultimately affords cyclopentadiene from polysilylated precursors. The crystal structure of (trimethylsilyl)cyclopentadienylrhodium dichloride dimer is also described.

Results

Reactions of Ruthenium Trichloride with Silylated Cyclopentadienes. We initially envisioned that the interaction of silylated cyclopentadienes with ruthenium trichloride might afford monocyclopentadienylruthenium dichloride complexes,[4] which would then afford synthetic entry to new half-sandwich ruthenium complexes. However, treatment of 3–4 equiv of (trimethylsilyl)cyclopentadiene (SiCpH) with hydrated ruthenium trichloride ($RuCl_3{\cdot}3H_2O$) in refluxing ethanol for 24 h, followed by workup, instead afforded ruthenocene (**1**) in 96% yield (eq 1). Ironically,



(1)

this is the highest yield yet reported for a preparation of this metallocene.[5] Similar results could be achieved in 2-propanol solvent. Reaction in several aprotic solvents afforded low, variable yields of **1** (dichloromethane (<5%), tetrahydrofuran (35%), acetonitrile (8%)). A protic solvent greatly increases the efficiency

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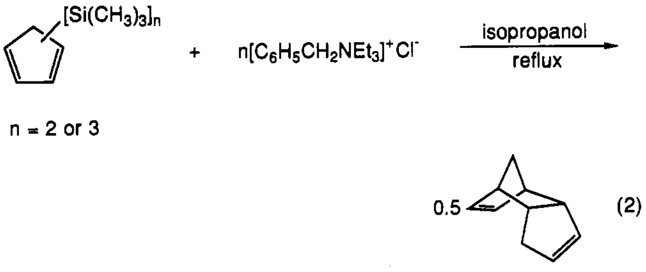
of the transformation. An excess of SiCpH (≥3 equiv) was required to achieve the maximum yields. When the reaction was conducted using 2.0 equiv of SiCpH, the yields of **1** ranged from 43 to 47%.

The reaction of hydrated ruthenium trichloride with 3 equiv of bis(trimethylsilyl)cyclopentadiene (Si_2CpH)[6] and tris(trimethylsilyl)cyclopentadiene (Si_3CpH)[6] was examined next. Surprisingly, both of these reactions afforded **1** in high yield (eq 1). There was no evidence for the anticipated 1,1′-bis(trimethylsilyl)ruthenocene and 1,1′,3,3′-tetrakis(trimethylsilyl)ruthenocene. An experiment was performed in which hydrated ruthenium trichloride was reacted with 3.0 equiv of Si_3CpH (99.8% pure by GLC) in refluxing 2-propanol for 0.5 h. Analysis of this solution by GLC and GLC/MS showed that when the reaction was about 25% complete, a 93:7 ratio of Si_3CpH:Si_2CpH was present. Additionally, **1** and (trimethylsilyl)ruthenocene had been produced in a 97:3 ratio. These results indicated that the silylated cyclopentadienes were being desilylated by a species present in the reaction mixture.

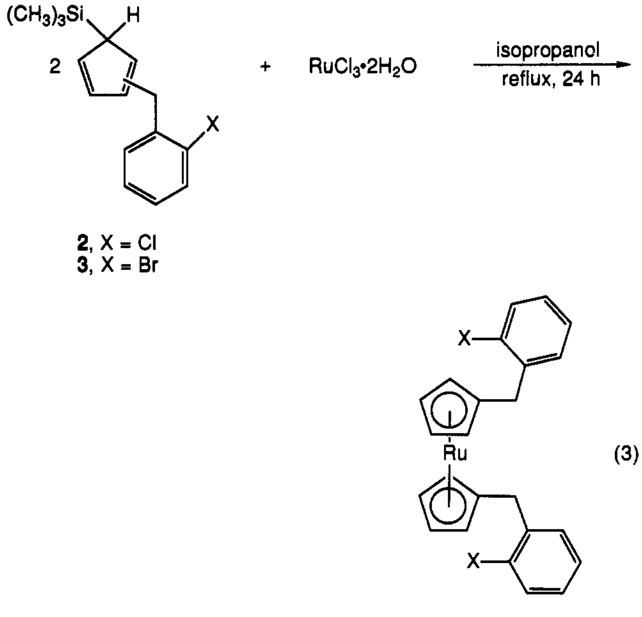
In order to gain a better understanding of the desilylation process, Si_2CpH and Si_3CpH were reacted with an ionic chloride ion source under conditions similar to those in the preparation of ruthenocene. Treatment of Si_2CpH with benzyltriethylammonium chloride (2 equiv) in refluxing 2-propanol for 1 h led to complete conversion to dicyclopentadiene (76%, eq 2). GLC analysis after 0.5 h revealed a 13:40:47 Si_2CpH:SiCpH:dicyclopentadiene mixture. A similar reaction of Si_3CpH and benzyltriethylammonium chloride (3 equiv) required 1.5 h for complete conversion to dicyclopentadiene (80%, eq 2), with GLC analysis after 1.0 h affording a 24:1:6:69 Si_3CpH:Si_2CpH:SiCpH:dicyclopentadiene mixture. Treatment of Si_2CpH with benzyltriethylammonium chloride (2 equiv) in refluxing 2-propanol for 1 h, followed by GLC/MS analysis, showed a peak corresponding to ethoxytrimethylsilane. However, its high volatility (bp 75 °C) made yield determination pointless. Refluxing Si_3CpH in 2-propanol for 4 h gave 5–10% conversion to Si_2CpH, which indicates that alcohols are sufficiently nucleophilic to desilylate Si_3CpH, although this reaction is sluggish relative to that of chloride ion. Refluxing Si_3CpH in 2-propanol containing 5% water for 4 h also gave 5–10% conversion to Si_2CpH. Hence, Si_2CpH and Si_3CpH are desilylated by chloride ion in a stepwise manner to ultimately afford dicyclopentadiene.



n = 2 or 3

n = 2, 76%
n = 3, 80%

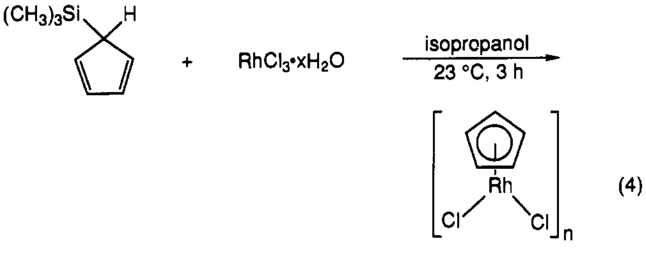
Synthesis of Substituted Ruthenocenes. It was envisioned that treatment of hydrated ruthenium trichloride with substituted (trimethylsilyl)cyclopentadienes would afford a useful synthetic route to substituted ruthenocenes,[7] since high yields of ruthenocene were obtained from the reaction of ruthenium trichloride with (trimethylsilyl)cyclopentadiene. The halobenzyl(trimethylsilyl)cyclopentadienes **2** and **3**, which were prepared by treatment of (trimethylsilyl)cyclopentadienyllithium with the appropriate *o*-halobenzyl halide, were reacted with ruthenium trichloride in refluxing 2-propanol for 24 h to afford the disubstituted ruthenocenes **4** and **5** in 92% and 86% yields, respectively (eq 3). The structures of **4** and **5** were established from the spectral and analytical data.



2, X = Cl
3, X = Br

4, X = Cl, 92%
5, X = Br, 86%

Reactions of Hydrated Rhodium Trichloride with Silylated Cyclopentadienes. It was anticipated that the reaction of silylated cyclopentadienes with rhodium trichloride ($RhCl_3 \cdot 2H_2O$) would afford entry into cyclopentadienylrhodium dichlorides. The chemistry of (pentamethylcyclopentadienyl)rhodium dichloride dimer has been extensively developed;[8] however, few other cyclopentadienyl analogs are available.[9] Accordingly, treatment of hydrated rhodium trichloride with SiCpH in 2-propanol at ambient temperature for 3 h afforded cyclopentadienylrhodium dichloride oligomer (**6**) as an orange powder which precipitated from the reaction medium in 93% yield (eq 4). The structure was established from spectral and analytical data. Complex **6** has been previously prepared in 66% yield from the reaction of hydrated rhodium trichloride with cyclopentadiene in methanol.[8d]



6, 93%

The facile formation of **6** raised the issue of whether it formed by a single-step insertion of a rhodium–chlorine bond into the carbon–silicon bond of SiCpH or by a two-step, chloride ion-induced desilylation of SiCpH to afford cyclopentadiene, which then reacted with rhodium(III) ion to afford **6**. To address this question, hydrated rhodium trichloride was reacted with freshly distilled cyclopentadiene (2 equiv) in 2-propanol at ambient

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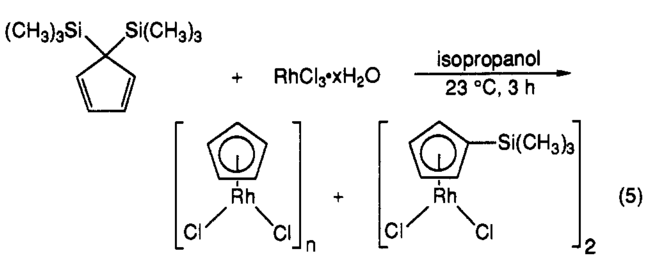
(6) Jutzi, P.; Sauer, R. *J. Organomet. Chem.* **1973**, *50*, C29. Miftakhov, M. S.; Tolstikov, G. A.; Lomakina, S. I. *Zh. Obshch. Khim.* **1976**, *46*, 2754. Frisch, K. C. *J. Am. Chem. Soc.* **1953**, *75*, 6050.

(7) For leading references to the synthesis of substituted ruthenocenes, see: Liles, D. C.; Shaver, A.; Singleton, E.; Wiege, M. *J. Organomet. Chem.* **1985**, *288*, C33. Albers, M. O.; Oosthuizen, H. E.; Robinson, D. J.; Shaver, A.; Singleton, E. *Ibid.* **1985**, *282*, C49. Albers, M. O.; Robinson, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1986**, *5*, 2199. Albers, M. O.; Liles, D. C.; Robinson, D. J.; Shaver, A.; Singleton, E.; Wiege, M. B.; Boeyens, J. C. A.; Levendis, D. C. *Ibid.* **1986**, *5*, 2321. Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1988**, *110*, 6130.

temperature for 3 h to afford **6** in 82% yield. The yield for this process was close to that obtained using SiCpH under similar conditions.

The reaction of hydrated rhodium trichloride with Si_2CpH was examined next. When the transformation was conducted using 2 equiv of the cyclopentadiene in isopropanol for 24 h at ambient temperature, the color gradually changed from deep red to light orange, and a small amount of an orange precipitate formed. Workup afforded a 27% yield of **6**, which was isolated as a spectroscopically pure orange powder upon filtration of the reaction solution (eq 5). Removal of the solvent from the filtrate afforded a 70% yield of (trimethylsilyl)cyclopentadienylrhodium dichloride dimer (**7**) as a light orange powder. The structure of **7** was deduced from spectral and analytical data and was further substantiated by an X-ray structure determination (vide infra). Unlike **6**, which was totally insoluble in most organic solvents, complex **7** exhibited moderate solubility in media such as dichloromethane, chloroform, and tetrahydrofuran.



6, 27% **7**, 70%

The observation of **6** in the reaction of hydrated rhodium trichloride with Si_2CpH implied that chloride ion-induced desilyltion of Si_2CpH was kinetically competitive with the formation of **7**. In an experiment conducted with 2 equiv of Si_2CpH, GLC analysis of the reaction solution after complete formation of **6** and **7** revealed a 92:8 ratio of Si_2CpH:SiCpH. No dicyclopentadiene was observed in the GLC trace. The presence of SiCpH was further evidence that a chloride ion-induced desilyltion process was operant. The fact that dicyclopentadiene was not observed is consistent either with its not being formed or with efficient trapping of monomeric cyclopentadiene by rhodium trichloride to form **6**.

The reaction of hydrated rhodium trichloride with Si_3CpH (2 equiv) in 2-propanol was explored as a possible route to (1,3-bis(trimethylsilyl)cyclopentadienyl)rhodium dichloride dimer (**8**). Unfortunately, a variety of conditions (ambient temperature, reflux) afforded variable mixtures of **6**, **7**, and a complex with spectral properties consistent with **8**. While complex **6** was easily isolated by filtration, **7** and **8** could not be separated by crystallization, due to their similar solubility properties. In view of these problems, further attempts at the synthesis of **8** were abandoned.

Structure of $[(\eta^5\text{-}C_5H_4Si(CH_3)_3)RhCl_2]_2$ (7). The crystal structure of **7** was determined in order to establish its nuclearity. X-ray data were collected under the conditions summarized in Table I. Bond lengths, bond angles, and positional parameters are summarized in Tables II and III. A perspective view is shown in Figure 1.

Table I. Experimental Crystallographic Data for **7**

chem formula	$C_8H_{13}Cl_2RhSi_2$
fw	339.175
space group	$P\bar{1}$
a (Å)	10.797(6)
b (Å)	11.204(4)
c (Å)	11.335(3)
α (deg)	79.23(2)
β (deg)	70.28(3)
γ (deg)	64.75(3)
V (Å^3)	1166.0(8)
Z	2
T, °C	18
ρ_{calcd} (g·cm^{-3})	1.772
λ (Å)	0.710 73
μ (cm^{-1})	19.58
trans coeff	0.912–0.655
$R(F_o)^a$	0.022
$R_w(F_o)^a$	0.027

[a] $R(F_o) = (\sum|\Delta F|/\sum|F_o|)$; $R_w(F_o) = [(\sum w|\Delta F|^2)/\sum wF_o^2]^{1/2}$.

Table II. Bond Lengths (Å) and Selected Bond Angles (deg) for **7**

Rh(1)–Cl(1)	2.4574(9)	C(1)–C(5)	1.428(5)
Rh(1)–Cl(2)	2.446(1)	C(1)–Si(1)	1.889(5)
Rh(1)–Cl(3)	2.373(1)	C(2)–C(3)	1.400(7)
Rh(1)–C(1)	2.146(5)	C(3)–C(4)	1.413(6)
Rh(1)–C(2)	2.154(5)	C(4)–C(5)	1.439(8)
Rh(1)–C(3)	2.136(5)	Si(1)–C(6)	1.862(6)
Rh(1)–C(4)	2.112(5)	Si(1)–C(7)	1.854(6)
Rh(1)–C(5)	2.107(5)	Si(1)–C(8)	1.857(4)
Rh(2)–Cl(1)	2.445(1)	C(9)–C(10)	1.436(7)
Rh(2)–Cl(2)	2.4565(8)	C(9)–C(13)	1.442(6)
Rh(2)–Cl(4)	2.376(1)	C(9)–Si(2)	1.889(4)
Rh(2)–C(9)	2.140(3)	C(10)–C(11)	1.424(7)
Rh(2)–C(10)	2.120(4)	C(11)–C(12)	1.412(8)
Rh(2)–C(11)	2.112(6)	C(12)–C(13)	1.409(7)
Rh(2)–C(12)	2.145(6)	Si(2)–C(14)	1.857(4)
Rh(2)–C(13)	2.145(5)	Si(2)–C(15)	1.851(6)
C(1)–C(2)	1.456(7)	Si(2)–C(16)	1.854(7)
Rh(1)–Cl(1)–Rh(2)	94.16(4)	Rh(1)–Cl(2)–Rh(2)	94.16(4)
Cl(1)–Rh(1)–Cl(3)	90.35(4)	Cl(1)–Rh(2)–Cl(2)	82.50(4)
Cl(1)–Rh(2)–Cl(4)	89.93(5)	Cl(2)–Rh(1)–Cl(3)	91.99(5)
Cl(2)–Rh(2)–Cl(4)	90.49(4)	Cl(1)–Rh(1)–Cl(2)	82.46(4)

Table III. Atomic Positional Parameters for **7**

atom	x	y	z
Rh(1)	0.26582(2)	0.12781(2)	0.17976(2)
Rh(2)	–0.04945(2)	0.23422(2)	0.08066(2)
Cl(1)	0.03535(8)	0.31847(7)	0.20858(7)
Cl(2)	0.20690(8)	0.09820(8)	–0.00015(8)
Cl(3)	0.38698(9)	0.26346(9)	0.05740(9)
Cl(4)	–0.0761(1)	0.06879(8)	0.24032(9)
C(1)	0.2713(3)	0.0895(3)	0.3710(3)
C(2)	0.2060(4)	0.0109(3)	0.3454(3)
C(3)	0.3042(5)	–0.0721(3)	0.2480(4)
C(4)	0.4327(4)	–0.0514(4)	0.2094(4)
C(5)	0.4125(3)	0.0481(4)	0.2861(3)
Si(1)	0.1842(1)	0.21793(9)	0.49270(9)
C(6)	0.2852(4)	0.1443(4)	0.6108(4)
C(7)	0.2025(5)	0.3736(4)	0.4170(4)
C(8)	–0.0068(4)	0.2420(4)	0.5608(3)
C(9)	–0.2595(3)	0.3792(3)	0.0867(3)
C(10)	–0.2374(4)	0.2581(3)	0.0411(4)
C(11)	–0.1198(4)	0.2281(4)	–0.0700(4)
C(12)	–0.0705(4)	0.3313(4)	–0.0977(3)
C(13)	–0.1544(3)	0.4232(3)	–0.0034(3)
Si(2)	0.3964(1)	0.4662(1)	0.23170(9)
C(14)	–0.5691(4)	0.5523(4)	0.1936(4)
C(15)	–0.3361(4)	0.5851(4)	0.2645(4)
C(16)	–0.4048(5)	0.3406(5)	0.3630(4)

The complex was a chlorine-bridged dimer, with a nonplanar Rh_2Cl_2 core. The torsion angles associated with the core were about 19.5° (Rh(1)–Cl(1)–Rh(2)–Cl(2) = –19.43(4)°; Rh(1)–Cl(2)–Rh(2)–Cl(1) = 19.52(4)°). The cyclopentadienyl ligands were trans in the dimer, apparently for steric reasons, and the trimethylsilyl groups within the molecule existed in an eclipsed conformation. The rhodium–chlorine distances in the Rh_2Cl_2 ring ranged between 2.445 and 2.457 Å, while the terminal rhodium–chlorine distances were 2.373(1) and 2.376(1) Å. The

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(8) (a) Churchill, M. R.; Julis, S. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 1137. (b) Churchill, M. R.; Julis, S. A. *Ibid.* **1978**, *17*, 3011. (c) Maitlis, P. M. *Acc. Chem. Res.* **1978**, *11*, 301. (d) Powell, J.; Shaw, B. L. *J. Chem. Soc. A* **1968**, 583. Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970. Faraone, F.; Marsala, V.; Tresoldi, G. *J. Organomet. Chem.* **1978**, *152*, 337.

(9) For example, see: May, S.; Reinsalu, P.; Powell, J. *Inorg. Chem.* **1980**, *19*, 1582.

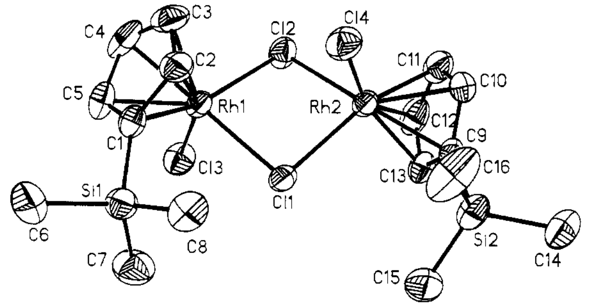

Figure 1. Perspective view of 7.

rhodium–rhodium distance was 3.590 Å. The rhodium–carbon distances averaged 2.131 Å (C(1)–C(5)) and 2.132 Å (C(9)–C(13)) and were consistent with idealized η^5 bonding. The carbon–carbon bond lengths in the cyclopentadienyl ligands were normal and averaged 1.427 Å (C(1)–C(5)) and 1.425 Å (C(9)–C(13)).

The overall dimeric structure of 7 is similar to those of the related structurally characterized dimers $\{[(\eta^5\text{-}C_5(CH_3)_5)RhCl]_2(\mu\text{-}Cl)_2\}$ (**9**)[8a] and $\{[(\eta^5\text{-}C_5(CH_3)_5)RhBr]_2(\mu\text{-}Br)_2\}$ (**10**).[8b] However, complex **7** possesses a nonplanar Rh_2Cl_2 core, while in **9** and **10** the Rh_2X_2 core is rigorously planar. Furthermore, the Rh–Rh distance in **7** is 3.590 Å, which is considerably shorter than the corresponding distances in **9** (3.719 Å) and **10** (3.848 Å).

Discussion

The present study documents the stepwise chloride ion-induced desilylation of silylated cyclopentadienes to ultimately afford cyclopentadiene and its dimer. Halide-promoted cleavage of C_{sp3}–Si bonds is best precedented for fluoride ion,[10] due to the high bond dissociation energy of the silicon–fluorine bond. The transition states for the reaction of silylated cyclopentadienes with chloride ion presumably contain considerable aromatic stabilization, which lowers the energy barrier for the desilylations. The alcohol solvent serves as a proton source for the cyclopentadienyl anions as well as a trap for the trimethylsilyl chloride that is formed.

In the case of hydrated ruthenium trichloride, treatment with SiCpH, Si_2CpH, and Si_3CpH in alcohol solvents afforded ruthenocene (**1**) in 85–96% yields. No evidence was obtained for the formation of 1,1′-bis(trimethylsilyl)ruthenocene (from Si_2CpH) or 1,1′,3,3′-tetrakis(trimethylsilyl)ruthenocene (from Si_3CpH), although a trace of (trimethylsilyl)ruthenocene was detected by GC/MS in the reaction of hydrated ruthenium trichloride with SiCpH. Hydrated ruthenium trichloride has been reported to react with cyclopentadiene in refluxing methanol to afford **1** in 80% yield.[5] Hence, the formation of **1** from SiCpH, Si_2CpH, and Si_3CpH can be most economically explained by the chloride ion-induced desilylation of the silylated cyclopentadienes to form cyclopentadiene, which then reacts with the ruthenium ion to afford **1**. Hydrated ruthenium trichloride is well-known to react in polar solvents to form a variety of complexes with chloride counterions,[11] which then provides the chloride ion for the desilylations. Ethanol and 2-propanol are documented agents for the reduction of Ru(III) to Ru(II) and undergo concomitant oxidation to acetaldehyde or acetone.[12] The rate of chloride ion-induced desilylation is clearly faster than the rate of reaction of the ruthenium ion with the silylated cyclopentadienes, since **1** was the nearly exclusive product.

The reactivity of hydrated rhodium trichloride toward silylated cyclopentadienes is different from that of hydrated ruthenium trichloride. Treatment of hydrated rhodium trichloride with SiCpH afforded cyclopentadienylrhodium dichloride oligomer (**6**) in nearly quantitative yield. Mechanistic sequences that are possible include direct reaction of SiCpH with rhodium trichloride to afford **6** or a two-step chloride ion-induced desilylation of SiCpH to give cyclopentadiene, followed by reaction of cyclopentadiene with Rh(III) ion to afford **6**. It was not possible to distinguish between these scenarios, since treatment of hydrated rhodium trichloride with cyclopentadiene afforded **6** in a yield similar to the process utilizing SiCpH. Treatment of rhodium trichloride with Si_2CpH afforded a 27% yield of **6** and a 70% ((trimethylsilyl)cyclopentadienyl)rhodium dichloride dimer (**7**). This product distribution indicates that a chloride ion-induced desilylation process is operant. The Rh(III) ion is more reactive toward the silylated cyclopentadienes than is the ruthenium ion, since the major product in the rhodium reactions (**7**) contains one trimethylsilyl group on the cyclopentadienyl ring.

The structure of **7** is similar to several pentamethylcyclopentadienyl analogs whose structures have been previously determined. The utility of $[Cp^*RhCl_2]_2$ as a starting material for rhodium chemistry has been amply documented.[8c] The simple synthesis of **7** provides an alternative soluble precursor for cyclopentadienylrhodium chemistry.

Thus, two distinct pathways exist in the reactions of silylated cyclopentadienes with transition metal halides. In early transition metals and in systems where the metal–halogen bond is not highly dissociated, silicon–carbon bond cleavage occurs to afford a cyclopentadienyl complex containing one less trimethylsilyl substituent than was present in the starting organic compound. However, in the later transition metal halides and in polar solvents, multiple desilylations ensue, which can lead to complexes containing unsubstituted cyclopentadienyl ligands from polysilylated precursors. The results described herein provide a mechanistic basis for understanding the various pathways exhibited in reactions of silylated hydrocarbons with ionizable transition metal halides.

Experimental Section

General Considerations. All organometallic reactions were performed under an atmosphere of argon or nitrogen using glovebox or Schlenk techniques. Benzene and diethyl ether were distilled from purple solutions of sodium/benzophenone. Dichloromethane was distilled from calcium hydride. Hexane was distilled from sodium. Ethanol (absolute) and 2-propanol were used as received without any further drying or purification. Chloroform-*d* and DMSO-d_6 were purified by vacuum-transfer from activated 4-Å molecular sieves. The silylated cyclopentadienes were prepared according to the literature procedure.[6] Hydrated ruthenium(III) chloride ($RuCl_3\cdot 3H_2O$) and hydrated rhodium(III) chloride ($RhCl_3\cdot 2H_2O$) were used as received from Johnson-Matthey. The organic reagents used to prepare the ligands were purchased from Aldrich Chemical Co.

^1H NMR and $^{13}C\{^1H\}$ NMR spectra were obtained on a General Electric QE-300 or GN-300 spectrometer in chloroform-*d* or DMSO-d_6. Infrared spectra were obtained on a Nicolet DX20 spectrophotometer either neat on sodium chloride plates or using potassium bromide as the medium. Mass spectra were obtained on a Kratos MS-50 or MS-80 spectrometer in the electron impact mode. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Melting points were obtained on a Haake Buchler HBI digital melting point apparatus and are uncorrected.

Preparation of Ruthenocene (1) by Reaction of Ruthenium(III) Chloride with (Trimethylsilyl)cyclopentadiene. A 50-mL Schlenk flask, equipped with condenser, stir bar, and rubber septum, was charged with hydrated ruthenium(III) chloride (0.207 g, 0.850 mmol), (trimethylsilyl)cyclopentadiene (0.535 g, 3.87 mmol), and absolute ethanol (10 mL). The mixture was refluxed for 24 h and then cooled to room temperature. The volatiles were removed under reduced pressure to give a dark oily solid. The solid was extracted with ether (50 mL). The ether layer was applied

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(11) For examples, see: Connick, R. E.; Fine, D. A. *J. Am. Chem. Soc.* **1960**, *82*, 4187. Farquhar, E. L.; Rusnock, L.; Gill, S. J. *Ibid.* **1970**, *92*, 416. Lever, F. M.; Powell, A. R. *J. Chem. Soc. A* **1969**, 1477. Prout, C. K.; Powell, H. M. *J. Chem. Soc.* **1962**, 137.

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to a 5-cm column of silica gel on a coarse frit and was eluted with ether (100 mL) to afford a pale yellow solution. Removal of the volatile components under reduced pressure, followed by vacuum-drying (24 h, 0.1 mm), afforded **1** as a pale yellow powder (0.19 g, 96%): mp 198–200 °C (lit.[4] mp 200 °C); HRMS (*m/z*) calcd for $C_{10}H_{10}Ru$ 231.981 97; found 231.9818.

Reaction of Hydrated Ruthenium(III) Chloride with Bis(trimethylsilyl)cyclopentadiene. Using the procedure outlined for (trimethylsilyl)cyclopentadiene, hydrated ruthenium(III) chloride (0.190 g, 0.780 mmol) and bis(trimethylsilyl)cyclopentadiene (0.517 g, 2.46 mmol) were reacted to afford **1** as an off-white powder (0.17 g, 95%).

Reaction of Hydrated Ruthenium(III) Chloride with Tris(trimethylsilyl)cyclopentadiene. Using the procedure outlined for (trimethylsilyl)cyclopentadiene, hydrated ruthenium(III) chloride (0.205 g, 0.842 mmol) and tris(trimethylsilyl)cyclopentadiene (0.731 g, 2.59 mmol) were reacted to afford **1** as an off-white powder (0.16 g, 85%).

GLC Analysis of the Reaction of Hydrated Ruthenium Trichloride with Tris(trimethylsilyl)cyclopentadiene. A 25-mL Schlenk flask, equipped with a condenser, stir bar, and rubber septum, was charged with hydrated ruthenium(III) chloride (0.044 g, 0.182 mmol), tris(trimethylsilyl)cyclopentadiene (0.156 g, 0.554 mmol), and 2-propanol (10 mL). The mixture was refluxed for 0.5 h. Upon cooling, the reaction solution was filtered through a 2-cm pad of Celite on a coarse glass frit to remove insoluble materials. The filtrate was analyzed by GLC and GLC/MS. For data, see Results.

General Procedure for GLC Analysis of the Reaction of Silylated Cyclopentadienes with Benzyltriethylammonium Chloride. A 25-mL round-bottomed flask, equipped with condenser, stir bar, and rubber septum, was charged with benzyltriethylammonium chloride (~0.18 mmol), the silylated cyclopentadiene (~0.06 mmol), and 2-propanol (2 mL). The solution was refluxed for a period of time ranging from 0.5 to 1.5 h. Upon cooling, the reaction solution was filtered through a 2-cm plug of silica on a coarse glass frit to remove the salts. GLC analyses were immediately conducted using these solutions. For data, see Results.

(*o*-Chlorobenzyl)(trimethylsilyl)cyclopentadiene (2). A 250-mL three-necked round-bottomed flask, equipped with stir bar, reflux condenser, nitrogen inlet, and septum, was charged with (trimethylsilyl)cyclopentadiene (5.034 g, 36.4 mmol) and benzene (50 mL). Then a 10.0 M solution of *n*-butyllithium in hexane (5.5 mL, 55 mmol) was added by syringe, and the resultant mixture was refluxed for 3 h. After the mixture cooled to room temperature 2-chlorobenzyl chloride (7.0 mL, 55 mmol) was added slowly by syringe. The solution was refluxed for an additional 12 h. Upon cooling, the reaction solution was quenched by addition of water (250 mL). The organic phase was separated from the mixture and was extracted with three 250-mL portions of hexane. The organic layers were combined, dried over anhydrous magnesium sulfate, and filtered to yield a clear pale yellow solution. Removal of the solvent under reduced pressure afforded a yellow liquid. Fractional distillation of this liquid afforded the desired product as a clear, colorless liquid (7.9 g, 82%): bp 100–110 °C (0.05 mm); IR (NaCl, cm^{-1}) 3092 (w), 3064 (w), 3020 (w), 2956 (m), 2899 (m), 1588 (w), 1573 (w), 1472 (m), 1444 (m), 1249 (vs), 1052 (m), 1040 (m), 985 (m), 961 (s), 868 (s), 838 (vs), 801(s), 751 (s), 739 (s), 715 (s); ^1H NMR ($CDCl_3$, δ) 7.46–7.21 (m, $C_6\boldsymbol{H}_4Cl$), 6.56 (s, $C_5\boldsymbol{HH'}H''H'''(Si(CH_3)_3)Ar$), 6.18 (s, $C_5HH'\boldsymbol{H''}H'''(Si(CH_3)_3)Ar$), 3.98 (s, $C\boldsymbol{H}_2Ar$), 3.40 (s, $C_5HH'H''\boldsymbol{H'''}Si(CH_3)_3)Ar$), 0.06 (s, $C_5HH'H''H'''(Si(C\boldsymbol{H}_3)_3)Ar$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 142.36 (s, quat Cp *C*), 138.80 (s, quat benzyl *C*), 134.12 (s, Cp *C*H), 134.04 (s, *C*Cl), 131.92 (s, Cp *C*H), 130.77 (s, Ar *C*H), 129.34 (s, Ar *C*H), 129.10 (s, Cp *C*H), 127.26 (s, Ar *C*H), 126.61 (s, Ar *C*H), 51.23 (s, *C*(H)($Si(CH_3)_3$)), 33.75 (s, *C*H_2Ar), –2.08 (s, $Si(\mathit{C}H_3)_3$); HRMS (*m/z*) calcd for $C_{15}H_{19}ClSi$ 262.094 45; found 262.0941.

(*o*-Bromobenzyl)(trimethylsilyl)cyclopentadiene (3). In a manner similar to the preparation of **2**, (trimethylsilyl)cyclopentadiene (5.034 g, 36.4 mmol), benzene (50 mL), a 10.0 M solution of *n*-butyllithium in hexane (6.0 mL, 60 mmol), and 2-bromobenzyl bromide (9.105 g, 36.4 mmol) were reacted to afford a clear, colorless liquid (7.6 g, 68%): bp 110–115 °C (0.05 mm); IR (NaCl, cm^{-1}) 3060 (w), 2955 (m), 2898 (m), 1467 (m), 1440 (m), 1249 (vs), 1044 (w), 1012 (s), 981 (s), 959 (s), 864 (s), 837 (vs), 802 (s), 752 (s), 730 (s), 714 (m); ^1H NMR ($CDCl_3$, δ) 7.56–7.03 (m, $C_6\boldsymbol{H}_4Cl$), 6.46 (s, $C_5\boldsymbol{HH'}H''H'''(Si(CH_3)_3)Ar$), 6.06 (s, $C_5HH'\boldsymbol{H''}H'''(Si(CH_3)_3)Ar$), 3.88 (s, $C\boldsymbol{H}_2Ar$), 3.28 (s, $C_5HH'H''\boldsymbol{H'''}(Si(CH_3)_3)Ar$), –0.05 s, (s, $C_5HH'H''H'''(Si(C\boldsymbol{H}_3)_3)Ar$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 142.32 (s, quat Cp *C*), 140.49 (s, quat benzyl *C*), 134.19 (s, Cp *C*H), 132.67 (s, Ar *C*H), 131.85 (s, Cp *C*H), 130.78 (s, Ar *C*H), 129.24 (s, Cp *C*H), 127.52 (s, Ar *C*H), 127.28 (s, A *C*H), 124.65 (s, *C*Br), 51.26 (s, *C*(H)($Si(CH_3)_3$)), 36.37 (s, *C*H_2Ar), –1.98 (s, $Si(\mathit{C}H_3)_3$); HRMS (*m/z*) calcd for $C_{15}H_{19}BrSi$ 306.043 99; found 306.0444.

Preparation of 1,1′-Bis((*o*-chlorobenzyl)cyclopentadienyl)ruthenium(II) (4). A 50-mL Schlenk flask, equipped with a condenser, stir bar, and rubber septum, was charged with hydrated ruthenium(III) chloride (0.174 g, 0.715 mmol), (*o*-chlorobenzyl)(trimethylsilyl)cyclopentadiene (0.662 g, 2.52 mmol), and 2-propanol (5 mL). The mixture was refluxed for 24 h. The volatiles were removed under reduced pressure, and the residue was extracted with dichloromethane (200 mL). The dichloromethane solution was filtered through a 2-cm pad of Celite on a coarse frit to afford a clear red-brown solution. Silica gel (30-mL dry volume) was added to the solution, and the volatiles were removed under reduced pressure to afford the silica gel impregnated with the crude product. The silica gel/product mixture was applied to a dry 4 cm × 20 cm silica gel column. The column was eluted with a 98:2 hexane:ethyl acetate mixture to afford a light yellow fraction. Removal of the volatile components under reduced pressure, followed by vacuum-drying (24 h, 0.1 mm), afforded **5** as an off-white solid (0.32 g, 92%): mp 132-133 °C; IR (KBr, cm^{-1}) 3087 (w), 3055 (w), 2930 (w), 2900 (w), 1639 (m), 1618 (m), 1467 (m), 1441 (m), 1420 (w), 1385 (s), 1315 (w), 1122 (w), 1084 (m), 1035 (s), 1023 (m), 920 (w), 825 (m), 804 (w), 758 (s), 752 (s); ^1H NMR ($CDCl_3$, δ) 7.40–7.14 (m, 2 $C_6\boldsymbol{H}_4Cl$), 4.60 (t, J = 1.5 Hz, 2 $C_5\boldsymbol{H}_2H'_2Ar$), 4.50 (t, J = 1.5 Hz, 2 $C_5H_2\boldsymbol{H'}_2Ar$), 3.69 (s, 2 $C\boldsymbol{H}_2Ar$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 139.63 (s, quat Ar *C*), 133.45 (s, Ar *C*Cl), 130.30 (s, Ar *C*H), 129.12 (s, Ar *C*H), 127.33 (s, Ar *C*H), 126.55 (s, Ar *C*H), 89.91 (s, quat Cp *C*), 72.16 (s, Cp *C*H), 70.46 (s, Cp *C*H), 32.93 (*C*H_2Ar); HRMS (*m/z*) calcd for $C_{24}H_{20}Cl_2Ru$ 479.997 91; found 479.9987. Anal. Calcd for $C_{24}H_{20}Cl_2Ru$: C, 60.01; H, 4.20. Found: C, 60.19; H, 4.32.

Preparation of 1,1′-Bis((*o*-bromobenzyl)cyclopentadienyl)ruthenium(II) (5). Using the general procedure for **4**, hydrated ruthenium(III) chloride (0.398 g, 1.63 mmol) and (*o*-bromobenzyl)(trimethylsilyl)cyclopentadiene (1.760 g, 5.75 mmol) were reacted to afford **5** as an off-white solid (0.80 g, 86%): mp 105–106 °C; IR (KBr, cm^{-1}) 3089 (w), 3083 (w), 2926 (m), 2893 (m), 1639 (m), 1618 (m), 1464 (s), 1438 (s), 1416 (m), 1384 (s), 1310 (m), 1259 (s), 1226 (w), 1158 (w), 1021 (s), 931 (m), 818 (m), 807 (s), 756 (s), 748 (s); ^1H NMR ($CDCl_3$, δ) 7.53–7.06 (m, 2 $C_6\boldsymbol{H}_4Br$), 4.56 (t, J = 1.5 Hz, 2 $C_5\boldsymbol{H}_2H'_2Ar$), 4.46 (t, J = 1.5 Hz, 2 $C_5H_2\boldsymbol{H'}_2Ar$), 3.65 (s, 2 $C\boldsymbol{H}_2Ar$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) 141.42 (s, quat Ar *C*), 132.50 (s, Ar *C*H), 130.36 (s, Ar *C*H), 127.66 (s, Ar *C*H), 127.28 (s, Ar *C*H), 124.20 (s, Ar *C*Br), 89.94 (s, quat Cp *C*), 72.30 (s, Cp *C*H), 70.54 (s, Cp *C*H), 35.67 (*C*H_2Ar); HRMS (*m/z*) calcd for $C_{24}H_{20}Br_2Ru$ 567.8969; found 567.8976. Anal. Calcd for $C_{24}H_{20}Br_2Ru$: C, 50.64; H, 3.54. Found: C, 50.59; H, 3.59.

(η^5-Cyclopentadienyl)rhodium Dichloride Oligomer (6). A 100-mL Schlenk flask was charged with hydrated rhodium trichloride (0.194, 0.789 mmol), (trimethylsilyl)cyclopentadiene (0.250 g, 1.81 mmol), 2-propanol (15 mL), and a stir bar and was fitted with a rubber septum. The mixture was stirred at ambient temperature for 3 h, during which time an orange powder precipitated. Hexane (30 mL) was added to the mixture, and the powder was isolated by filtration onto a fine glass frit. The orange powder was suspended in dichloromethane (150 mL) in a 250-mL round-bottomed flask containing a stir bar. The mixture was stirred for 12 h to extract undesired impurities. Filtration of the mixture onto a fine glass frit, followed by vacuum-drying of the filtrate, afforded **6** as a bright orange powder (0.18 g, 93%): mp >300 °C dec; IR (KBr, cm^{-1}) 3102 (m), 1618 (m), 1413 (s), 1385 (s), 1106 (w), 1068 (w), 1009 (w), 847 (s); ^1H NMR (DMSO-d_6, δ) 6.06 (s, $C_5\boldsymbol{H}_5$); ^{13}C NMR (DMSO-d_6, ppm) 87.13 (d, J_{C-Rh} = 6.6 Hz, C_5H_5). The material could not be obtained in analytically pure form due to its lack of solubility. Anal. Calcd for $C_5H_5Cl_2Rh$: C, 25.14; H, 2.11. Found: C, 26.07; H, 2.03.

Reaction of Hydrated Rhodium Trichloride with Cyclopentadiene. A 50-mL Schlenk flask was charged with hydrated rhodium trichloride (0.102 g, 0.416 mmol), freshly distilled cyclopentadiene (0.055 g, 0.832 mmol), 2-propanol (25 mL), and a stir bar and was fitted with a rubber septum. The mixture was stirred at ambient temperature for 3 h. Workup as above afforded **6** as a bright orange powder (0.082 g, 82%).

(η^5-(Trimethylsilyl)cyclopentadienyl)rhodium Dichloride Dimer (7). A 100-mL Schlenk flask was charged with hydrated rhodium trichloride (0.201 g, 0.820 mmol), bis(trimethylsilyl)cyclopentadiene (0.351 g, 1.67 mmol), 2-propanol (5 mL), and a stir bar and was fitted with a rubber septum. The mixture was stirred at ambient temperature for 24 h. The reaction mixture was filtered through a fine glass frit to afford an orange solid and a red-orange filtrate. The orange solid was washed with 2-propanol (20 mL) and dichloromethane (20 mL) and was then vacuumdried to afford **6** as a medium orange powder (0.052 g, 27%). The filtrate was evaporated to afford an orange powder. This material was dissolved in dichloromethane (50 mL), and the solution was filtered through a 1-cm pad of Celite on a coarse glass frit to separate insoluble material. Removal of the volatile components under reduced pressure followed by vacuum-drying for 1 h afforded **7** as a spectroscopically pure powder (0.164 g, 70%). An analytical sample was obtained by diffusion of hexane into a 1,2-dichloroethane solution to afford orange-red needles: mp 194–196 °C dec; IR (KBr, cm^{-1}) 3088 (m), 2955 (w), 2897 (w), 1637 (m), 1618 (m), 1414 (m), 1385 (s), 1253 (m), 1158 (m), 1023 (w), 887 (m), 848 (vs), 759 (m), 702 (w), 631 (w), 605 (w); ^1H NMR (chloroform-*d*, δ) 5.76 (s, $C_5\boldsymbol{H}_2H'_2(Si(CH_3)_3)$), 5.58 (s, $C_5H_2\boldsymbol{H}'_2(Si(CH_3)_3)$), 0.39 (s, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR (DMSO-d_6, ppm) 91.85 (d, J_{C-Rh} = 7.2 Hz, SiCp *C*H), 89.72 (d, J_{C-Rh} = 7.2 Hz, SiCp *C*H), 87.72 (d, J_{C-Rh} = 7.2 Hz, $CSi(CH_3)_3$). Anal. Calcd for $C_{16}H_{26}Cl_4Rh_2Si_4$: C, 30.89; H, 4.21. Found: C, 30.68; H, 4.09.

GLC analysis of the reaction solution, prior to the above workup, revealed a 92:8 ratio of (trimethylsilyl)cyclopentadiene:bis(trimethylsilyl)cyclopentadiene. For details, see Results.

X-ray Crystal Structure Determination of 7. The single-crystal diffraction experiment was performed at ambient temperature on a suitable crystal grown by slow diffusion of hexane into a 1,2-dichloroethane solution of **7** at ambient temperature. Details of the data collection are given in Table I. Cell constants were obtained from 25 high-angle ($2\theta > 20°$) reflections. During data collection, periodically remeasured standard reflections varied 2%. The orientation was checked midway through data collection by recentering. Absorption corrections were empirical, based upon a number of ψ scans.[13a] Lp corrections were applied, and neutral-atom scattering factors and corrections for anomalous dispersion were taken from ref 13b.

The structure was solved by Patterson methods and refined in a full matrix, minimizing $\sum w(F_o - |F_c|)^2$.[13c] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were placed in observed positions and were held invariant. No correction for secondary extinction was made. Final positional parameters are given in Table III. Further data are contained in the supplementary material.

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Supplementary Material Available: Tables S1-S5, listing full experimental details for data collection and refinement, thermal parameters, hydrogen positional parameters, complete bond angles, and least squares planes for **7** (8 pages). Ordering information is given on any current masthead page.

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