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Synthesis and Characterization of 1-Transition Metal Complex Substituted-2,3,4,5-Tetraphenyl-1-Silacyclopentadienyl Complexes and Generation of Transition Metal Complex-Substituted Silylene

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Received January 22, 1994

New silicon-monosubstituted (η^4 -2,3,4,5-tetraphenyl-1-silacyclopentadiene)transition metal complexes are described. (7-Alkyl-7-silanorbornadienyl)MLn(Alkyl = Methyl : MLn = CpRu(CO)₂ ; Alkyl = Methyl : MLn = CpNi(CO) ; Alkyl = Ethyl : MLn = CpNi(CO)) complexes were prepared from the corresponding silole-transition metal complexes with dimethyl acetylenedicarboxylate. Cycloaddition products were obtained with 2,3-dimethyl-1,3-butadiene, 2,3-butanedione, and 1,4-benzoquinone through the ruthenium-substituted silylene. We have determined the crystal structure of (1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)cyclopentadienyldicarbonylruthenium by using graphite monochromated Mo-K α radiation. The compound was crystallized in the monoclinic space group *P*2₁/*c* with *a* = 9.838(1), *b* = 15.972(3), *c* = 18.327(3) Å, and β = 94.28(1)°. The ruthenium moiety CpRu(CO)₂ on silicon is in an axial position.

Introduction

Transition metal complexes of nonfunctional siloles have been well documented,¹ and the silole functions as an η^4 -li-

gand in all complexes reported thus far.² Transition-metal complexes of siloles [Ph₄C₄Si(R)MLn] draw our attention because they are presumed to function as a silylene precursor or as precursors for the generation or detection of an

η^5 -silacyclopentadienyl containing transition metal complex. Recently, West and coworker³ described the synthesis of (7-methyl-7-silanorbornadienyl)FeCp(CO)₂ complex and a preliminary investigation of its activity as a silylene source. We also reported the synthesis of (silole-transition metal complex) Fe(CO)₃.⁴ Nevertheless, little was known about the syntheses of a variety of silole containing transition-metal complexes and a study of generation and trapping of silylene containing transition-metal complexes. In view of the importance of transition-metal complexes of silole as a silylene precursor, we wish to prepare a variety of siloles containing transition metal complexes.

In this paper, we wish to report the preparation of transition metal complex-substituted silole and generation of silylene precursor containing transition metal complexes.

Experimental Section

All manipulations of air-sensitive materials were carried out under an argon atmosphere with use of standard Schlenk or vacuum line technique or a Mebraun MB150 glovebox. ¹H-NMR spectra were recorded on a Bruker WM-250 spectrometer in CDCl₃. Chemical shifts are given in parts per million relative to tetramethylsilane for ¹H-NMR spectra. IR spectra were obtained by using a Perkin-Elmer 1310 instrument. Mass spectra were measured on a high resolution VG70-VSEG spectrometry. Elemental analyses were carried out at the Basic Science Research Center and University of Liverpool. Reagent grade tetrahydrofuran (THF), ether, toluene, hexane, and benzene were distilled under argon from sodium-benzophenone ketyl. The Ph₄C₄SiMeCl and Ph₄C₄SiEtCl were prepared according to literature methods.⁵ [CpFe(CO)₂]₂, Co₂(CO)₈, [CpRu(CO)₂]₂, SiMeCl₃, and SiEtCl₃ were obtained from Strem Chemicals and Aldrich and used without further purification. The NaCpFe(CO)₂,⁶ NaCpRu(CO)₂, and KCpNi(CO)⁷ were prepared according to literature methods.

Preparation of (1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)cyclopentadienyldicarbonylruthenium (I). A 0.29 g (0.65 mmol) of [CpRu(CO)₂]₂ in THF (20 ml) was stirred with sodium amalgam prepared from 1 ml of Hg and 0.13 g (5.65 mmol) of Na. After 2 hr, this solution was transferred to a stirred THF (15 ml) solution of 1,1-methyl, chloro-2,3,4,5-tetraphenylsilacyclopentadiene (0.55 g, 1.29 mmol). The solution was stirred for 3 hr at room temperature. The solution was filtered and evaporated to dryness. To the resulting powder was added the toluene (5 ml) and hexane (30 ml). After the solution was filtered, the resulting yellow solution was left in a refrigerator at -20°C. The yellow product was collected and dried. The yield was 23%. ¹H-NMR (CDCl₃) δ 7.5-6.8 (m, 20H, aromatic), 4.48 (s, 5H, Cp), 1.16 (s, 3H, CH₃); IR (on KBr pellet; cm⁻¹) ν (CO) 1992, 1943; mass spectrum, m/e (relative intensity) 621 (M⁺, 22), 565 (M⁺-2CO, 64), 399 (M⁺-RuCp(CO)₂, 17). Anal. Calcd. for C₃₆H₂₈O₂SiRu: C, 69.53; H, 4.51. Found: C, 68.71; H, 4.29.

Preparation of (1-ethyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)cyclopentadienyldicarbonylruthenium (II). The same procedure was taken as described in the preparation of I. The yield was 28%. ¹H-NMR (CDCl₃) δ 7.5-6.6 (m, 20H, aromatic), 4.56 (s, 5H, Cp), 1.36-1.04 (m, 5H,

CH₂CH₃); IR (on KBr pellet; cm⁻¹) ν (CO) 1990, 1942; mass spectrum, m/e (relative intensity) 635 (M⁺, 16), 579 (M⁺-2CO, 73), 413 (M⁺-RuCp(CO)₂, 32). Anal. Calcd. for C₃₇H₃₀O₂-SiRu: C, 69.89; H, 4.76. Found: C, 69.21; H, 4.54.

Preparation of (1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)cyclopentadienylcarbonylnickel (IV). A 0.28 g (0.98 mmol) of [CpNiCO]₂ in 15 ml of THF was stirred with K (0.15 g, 3.8 mmol). After 2.5 hr, this solution was added to a stirred THF (20 ml) solution of 1,1-methyl, chloro-2,3,4,5-tetraphenylsilacyclopentadiene (0.55 g, 1.29 mmol). The reaction was continued for 4 hr at room temperature. The solution was filtered and evaporated to dryness. The reddish powder was dissolved in toluene (5 ml) and the hexane (30 ml) was added. After the solution was filtered, the resulting yellow solution was left in a refrigerator at -20°C. The yellowish-brown product was collected and dried. The yield was 18%. ¹H-NMR (CDCl₃) δ 7.6-6.9 (m, 20H, aromatic), 4.72 (s, 5H, Cp), 0.18 (s, 3H, CH₃); IR (on KBr pellet; cm⁻¹) ν (CO) 1962; mass spectrum (relative intensity) 551 (M⁺, 8), 523 (M-CO, 83), 399 (M-NiCp Co, 32). Anal. Calcd. for C₃₅H₂₈OSiNi: C, 76.24; H, 5.12. Found: C, 75.84; H, 5.02.

Preparation of (1-ethyl-2,3,4,5-tetraphenyl-silacyclopentadienyl)cyclopentadienylcarbonylnickel (V). The same procedure was taken as described in the preparation of IV. The yield was 22%. ¹H-NMR (CDCl₃) δ 7.4-6.7 (m, 20H, aromatic), 4.54 (s, 5H, Cp), 1.36-1.12 (m, 5H, CH₂CH₃); IR (on KBr pellet; cm⁻¹) ν (CO) 1958; mass spectrum, m/e (relative intensity) 565 (M⁺, 8), 537 (M⁺-CO, 54), 413 (M⁺-NiCpCO, 23). Anal. Calcd. for C₃₆H₃₀OSiNi: C, 76.48; H, 5.35. Found: C, 75.94; H, 5.18.

Preparation of [1-methyl-4,5,6,7-tetraphenyl-2,3-bis(methoxycarbonyl)-1-silanorbornadienyl]cyclopentadienyldicarbonylruthenium (VI). Complex I (0.2 g, 0.32 mmol) was refluxed in the presence of dimethyl acetylenedicarboxylate (0.23 g, 1.62 mmol) in benzene (25 ml) for 24 hr. After the reaction mixture was allowed to cool to room temperature, the solution was put into the refrigerator. The resulting yellow crystalline product was filtered and dried. The yield was 78%. ¹H-NMR (CDCl₃) δ 7.6-6.8 (m, 20H, aromatic), 4.83 (s, 5H, Cp), 3.42 (s, 6H, CH₃), 1.08 (s, 3H, CH₃); IR (on KBr pellet; cm⁻¹) ν (CO) 2008, 1962, 1720. Anal. Calcd. for C₄₂H₃₄O₆SiRu: C, 66.04; H, 4.46. Found: C, 66.82; H, 4.52.

Preparation of [1-methyl-4,5,6,7-tetraphenyl-2,3-bis(methoxycarbonyl)-1-silanorbornadienyl]cyclopentadienylcarbonylnickel (VII). The same procedure was taken as described in the preparation of VI. The yield was 26%. ¹H-NMR (CDCl₃) δ 7.4-6.6 (m, 20H, aromatic), 4.75 (s, 5H, Cp), 3.38 (s, 6H, CH₃), 1.18 (s, 3H); IR (on KBr pellet; cm⁻¹) ν (CO) 1954, 1770 (s, br). Anal. Calcd. for C₄₁H₂₇O₅SiNi: C, 71.74; H, 3.94. Found: C, 71.32; H, 3.72.

Preparation of [1-ethyl-4,5,6,7-tetraphenyl-2,3-bis(methoxycarbonyl)-1-silanorbornadienyl]cyclopentadienylcarbonylnickel (VIII). The same procedure was taken as described in the preparation of VI. The yield was 18%. ¹H-NMR (CDCl₃) δ 7.6-6.7 (m, 20H, aromatic), 4.64 (s, 5H, Cp), 3.42 (s, 6H, CH₃), 1.28-1.12 (m, 5H, CH₂CH₃); IR (on KBr pellet; cm⁻¹) ν (CO) 1968, 1770 (s, br). Anal. Calcd. for C₄₂H₃₄O₅SiNi: C, 71.52; H, 4.82. Found: C, 71.97; H, 4.49.

Reaction of VI with 2,3-dimethyl-1,3-butadiene (J).

The mixture of VI (0.3 g, 0.47 mmol) and 2,3-dimethyl-1,3-butadiene (2.83 mmol) in xylene (10 mL) was refluxed for 6h. After evaporation of the solvent, the product was chromatographed on neutral silicagel with use of hexane(95%)/ether(5%) mixtures as eluent. The trapping pale yellow product J is eluted first in 22% yield; pale yellow oil; $^1\text{H-NMR}$ (CDCl_3) δ 4.42 (s, 5H, Cp), 1.39 (s, 6H, CH_3), 1.12 (s, 4H, CH_2), 0.82 (s, 3H, CH_3); IR (on KBr pellet; cm^{-1}) ν (CO) 1996, 1948. Anal. Calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_2\text{SiRu}$: C, 48.40; H, 5.22. Found: C, 48.02; H, 5.04.

Reaction of VI with 2,3-butanedione (K). The reaction mixture of VI (0.3 g, 0.47 mmol) was refluxed in xylene (10 mL) for 6h. The product K was chromatographed on neutral silicagel with use of hexane(95%)/ether(5%) mixtures as eluent. The pale yellow product was obtained in 32% yield. $^1\text{H-NMR}$ (CDCl_3) δ 4.73 (s, 5H, Cp), 1.54 (s, 6H, CH_3), 1.12 (s, 3H, CH_3); IR (on KBr pellet; cm^{-1}) ν (CO) 1984, 1936. Anal. Calcd. for $\text{C}_{12}\text{H}_{14}\text{O}_4\text{SiRu}$: C, 41.02; H, 4.02. Found: C, 39.37; H, 3.92.

Reaction of VI with 1,4-butanedione (L). The same procedure was taken as described in the preparation of J except. 1,4-benzoquinone as trapping agent. After chromatography with hexane(90%)/ether(10%), L was obtained in 24% yield. Colorless oil; $^1\text{H-NMR}$ (CDCl_3) δ 7.8-7.0 (m, 4H, Ph), 4.67 (s, 5H, Cp), 1.08 (s, 3H, CH_3); IR (on KBr pellet; cm^{-1}) ν (CO) 1981, 1932. Anal. Calcd. for $\text{C}_{14}\text{H}_{12}\text{O}_4\text{SiRu}$: C, 45.03; H, 3.24. Found: C, 44.74; H, 3.08.

Crystall structure of (I). The crystal of (I) was grown from hexane at -20°C . The crystallized compound possesses in the monoclinic space group $P2_1/c$ (systematic absences h 01: $1=0$ dd) with $a=9.838(1)$, $b=15.972(3)$, $c=18.327(3)$ Å, $\beta=94.28(1)^\circ$ $V=2944(1)$ Å³, $Z=4$ and $d_{\text{calc}}=1.549$ g/cm³. The cell constants were determined from a least squares fit of the setting angles for 25 accurately centered reflections. X-ray intensity data were collected on an Enraf-Nonius CAD 4 diffractometer employing graphite-monochromated Mo-K α radiation ($\lambda=0.71073$ Å) and using the ω -2 θ scan technique. A total of 4827 reflections were measured over the ranges: $4 \leq 2\theta \leq 52.0^\circ$, $0 \leq h \leq 10$, $-20 \leq k \leq 0$, $-23 \leq l \leq 23$. Three standard reflections measured every 3500 sec of X-ray exposure showed no intensity decay over the course of data collection.

The intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied. Of the reflections measured a total of 4327 unique reflections with $F^2 < 3\sigma(F^2)$ were used during subsequent structure refinement.

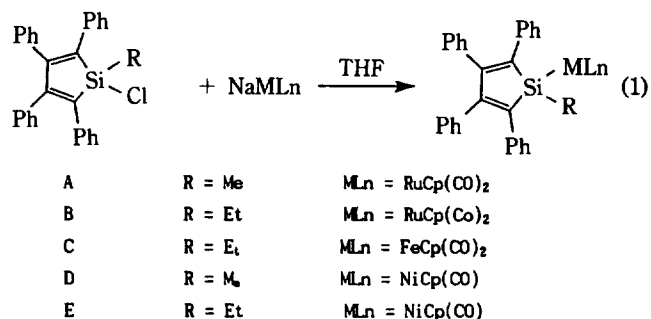
The structure was solved by standard heavy atom Patterson techniques followed by weighted Fourier syntheses. Refinement was by full-matrix least squares techniques based on F to minimize the quantity $\sum W(|F_o| - |F_c|)^2$ with $w=1/\sigma^2(F)$.

Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as constant contributions to the structure factors and were not refined. Refinement converged to $R=0.038$ and $R_w=0.050$.

Results and Discussion

The silole-transition metal complexes have been prepared according to the general Eq. (1).

The reaction of silole with NaRuCp(CO)_2 at room temper-



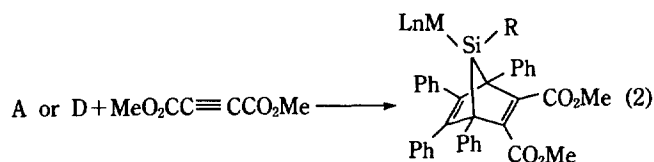
ature gave a pale yellow solution. The ruthenium-silole complex A was isolated as air-stable yellow solid in 23% yield. The structure of compound A was deduced from its $^1\text{H-NMR}$, IR and mass spectra. The $^1\text{H-NMR}$ spectrum of A exhibits resonances of Cp at δ 4.48 and CH_3 at δ 1.16, which are closely comparable to those of (1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)cyclopentadienyldicarbonylruthenium. In addition to that, there are peaks at δ 7.5-6.8, assigned to phenyl hydrogens. The infrared spectrum of A clearly indicates the presence of moiety of CpRu(CO)_2 . Two peaks at 1992 and 1943 cm^{-1} are CO stretching frequencies, as found in the complex $\text{CpRu(CO)}_2\text{SiMe}_3$.⁸ The peaks at 818 cm^{-1} and 2932 cm^{-1} are assigned to the Cp and CH_3 , respectively. The compound A was robust enough to give the expected molecular ion of m/e (621) in its electron impact mass spectrum, followed by the fragmentation ions of M^+-2CO and $\text{M}^+-\text{RuCp(CO)}_2$.

The spectral patterns of compound B is quite similar to those of A. Although these data support their formulation as complexes with the ruthenium metal coordinated to the silole $\text{CpRu(CO)}_2(\text{Ph}_4\text{C}_4\text{SiX})$, the ruthenium moiety CpRu(CO)_2 on silicon center is not certain as to whether it is located in an *exo* or *endo*-position. From our previous crystal structure of $\text{CpFe(CO)}_2(\text{Ph}_4\text{C}_4\text{SiMe})\text{Fe(CO)}_3$, it was found that the bulky iron moiety was in an *exo* position.⁴ Similarly, the moiety of CpRu(CO)_2 is presumed to be located in an *exo* position. The compound C was prepared by the reaction of silole $\text{Ph}_4\text{C}_4\text{Si(Et)Cl}$ with NaCpFe(CO)_2 . The $^1\text{H-NMR}$ spectrum of C was quite similar to that of (1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)cyclopentadienyldicarbonylruthenium except ethyl instead of methyl. Two peaks at 1996 and 1951 cm^{-1} in the infrared spectrum are assigned to CO stretching frequencies. The values are close to those of $\text{Ph}_4\text{C}_4\text{Si(Me)CpFe(CO)}_2$. It is interesting to note that Weiss and coworker⁹ recently prepared the complex $\text{Ph}_4\text{C}_4\text{GeCl[FeCp(CO)}_2]$ from the reaction of $\text{Ph}_4\text{C}_4\text{GeCl}_2$ and NaCpFe(CO)_2 .

The nickel-silole complex was prepared through the reaction of silole and KNiCp(CO) . The reaction of silole $\text{Ph}_4\text{C}_4\text{Si(Me)Cl}$ with KNiCp(CO) at room temperature gave a yellowish brown solution. The nickel-silole complex D was isolated as yellowish-brown solid in 18% yield. The $^1\text{H-NMR}$ spectrum of D exhibits resonances of Cp at δ 4.78 and CH_3 at 0.18, which are quite close to those of $\text{Me}_3\text{SiNiCp(CO)}_3$.¹⁰ In addition to that, there are peaks at δ 7.6-6.9, assigned to phenyl hydrogens. IR absorptions due to the CO and Cp stretch are observed at 1962 cm^{-1} and 808 cm^{-1} , respectively. The spectral data of the compound E were quite similar to those of compound D. On the other hand, the reaction of silole with NaMoCp(CO)_3 and NaMn(CO)_5 gave no reaction due presumably to the steric hindrance. The reaction of silole with NaCo(CO)_4 was decomposed to cobalt dimer and

unidentified compound, due probably to the oxidation potential. In contrast, it is interesting to note that the reaction of $[\text{C}_4\text{H}_2\text{Ph}_2\text{Si}(\text{H})\text{Me}]\text{Fe}(\text{CO})_3$ with $\text{Co}_2(\text{CO})_8$ leads to the formation of the *exo*-silyltetracarbonylcobalt complex.¹¹

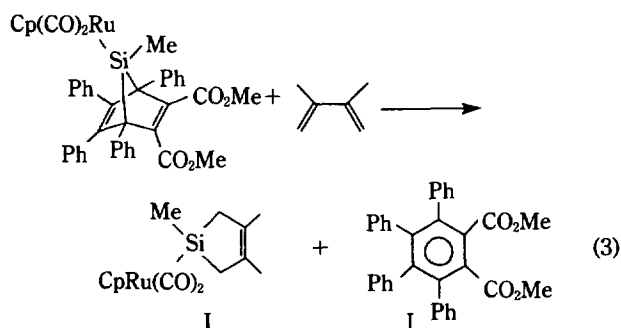
In spite of the presence of electronegative phenyl substituents and the steric hindrance of the metal complex, complexes **A** and **D** reacted as a diene. Dimethyl acetylenedicarboxylate reacted with **A** and **D** to give 7-silanorbornadienes **F** and **G** Eq. (2).



F	$\text{MLn} = \text{RuCp}(\text{CO})_2$	$\text{R} = \text{CH}_3$
G	$\text{MLn} = \text{NiCp}(\text{CO})$	$\text{R} = \text{CH}_3$
H	$\text{MLn} = \text{NiCp}(\text{CO})$	$\text{R} = \text{C}_2\text{H}_5$

The 7-silanorbornadiene **F** was isolated as air-stable pale yellow solid in 52% yield. The structure of compound **F** was deduced from ^1H -NMR, IR and mass spectra. The ^1H -NMR spectrum of **F** exhibits resonances of Cp at δ 4.83 and CO_2Me at δ 3.42, in addition to those of CH_3 at δ 1.08 and Ph at δ 7.5-6.8. The infrared spectrum of **F** on pellet shows strong absorptions at 2008 cm^{-1} and 1962 cm^{-1} which are assigned to the CO stretching mode. It is interesting to note that the CO stretching frequency is relatively high compared with that of compound (7-methyl-7-silanorbornadienyl) $\text{FeCp}(\text{CO})_2$. In addition to that, the CO-ester stretching peak was appeared at 1720 cm^{-1} . The value is very close to that of the compound [1,4,5,7-tetraphenyl-2,3-bis(methoxycarbonyl)-7-methyl-7-silanorbornadienyl]cyclopentadienyldicarbonyliron. The compound **G** is straightforwardly assigned. The spectral data of **G** is quite similar to that of **F**. The infrared spectrum of **G** shows a strong absorption at 1945 cm^{-1} , assigned to the CO stretching mode. The ^1H -NMR spectrum of **G** is quite similar to that of **F**. On the other hand, the reaction of **B** and **C** with dimethyl acetylenedicarboxylate proceeded to give incomplete 7-silanorbornadienes due probably to the steric hindrance.

Trapping of Silylene. In order to test for trapping of silylene, the ruthenium-substituted silanorbornadiene **F** was heated in the presence of 2,3-dimethyl-2-butene under these condition,



producing 22% of the silacyclopentene together with dimethyl-3,4,5,6-tetraphenylphthalate. The structure of **J** was deduced from the conventional method. The low yield of silylene trapping complex may be attributable to the instability of product formed at the reaction temperature. An analogous

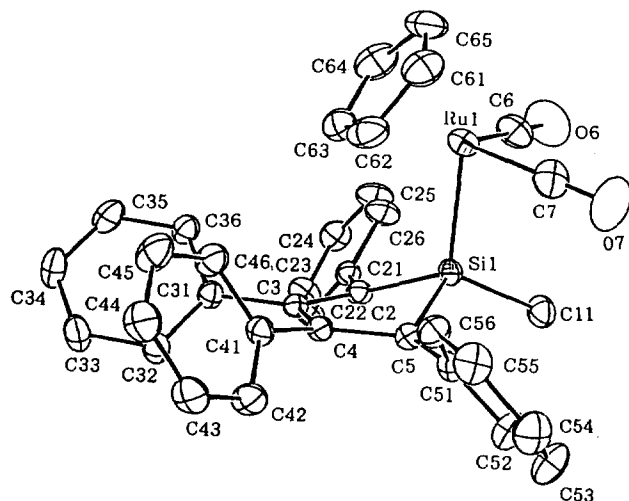
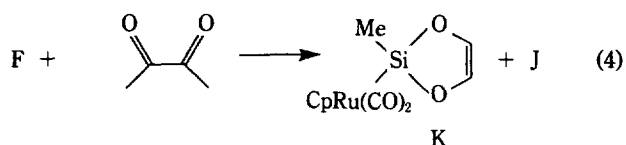


Figure 1. Structure and atom labelling of (I).

Table 1. Bond Distances (\AA)

Ru1-Si1	2.372(1)	C4-C41	1.498(3)	C41-C46	1.384(4)
Ru1-C6	1.743(3)	C5-C51	1.497(3)	C42-C43	1.390(4)
Ru1-C7	1.742(3)	C6-O6	1.144(3)	C43-C44	1.372(5)
Ru1-C61	2.206(4)	C7-O7	1.150(4)	C44-C45	1.376(4)
Ru1-C62	2.103(3)	C21-C22	1.386(4)	C45-C46	1.380(4)
Ru1-C63	2.108(3)	C21-C26	1.392(4)	C51-C52	1.388(3)
Ru1-C64	2.106(3)	C23-C24	1.376(4)	C51-C56	1.382(4)
Ru1-C65	2.211(4)	C24-C25	1.370(4)	C52-C53	1.379(4)
Ru1-C2	1.907(2)	C25-C26	1.382(4)	C53-C54	1.380(5)
Ru1-C5	1.893(2)	C31-C32	1.392(3)	C54-C55	1.372(4)
Ru1-C11	1.902(3)	C31-C36	1.388(3)	C55-C56	1.379(4)
C2-C3	1.440(3)	C32-C33	1.382(4)	C61-C62	1.408(5)
C2-C21	1.494(3)	C33-C34	1.376(4)	C62-C63	1.381(5)
C3-C4	1.442(3)	C34-C35	1.374(4)	C63-C64	1.383(5)
C3-C31	1.501(3)	C35-C36	1.384(4)	C64-C65	1.400(5)
C4-C5	1.442(3)	C41-C42	1.382(3)	C65-C66	1.388(5)

cyclic compound was obtained in the 32% yield by the reaction of **F** and 2,3-butanedione as shown in Eq. (4).

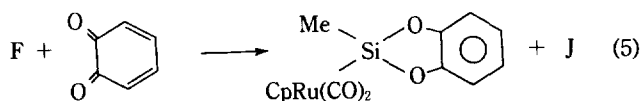


The cyclic formation may be attributed to the diradical generation in the oxygen atom. The attachment of silylene and oxygen radical may be concomitant with formation of two radicals. The mechanistic pathways were confirmed by the well known reaction.¹² It was well known that dione was reacted with the divalent compound to produce the cyclic compound.¹³ Similarly, the reaction of 1,4-benzoquinone with **F** in refluxing xylene was produced the cyclic compound as shown in Eq. (5).

The mechanistic pathways are presumed to proceed by the divalent generation as the 2,3-butanedione. On the other hand, reactions of **F** with triethyl silane, methylphenylketone

Table 2. Bond Angles (deg)

Sil-Rul-C6	88.2(1)	C2-Sil-C11	142.4(1)	C4-C41-C42	123.2(2)
Sil-Rul-C7	84.1(1)	C5-Sil-C11	132.0(1)	C4-C41-C46	118.3(2)
Sil-Rul-C61	135.4(1)	Sil-C2-C3	109.3(2)	C42-C41-C46	118.2(2)
Sil-Rul-C62	99.1(1)	Sil-C2-C21	124.4(2)	C41-C42-C43	120.8(2)
Sil-Rul-C63	90.8(1)	C3-C2-C21	124.7(2)	C42-C43-C44	120.1(2)
Sil-Rul-C64	119.8(1)	C2-C3-C4	112.2(2)	C43-C44-C45	118.3(3)
Sil-Rul-C65	155.8(1)	C2-C3-C31	126.7(2)	C44-C45-C46	119.2(3)
C6-Rul-C7	91.0(1)	C4-C3-C31	121.8(2)	C41-C46-C45	120.7(2)
C6-Rul-C61	138.2(2)	C3-C4-C5	113.2(2)	C5-C51-C52	120.0(2)
C6-Rul-C62	158.3(1)	C3-C4-C41	122.3(2)	C5-C51-C56	120.7(2)
C6-Rul-C63	121.2(1)	C5-C4-C4	124.7(2)	C52-C51-C56	118.8(2)
C6-Rul-C64	94.0(1)	Sil-C5-C4	107.9(1)	C51-C52-C53	120.8(3)
C6-Rul-C65	103.2(1)	Sil-C4-C51	126.2(2)	C52-C53-C54	120.4(3)
C7-Rul-C61	95.2(1)	C4-C5-C51	120.2(2)	C53-C54-C55	119.8(3)
C7-Rul-C62	108.8(1)	Rul-C6-O6	177.5(3)	C54-C55-C56	119.2(3)
C7-Rul-C63	147.3(1)	Rul-C7-O7	177.9(3)	C51-C56-C55	120.2(2)
C7-Rul-C64	156.1(1)	C2-C21-C22	125.5(2)	Rul-C61-C62	68.7(2)
C7-Rul-C65	118.2(1)	C2-C21-C26	118.3(2)	Rul-C61-C65	70.8(2)
C61-Rul-C62	39.8(1)	C22-C21-C26	117.2(2)	C62-C61-C65	106.2(3)
C61-Rul-C63	64.8(1)	C21-C22-C23	120.4(2)	Rul-C62-C61	70.8(2)
C61-Rul-C64	65.2(1)	C22-C23-C24	121.3(3)	Rul-C62-C63	71.8(2)
C61-Rul-C65	37.8(1)	C23-C24-C25	119.2(3)	C61-C62-C63	107.4(3)
C62-Rul-C63	38.1(1)	C24-C25-C26	121.4(3)	Rul-C63-C62	71.2(2)
C62-Rul-C64	64.1(1)	C21-C26-C25	120.7(2)	Rul-C63-C64	70.8(2)
C62-Rul-C65	64.2(1)	C3-C31-C32	121.2(2)	C62-C63-C64	106.8(3)
C63-Rul-C64	39.8(1)	C3-C32-C36	120.2(2)	Rul-C64-C63	70.4(2)
C63-Rul-C65	65.7(1)	C32-C31-C36	117.7(2)	Rul-C64-C65	70.8(2)
C64-Rul-C65	39.4(1)	C31-C32-C33	120.0(2)	C63-C64-C65	109.4(3)
Rul-Sil-C2	121.7(1)	C32-C33-C34	120.2(3)	Rul-C65-C61	70.2(2)
Rul-Sil-C5	115.4(1)	C33-C34-C35	119.0(3)	Rul-C65-C64	70.8(2)
Rul-Sil-C11	107.2(1)	C34-C35-C36	119.7(2)	C61-C65-C64	108.5(3)
C2-Sil-C5	85.8(1)	C31-C36-C35	120.2(2)		



and phenyltrimethoxysilane gave unidentified products.

Crystallographic work. To get a geometrical information of the complex (I) in the solid state, X-ray diffraction work was carried out. The structure and atom labelling of the (1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)cyclopentadienyldicarbonylruthenium are shown in Figure 1. Selected interatomic distances and bond angles are listed in Table 1 and 2, respectively. The four carbon atoms C2, C3, C4, and C5 constituting the diene portion of the five-membered ring containing the silicon atom are almost coplanar. SilC2C3C4C5 butadiene dihedral angle has opened up to 47.8°, so that the silicon atom is out of the diene plane by 0.957 Å. This value is relatively large compared with those of the complexes Ru(C₄Ph₂H₂SiMe₂)(CO)₃,¹⁴ [CoCC₄Me₂H₂SiMe₂)(PMe₃)₃]¹⁵ and (η⁴-*exo*-phenyl-endo-chloro-2,3,4,5-tetraphenyl-1-silacyclopentadienyl) tricarbonylruthenium,¹⁶ where the dihedral angle is 32°, 41.3°, and 41.8°, respectively.

The difference may be attributable to the steric bulkiness

of the ruthenium moiety. The ruthenium moiety on silicon is in an axial position. The geometry of (I) is quite similar to that of (η⁴-*exo*-cyclopentadienyldicarbonylruthenium-1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)tricarbonylruthenium. The carbon-carbon bond distances in the five-membered ring on the silole show considerable conjugation. The bond distances of C2-C3 (1.440 Å), C3-C4 (1.441 Å), C4-C5 (1.442 Å) is slightly shorter than the single C-C bond (1.462 Å).

Acknowledgement. The work was supported by grants from the Korea Science and Engineering Foundation.

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Synthesis and Characterization of Tetrathiafulvalene Charge Transfer Compounds with Iron and Antimony Halides

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Received January 24, 1994

The charge transfer compounds $(\text{TTF})_4\text{FeCl}_3 \cdot \text{CH}_3\text{OH}$, $(\text{TTF})_4\text{SbCl}_4$ and $(\text{TTF})_5(\text{SbBr}_4)_2 \cdot \text{CH}_3\text{COCH}_3$ were prepared from reactions of the TTF (tetrathiafulvalene) and metal halides. The compounds were characterized by spectroscopic (UV, IR, EPR and XPS) methods, magnetic susceptibility and electrical conductivity measurements. The *d.c* electrical conductivities of the pressed pellets are in the order of 10^{-1} – 10^{-3} Scm^{-1} , which lies in the range of semiconductor region at room temperature. It means that the partially ionized TTF has stacked in low-dimensional chain in each compound. Spectroscopic properties also indicate that TTF molecules are partially ionized and charge transfer has occurred from $(\text{TTF})_n$ to Fe(III) center in $(\text{TTF})_4\text{FeCl}_3 \cdot \text{CH}_3\text{OH}$ whereas to the $-\text{SbX}_4^-$ entity in $(\text{TTF})_4\text{SbCl}_4$ and $(\text{TTF})_5(\text{SbBr}_4)_2 \cdot \text{CH}_3\text{COCH}_3$. The EPR *g* values are consistent with TTF radical formation and EPR linewidths suggest the delocalization of unpaired electrons along TTF stacks. A signal arising from metal (Fe and Sb) ions were not detected in EPR spectra, indicating that metal ion is in the diamagnetic state in each compound. The diamagnetic state was also examined by the magnetic susceptibility measurement. The magnetic properties reveal the significant interaction between the TTF^+ radical cations in the stacks. The oxidation state of metal ions was also investigated by XPS spectra.

Introduction

TTF (Tetrathiafulvalene) and its analogues have been used as electron donors to form highly electroconductive charge transfer complexes.¹ The complexes contain simple halides,² pseudohalides³ and some organic materials^{1,4} as an electron acceptor. Relatively less work has been done in charge transfer compounds containing transition metals.

Recently we have prepared TTF complexes with the metal halides FeCl_3 , FeBr_3 and the hydrated salts of RuCl_3 , RhCl_3 , and IrCl_4 .⁵ TTF π stacks were revealed to exhibit semiconducting behavior in each compound. The compounds formed with FeCl_3 and FeBr_3 with the formulas $(\text{TTF})_2\text{FeCl}_3$ and $(\text{TTF})_3\text{FeBr}_3$ were especially interesting since the magnetic interaction along TTF stacks in $(\text{TTF})_3\text{FeBr}_3$ was greater than that in $(\text{TTF})_2\text{FeCl}_3$ and the electrical conductivity of $(\text{TTF})_3\text{FeBr}_3$ was also greater than that of $(\text{TTF})_2\text{FeCl}_3$. It was concluded that the magnetic interaction could provide an important information in design of conductive materials.

Furthermore, $(\text{TTF})_5\text{Fe}(\text{NO}_3)_3$ is also reported.⁶ Iron existed in diamagnetic +2 state and unpaired electrons were delocalized along TTF stacks in $(\text{TTF})_5\text{Fe}(\text{NO}_3)_3$. Small temperature-independent paramagnetism was observed as a result of significant magnetic interaction along TTF chains.

In this study, $(\text{TTF})_4\text{FeCl}_3 \cdot \text{CH}_3\text{OH}$ is prepared from TTF and hydrated FeCl_3 in methanol solution as the extension of the study of TTF charge transfer compound containing transition metals. $(\text{TTF})_4\text{SbCl}_4$ and $(\text{TTF})_5(\text{SbBr}_4)_2 \cdot \text{CH}_3\text{COCH}_3$ are also synthesized in acetone solution. These compounds draw our interest since Fe(III) is reduced to Fe(II) state in $(\text{TTF})_4\text{FeCl}_3 \cdot \text{CH}_3\text{OH}$ as a result of charge transfer from TTF donor to iron, while charge transfer has occurred from $(\text{TTF})_n$ to the $-\text{SbX}_4^-$ ($X = \text{Cl}, \text{Br}$) entity in $(\text{TTF})_4\text{SbCl}_4$ and $(\text{TTF})_5(\text{SbBr}_4)_2 \cdot \text{CH}_3\text{COCH}_3$. Their electrical and magnetic properties are quite different from each other. The compounds are also characterized by EPR, X-ray photoelectron, electronic absorption and vibrational spectroscopy.