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Synthesis and X-Ray Structure of an Iridocenium(1+) Dichlorobis(pentamethylcyclopentadienyl)samarate(1−) Complex: $[Ir(C_5Me_5)_2][Sm(C_5Me_5)_2Cl_2]$

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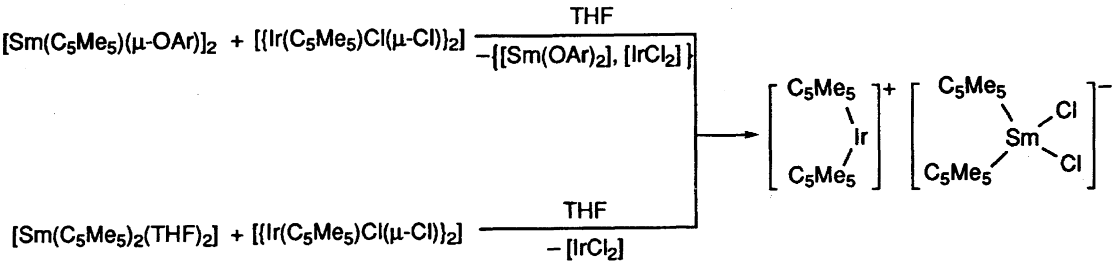
Reaction of $[\{Sm(C_5Me_5)(\mu\text{-}OAr)\}_2]$ (Ar = 2,6-(t-Bu)$_2$-4-MeC$_6$H$_2$) or $[Sm(C_5Me_5)_2(thf)_2]$ with 1 equiv of $[\{Ir(C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ in THF gave the "ate" complex $[Ir(C_5Me_5)_2][Sm(C_5Me_5)_2Cl_2]$ (**1**) as orange-red crystals in 60—74% yields (based on Sm). Complex **1** represents the first example of a structurally characterized metallocenium lanthanocene dihalide complex. Crystal data for **1**: monoclinic, space group $P2_1/m$ (No. 11), $a = 9.781(4)$, $b = 14.956(4)$, $c = 13.842(5)$ Å, $\beta = 93.38(3)°$, $V = 2021(1)$ Å^3, $Z = 2$, $D_c = 1.57$ g cm^{-3}, $R = 7.75\%$, $R_W = 9.23\%$, GOF = 1.12.

The chlorometallocene(III) complexes of the lanthanide metals are among the most fundamental organolanthanide compounds.[1] These compounds can be generally grouped into four classes based on structural features: (1) solvated monomer $[LnCp'_2Cl(thf)]$ (Ln = lanthanide metal, Cp′ = substituted or unsubstituted cyclopentadienyl);[2] (2) homometallic dimer $[\{LnCp'_2(\mu\text{-}Cl)\}_2]$;[3,4] (3) heterometallic dimer $[LnCp'_2(\mu\text{-}Cl)_2ML_2]$ (M = alkali metal, L = thf, OEt$_2$, or L$_2$ = dme);[5] and (4) anionic dichlorometallocene $[Ph_4E][LnCp'_2Cl_2]$ (E = N, P, As).[6] Among all these types of compounds, the anionic dichlorometallocene complexes are the least extensively studied, and only one complex, $[Ph_4As][Nd\{C_5H_3(SiMe_3)_2\}_2Cl_2]$, has been structurally characterized.[6] On the other hand, although the eighteen-electron metallocenium $[MCp'_2]^+$ cations of group 9 metals have been known for a long time,[7,8] structurally characterized examples of these species have been mostly limited to those of cobalt and rhodium,[9] while structurally well-defined iridocenium cation species are surprisingly scarce.[10] In this paper, we report the synthesis and structural characterization of an iridocenium(1+) dichlorobis(pentamethylcyclopentadienyl)samarate(1−) complex, $[Ir(C_5Me_5)_2][Sm(C_5Me_5)_2Cl_2]$ (**1**), which is isolated from the reaction of $[\{Sm(C_5Me_5)(\mu\text{-}OAr)\}_2]$ (Ar = 2,6-(t-Bu)$_2$-4-MeC$_6$H$_2$)[11a] or $[Sm(C_5Me_5)_2(thf)_2]$[12] with 1 equiv of $[\{Ir(C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$. To our knowledge, this complex represents the first example of a structurally characterized metallocenium lanthanocene dihalide complex.[13]

Results and Discussion

In our previous studies on samarium(II) complexes bearing mixed C$_5$Me$_5$/OAr ligands (Ar=2,6-di-t-butylphenyls),[11] we observed that the reaction of $[\{Sm(C_5Me_5)(\mu\text{-}OAr)\}_2]$ with 2 equiv of C$_5$Me$_5$K in THF yielded a novel addition product, $[\{\mu,\eta^5\text{-}C_5Me_5)Sm(OAr)(\mu,\eta^5\text{-}C_5Me_5)K(thf)_2\}_\infty]$, in which the "C$_5Me_5$K" unit acted as a neutral coordination ligand.[11a] In an attempt to see how the central Sm(II) ion in "(C$_5$Me$_5$)SmOAr" would interact with a "(C$_5$Me$_5$)M" unit of a late transition metal, reaction of $[\{Sm(C_5Me_5)(\mu\text{-}OAr)\}_2]$ (Ar = 2,6-(t-Bu)$_2$-4-MeC$_6$H$_2$) with 1 equiv of $[\{Ir(C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ in THF was carried out. Unexpectedly, the orange-red complex $[Ir(C_5Me_5)_2][Sm(C_5Me_5)_2Cl_2]$ (**1**) was isolated from this reaction. The similar reaction of $[Sm(C_5Me_5)_2(thf)_2]$[12] with $[\{Ir(C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ also gave **1** in 74% isolated yield (based on Sm) (Scheme 1). An X-ray analysis has revealed that **1** is an "ate" complex which consists of a $[Sm(C_5Me_5)_2Cl_2]^-$ anion and a $[Ir(C_5Me_5)_2]^+$ cation (Fig. 1, Table 1). The whole molecule possesses a mirror symmetry. The mirror plane contains Sm(1), Ir(1), C(3), C(6), C(9), C(12), C(15), C(18), C(21), and C(24), and



Scheme 1.

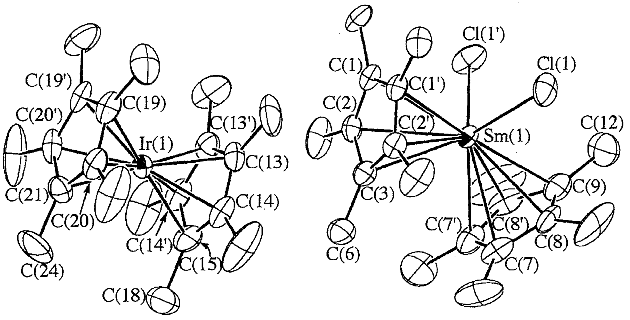


Fig. 1. ORTEP Drawing of **1**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1**

Sm(1)–Cl(1)	2.665(7)	Sm(1)–C(1)	2.78(2)
Sm(1)–C(2)	2.75(2)	Sm(1)–C(3)	2.79(3)
Sm(1)–C(7)	2.78(3)	Sm(1)–C(8)	2.73(2)
Sm(1)–C(9)	2.76(4)	Ir(1)–C(13)	2.19(3)
Ir(1)–C(14)	2.18(3)	Ir(1)–C(15)	2.21(3)
Ir(1)–C(19)	2.20(2)	Ir(1)–C(20)	2.17(3)
Ir(1)–C(21)	2.17(3)		
Cl(1)–Sm(1)–Cl(1′)		98.1(3)	
Cp*(centroid)–Sm–Cp*(centroid)		135.5	
Cp*(centroid)–Ir–Cp*(centroid)		178.6	

bisects the C(1)–C(1′), C(7)–C(7′), C(13)–C(13′), C(19)–C(19′), and Cl(1)···Cl(1′) bonds. The average bond distances of the Sm–C(Cp*) (2.77 Å) and Sm–Cl bonds (2.665(7) Å) in **1** can be compared, respectively, to those of the Nd–$C_5H_3(SiMe_3)_2$ (2.78 Å) and Nd–Cl bonds (2.668(3) Å) found in another lanthanide dichlorometallocene(III) complex, $[Ph_4As][Nd\{C_5H_3(SiMe_3)_2\}_2Cl_2]$,[6)] since the Sm^{3+} radius is only 0.03 Å shorter than that of Nd^{3+}.[14)] The average Sm–C(Cp*) bond distance in **1** (2.77 Å) is slightly longer than those found in other bis(pentamethylcyclopentadienyl)halogenosamarium(III) complexes such as $[Sm(C_5Me_5)_2Cl(thf)]$ (2.72 Å),[2b)] $[Sm(C_5Me_5)_2I(thf)]$ (2.73 Å),[2b)] $[\{Sm(C_5Me_5)_2(\mu\text{-}Cl)\}_3]$ (2.73 Å),[4)] and $[\{Sm(C_5Me_5)_2Cl\}_2(\mu\text{-}Cl)\}^-$ (2.72 Å),[4)] while the Sm–Cl bond distances in **1** (2.665(7) Å) are significantly shorter than that in $[Sm(C_5Me_5)_2Cl(thf)]$ (2.738(8) Å),[2b)] but comparable with those of the terminal Sm–Cl bonds in $[\{Sm(C_5Me_5)_2Cl\}_2(\mu\text{-}Cl)]^-$ (av. 2.64 Å).[4)] The angle of the ∠Cp*(ring centroid)–Sm–Cp*(ring centroid) in **1** (135.5°) is comparable with those found in $[Sm(C_5Me_5)_2Cl(thf)]$ (135°),[2b)] $[Sm(C_5Me_5)_2I(thf)]$ (137°),[2b)] and $[\{Sm(C_5Me_5)_2Cl\}_2(\mu\text{-}Cl)]^-$ (134.5°),[4)] but larger than that found in $[\{Sm(C_5Me_5)_2(\mu\text{-}Cl)\}_3]$ (127.9°)[4)] and that of the ∠Cp′(ring centroid)–Nd–Cp′(ring centroid) in $[Ph_4As][Nd(Cp')_2Cl_2]$ ($Cp' = C_5H_3(SiMe_3)_2$ (126.3°).[6)] The angle of the ∠Cl–Sm–Cl in **1** (98.1(3)°) is significantly larger than that in $[\{Sm(C_5Me_5)_2(\mu\text{-}Cl)\}_3]$ (82.8(2)°),[4)] but comparable with that of the ∠Cl–Nd–Cl in $[Ph_4As][Nd\{C_5H_3(SiMe_3)_2\}_2Cl_2]$, (99.3(1)°).[6)] The average bond distance of the Ir–C(Cp*) bonds in **1** (2.186(3) Å) is slightly longer than those in $[\{Ir(C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ (2.132(16) Å)[15)] and $[\{Ir(C_5Me_5)Br(\mu\text{-}Br)\}_2]$ (2.148(13) Å),[16)] but comparable with those in $[Ir(C_5Me_5)_2][BPh_4]$ (2.193(7) Å),[10a)] $[Ir(Cp)(Cp')][BF_4]$ (Ir–C(Cp): 2.186(6) Å, Ir–C(Cp′): 2.173(5) Å, $Cp = C_5H_5$, $Cp' = C_5Me_4Et$),[10b)] $[Ir(Cp)(Cp')][Zr(Cp)(NH^tBu)(OTf)_3(thf)]$ (Ir–C(Cp): 2.18(1) Å), Ir–C(Cp′): 2.16(1) Å, $Cp = C_5H_5$, $Cp' = C_5Me_4Et$),[10b)] and $[Ir(C_5)Me_5)(bpy)Cl]^+$ (2.156(10) Å, bpy = 2,2′-bipyridine).[17)] In contrast with the staggered conformation of the Cp* ligands in $[Ir(C_5Me_5)_2][BPh_4]$ (rotated by 23.8°),[10a)] the two Cp* ligands in the $[(C_5Me_5)_2Ir]^+$ unit in **1** are almost completely eclipsed, with the torsion angles between the two most eclipsed Me groups being less than 2°. The two Cp* ring planes in the $[Ir(C_5Me_5)_2]^+$ unit in **1** are almost parallel to each other, with a dihedral angle of 1.4°. This is similar to what was observed in $[Ir(C_5Me_5)_2][BPh_4]$,[10a)] $[Ir(Cp)(Cp')][BF_4]$,[10b)] and $[Ir(Cp)(Cp')][Zr(Cp)(NH^tBu)(OTf)_3(thf)]$.[10b)]

Complex **1** was soluble in benzene. Its ^1H NMR spectrum in C_6D_6 showed a singlet at $\delta = 1.79$ for the $[Ir(C_5Me_5)_2]^+$ cation and a singlet at $\delta = 1.39$ for the $[Sm(C_5Me_5)_2Cl_2]^-$ anion. The latter was 0.19—0.23 ppm downfield shifted from those for the C_5Me_5 groups in $[Sm(C_5Me_5)_2Cl(thf)]$ ($\delta = 1.20$) and $[Sm(C_5Me_5)_2I(thf)]$ ($\delta = 1.16$),[2b)] but comparable with that in $[Sm(C_5Me_5)_2(\mu\text{-}Cl)_2Li(thf)_2]$ ($\delta = 1.37$).[2b)]

The formation of **1** in the present reactions was apparently accompanied by oxidation of Sm(II) to Sm(III), chloride (Cl^-) transfer from Ir to Sm, and ligand redistribution at the Ir center, although detailed mechanisms were not very clear. It has previously been reported that the reaction of $[Sm(C_5Me_5)_2(thf)_2]$ with an organic halide such as ^tBuCl afforded $[Sm(C_5Me_5)_2Cl(thf)]$ in high yield.[2b)] The reaction of $[Sm(C_5Me_5)_2(thf)_2]$ with $[\{Ir(C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ could give $Sm(C_5Me_5)_2Cl$ through one electron transfer from Sm(II) to Ir(III). Chloride (Cl^-) abstraction by the Lewis acidic Sm(III) center in $Sm(C_5Me_5)_2Cl$ from a C_5Me_5-coordinated iridium chloride species would afford the $[Sm(C_5Me_5)_2Cl_2]^-$ anion,[6)] while ligand redistribution of the iridium species could probably give the $[Ir(C_5Me_5)_2]^+$ cation.

Experimental

All experiments were performed under an atmosphere of dry and oxygen-free argon by using standard Schlenk technique or under a nitrogen atmosphere in an Mbraun glove box. ^1H NMR spectra were recorded on a JNM-EX 270 (FT, 270 MHz) spectrometer and are reported in ppm downfield from tetramethylsilane. Elemental analyses were performed by the chemical analysis laboratory of The Institute of Physical and Chemical Research (RIKEN). Tetrahydrofuran (THF), toluene and hexane were distilled from sodium/benzophenone ketyl, degassed by the freeze-thaw method (three times) and dried over fresh Na chips in the glove box. C_6D_6 was degassed by the freeze-thaw method (three times) and dried over fresh Na chips in the glove box. $[\{Ir(C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ was purchased from Aldrich. $[\{Sm(C_5Me_5)(\mu\text{-}OAr)\}_2]$[11a)] and $[Sm(C_5Me_5)_2(thf)_2]$[12)] were prepared according to literature.

Synthesis of $[Ir(C_5Me_5)_2][Sm(C_5Me_5)_2Cl_2]$ (1). To a THF suspension (10 mL) of $[\{Ir(C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ (169 mg, 0.212 mmol) was added a purple solution of $[Sm(C_5Me_5)_2(thf)_2]$ (110 mg, 0.195 mmol). This mixture was then stirred at room temperature for 2 h to give a brown solution. The solvent was evaporated and the residue was extracted with 10 mL of toluene. Reduction of the solution volume under reduced pressure and addition of hexane precipitated **1** as orange-red blocks (137 mg, 0.144 mmol, 74% yield based on Sm). The similar reaction of [{Sm(C_5Me_5)(μ-OAr)}$_2$] (101 mg, 0.100 mmol) with [{Ir(C_5Me_5)Cl(μ-Cl)}$_2$] (84 mg, 0.105 mmol) also gave **1** (60 mg, 0.062 mmol). ^{1}H NMR (C_6D_6, 22 °C) $\delta = 1.79$ (s, 30 H, (C_5Me_5)$_2$Ir), 1.39 (s, 30 H, (C_5Me_5)$_2$Sm). Anal. Calcd for $C_{40}H_{60}Cl_2IrSm$: C, 50.34; H, 6.34%. Found: C, 50.78; H, 6.50%.

Crystallographic Study of [Ir(C_5Me_5)$_2$][Sm(C_5Me_5)$_2$Cl$_2$] (1). An orange-red crystal (4.4×4.0×3.5 mm) was sealed in a thin-walled glass capillary under N_2 atmosphere and mounted on a Mac Science MXC3K diffractometer (Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å, graphite monochromator, ω–2θ scan, 20 °C). Lattice constants and orientation matrix were obtained by least-squares refinement of 22 reflections with $30° \leq 2\theta \leq 35°$. Three reflections were monitored periodically as a check for crystal decomposition or movement and no significant decay was observed. The data were corrected for X-ray absorption effects. The structure was solved by direct methods using SIR92 in the Crystan-GM software package. Refinements were performed anisotropically for all non-hydrogen atoms by the block diagonal least squares method. No attempt to locate the hydrogen atoms was made. Neutral atomic scattering factors were taken from the International Tables for X-ray Crystallography.[18] The residual electron densities were of no chemical significance. Crystal data, data collection, and processing parameters are given in Table 2.

Supporting Data. Atomic coordinates, thermal parameters, bond distances and angles, and a packing diagram for **1** (9 pages) are deposited as Document No. 71033 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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Table 2. Crystallographic Data for **1**

Formula	$C_{40}H_{60}Cl_2IrSm$
FW	954.45
Cryst system	Monoclinic
Space group	$P2_1/m$ (No. 11)
a/Å	9.781(4)
b/Å	14.956(4)
c/Å	13.842(5)
β/deg	93.38(3)
V/Å^3	2021(1)
Z	2
D_{calcd} / g cm^{-3}	1.57
Radiation λ / Å	Mo $K\alpha$ 0.71073
μ / cm^{-1}	48.774
Data collect	$\pm h$, $+k$, $+l$
Scan speed / deg min^{-1}	6
2θrange / deg	3—55
No. of obsd reflns	5256
No. of unique reflns	4821
No. of reflns with $I_o \geq 3\sigma(I_o)$	3367
No. of variables	214
R/%[a)]	7.75
R_w/%[b)]	9.23
GOF	1.12

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

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