Tris(solvent) iridium complex supported by the η^5-pentamethylcyclopentadienyl ligand. Refinement of $[Ir(\eta^5\text{-}C_5Me_5)(Me_2CO)_2(H_2O)](BF_4)_2$

Masahiko Maekawa,*[,a] Yusaku Suenaga,[a,b] Takayoshi Kuroda-Sowa,[b] Megumu Munakata[b] and Hisashi Konaka[b]

[a]*Research Institute for Science and Technology, Kinki University, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan*
[b]*Department of Chemistry, Kinki University, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan*

(Received, December 12, 2003)

Abstract

Yellow single crystals of tris(solvent) Ir complex $[Ir(\eta^5\text{-}C_5Me_5)(Me_2CO)_2(H_2O)](BF_4)_2$ were collected and the structure was refined crystallographically. The Ir atom supported by the $\eta^5\text{-}C_5Me_5$ fragment is bonded to two Me_2CO molecules and one aqua molecule in a unique three-legged piano stool coordination mode.

Key words: Iridium complexes, Cyclopentadienyl complexes, Acetone complexes, Aqua complexes, Crystal structures

1. Introduction

It has been known that dichloro-bridged binuclear Rh and Ir complexes $[M(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)(Cl)]_2$ (M=Rh and Ir) play a prominent role as starting materials in organometallic chemistry and because of their relevance in catalysis.[1,2] The reaction of $[M(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)(Cl)]_2$ with a suitable Ag salt in organic solvent and aqueous solution could produce the intermediate $[M(\eta^5\text{-}C_5Me_5)(\text{solvent})_3]^{2+}$. The solvated complexes can be regarded as "tripod connectors" in which the $\eta^5\text{-}C_5Me_5$ ligand remains firmly attached, whereas three weakly bound solvent molecules occupy the three legs of the tripod. The coordinated solvent molecules can be displaced by a wide range of donor ligands under extremely mild conditions. A variety of organometallic compounds with a half-sandwich structure have been prepared by the reaction of $[M(\eta^5\text{-}C_5Me_5)(\text{solvent})_3]^{2+}$ with an appropriate organic ligand and their structures and properties have been physicochemically characterized.[1,2] However, the intermediate $[M(\eta^5\text{-}C_5Me_5)(\text{solvent})_3]^{2+}$ is hardly isolated or characterized due to their high reactivity. We have so far interested in the reaction of the intermediate $[M(\eta^5\text{-}C_5Me_5)(\text{solvent})_3]^{2+}$ and various aromatic ligands such as [2.2]paracyclophane (pcp) and terphenyl (tp).[3-5] The structure and property of resultant compounds have been determined. Here, on the reaction of $[Ir(\eta^5\text{-}C_5Me_5)(solvent)_3]^{2+}$ with *o*-tp,[3] we obtained yellow single crystals of tris(solvent) Ir complex $[Ir(\eta^5\text{-}C_5Me_5)(Me_2CO)_2(H_2O)](BF_4)_2$ (**1**) as a by-product and examined it crystallographically. More recently Rh and Ir complexes $[M(\eta^5\text{-}C_5Me_5)(Me_2CO)_2(H_2O)](BF_4)_2$ (M=Rh and Ir) which were prepared by another procedures have been structurally characterized.[6] This study concerns as the refinement of crystal structure mentioned above.

2. Experimental

All experimental procedures are carried out under Ar. The precursor Ir complex $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)(Cl)]_2$ (79.7 mg, 0.1 mmol) and $AgBF_4$ (77.8 mg, 0.4 mmol) were mixed in Me_2CO (10 ml) for 30 min and the yellow suspension was filtered to remove AgCl. The Me_2CO solution of intermediate $[Ir(\eta^5\text{-}C_5Me_5)(Me_2CO)_3]^{2+}$ was added to *o*-tp (4.6 mg, 0.2 mmol). After stirring for 15min, the reaction solution was again filtrated. Each 2 ml sample solution was layered by hexane in 7 mm diameter glass tubes and then was sealed under Ar. The reaction solution was allowed to stand at room temperature for 2 weeks. The yellow needle crystals of **1** were collected.

A yellow crystal of **1** was attached to the end of a glass fiber and mounted on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo-K_α radiation (λ=0.71069 Å). The detailed measurement conditions and crystal data are listed in Table 1. The data were collected at -150 °C to a maximum 2θ value of 55.0°. Of the 16655 reflections which were collected, 4828 were unique (R_{int}=0.026). The linear absorption coefficient, μ, for Mo-K_α radiation is 61.0 cm^{-1}. A symmetry-related absorption correction using the program *REQAB* was applied which resulted in transmission factors ranging from 0.46 to 0.54. The data were corrected for Lorentz and polarization effects. The structure was solved by heavy-atom Patterson method (*DIRDIR94-PATTY*) and expanded using Fourier technique.[7] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The BF_4^- anion including B(2) atom disordered. The final cycle of the full-matrix least-squares refinement was based on 4828 observed reflections (I>2σ(I)) and 380 variable parameters. The reliability factors are defined as $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R_w=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. The final R and R_w values were 0.019 and 0.045, respectively. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.36 and -0.63 e$Å^{-3}$, respectively. The atomic-scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography, Vol. IV.[8] All of the calculations were performed using the program *teXsan*, crystallographic software package of Molecular Structure Corporation.[9] Selected positional parameters are listed in Table 2.

Table 1. Crystal and experimental data of **1**.

Formula	$IrF_8O_3C_{16}B_2H_{29}$
Formula weight	635.23
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	10.142(2)
b (Å)	13.915(3)
c (Å)	15.978(3)
β (°)	99.493(3)
V ($Å^3$)	2224.0(8)
Z	4
D_{calc} (gcm^{-3})	1.897
μ_{eff} (cm^{-1})	61.0
Radiation	Mo-K_α (0.7107Å)
Measurement method	ω-2θ
No. of reflections measured	16655 (total) 4828 (unique)
No. Observations	4193 (all data)
R	0.019
R_w	0.045

Table 2. Selective atomic coordinate and equivalent isotropic thermal parameters B_{eq} ($Å^2$) of non-hydrogen atoms.

atom	X	y	Z	Beq
Ir(1)	0.14553(1)	0.09935(1)	0.28461(1)	0.983(3)
F(1)	0.2411(2)	0.1471(2)	0.6673(1)	2.86(4)
F(2)	0.4257(2)	0.0621(2)	0.6531(2)	3.35(4)
F(3)	0.4474(2)	0.2143(2)	0.7054(1)	2.77(3)
F(4)	0.3642(2)	0.1897(2)	0.5670(1)	3.52(4)
F(5)	0.7140(2)	0.3970(2)	0.5363(2)	4.35(5)
F(6)	0.9040(4)	0.3730(3)	0.4798(3)	3.5167(10)
F(7)	0.9077(7)	0.3262(6)	0.5673(5)	6.1(2)
F(8)	0.8667(5)	0.2764(4)	0.5870(3)	4.2(1)
F(9)	0.7122(9)	0.2476(5)	0.5386(5)	7.7(2)

F(10)	0.7467(4)	0.2580(3)	0.4580(3)	3.40(8)
F(11)	0.7874(7)	0.3247(7)	0.4358(3)	5.9(2)
O(1)	0.3054(2)	0.0932(1)	0.2144(1)	1.47(3)
O(2)	0.2598(2)	0.2196(1)	0.3409(1)	1.26(3)
O(3)	0.0726(2)	0.2211(2)	0.2076(1)	1.72(4)
C(1)	-0.0431(3)	0.0511(2)	0.3121(2)	1.47(5)
C(2)	0.0088(3)	-0.0174(2)	0.2573(2)	1.51(5)
C(3)	0.1349(3)	-0.0528(2)	0.3027(2)	1.40(4)
C(4)	0.1628(3)	-0.0052(2)	0.3833(2)	1.36(4)
C(5)	0.0519(3)	0.0603(2)	0.3892(2)	1.41(4)
C(6)	-0.1734(3)	0.1023(3)	0.2919(2)	2.17(5)
C(7)	-0.0617(4)	-0.0516(3)	0.1732(2)	2.18(5)
C(8)	0.2242(4)	-0.1241(2)	0.2704(2)	2.15(5)
C(9)	0.2780(3)	-0.0239(3)	0.4517(2)	2.00(5)
C(10)	0.0419(4)	0.1256(3)	0.4624(2)	2.09(5)
C(11)	0.3188(3)	0.0869(2)	0.1389(2)	1.69(5)
C(12)	0.2049(4)	0.0933(3)	0.0682(2)	2.72(6)
C(13)	0.4557(4)	0.0754(3)	0.1197(3)	2.49(6)
C(14)	0.3801(3)	0.2314(2)	0.3694(2)	1.35(4)
C(15)	0.4272(3)	0.3299(2)	0.3957(2)	2.11(5)
C(16)	0.4804(3)	0.1527(3)	0.3792(2)	2.02(5)
B(1)	0.3726(3)	0.1526(3)	0.6484(2)	1.78(5)
B(2)	0.7951(4)	0.3257(3)	0.5160(2)	2.49(7)

3. Results and discussion

According to experimental section, the reaction of intermediate [Ir(η^5-C_5Me_5)(solvent)$_3$]$^{2+}$ with *o*-tp ligand afforded yellow single crystals of [Ir(η^5-C_5Me_5)(Me_2CO)$_2$(H_2O)](BF_4)$_2$ (**1**). On the other hand, our previous study described that the reaction of [Ir(η^5-C_5Me_5)(solvent)$_3$]$^{2+}$ with *m*-tp ligand to afford mononuclear Ir complex [Ir(η^5-C_5Me_5)(*m*-tp)](BF_4)$_2$.[3] Rh and Ir [M(η^5-C_5Me_5)(pcp)](BF_4)$_2$ (M=Rh and Ir) were also produced by the reaction of [M(η^5-C_5Me_5)(solvent)$_3$]$^{2+}$ and pcp ligand.[4,5] These facts demonstrated that the coordination affinity of [Ir(η^5-C_5Me_5)(solvent)$_3$]$^{2+}$ to *o*-tp ligand is lower, in comparison with that to *m*-tp and pcp ligands.

The structure of the cation moiety of **1** is shown in Figure 1, together with the atomic labeling scheme. Amouri, et al. prepared complex **1** by another procedure and the preliminary structure was more recently reported.[6] The present structure is essentially same to the reported one. Most interesting feature is that the Ir atom is coordinated by two acetone molecules and one aqua molecule in a unique three-legged piano stool coordination mode. The Ir atom is also supported by the η^5-C_5Me_5 fragment to provide a half-sandwich structure. Our Survey in SciFinder describes that there are a few crystallographic study of Ir η^5-C_5Me_5 complexes having the three-legged piano stool coordination mode: [Ir(η^5-C_5Me_5)(Me_2CO)$_2$(H_2O)](BF_4)$_2$,[6] [Ir(η^5-C_5Me_5)(py)$_3$](BF_4)$_2$,[6] [Ir(η^5-C_5Me_5)(NO_3)$_2$],[6] [Ir(η^5-C_5Me_5)(CN)$_3$](H_3O)•Me_2CO[10] and [Ir(η^5-C_5Me_5)(Cl)(Ph_2PCH_2SPh)]BF_4.[11] Moreover, Ir complexes possessing two coordinated acetone molecules identified structurally is rare, which have been only found in two examples of [Ir(η^5-C_5Me_5)(Me_2CO)$_2$(H_2O)](BF_4)$_2$[6] and [Ir(H)$_2$(Me_2CO)$_2$(PPh_3)$_2$]BF_4.[12] Since the isolation of the intermediate [M(η^5-C_5Me_5)(solvent)$_3$]$^{2+}$ has been limited due to the high lability,[3] The crystallographic study of **1** is of significance to solve a reaction mechanism. This is a first crystal structure of tris(solvent) iridium complex.[6]

The average Ir-C(η^5-C_5Me_5) distance of 2.134 Å is within those (2.105—2.238 Å) of other Ir η^5-C_5Me_5 complexes in the piano stool coordination mode.[6,10,11] The Ir-O(H_2O) of 2.153(2) Å is longer than those (2.120(2), 2.146(2) Å) of other Ir-O(Me_2CO) distances. The average Ir-O(Me_2CO) distance of 2.133 Å is slightly shorter than that (2.228 Å) of the Ir acetone complex [Ir(H)$_2$(Me_2CO)$_2$(PPh_3)$_2$]BF_4.[12] In the packing view, we could not find a specific intra- or inter-molecular π-π interaction. The detailed selected bond distances and bond angles are listed in Table 3.

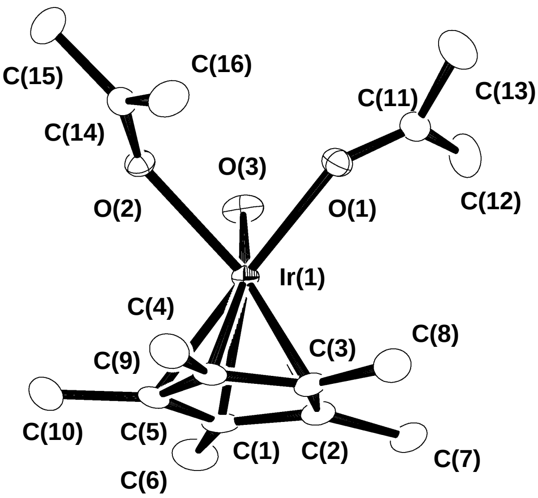

Figure 1. The cation moiety of **1** and the atomic labeling scheme. The two BF_4 anions were omitted.

Table 3. Selected bond distances (Å) and angles (°) of **1**.

Ir(1)-O(1)	2.120(2)	Ir(1)-O(2)	2.146(2)
Ir(1)-O(3)	2.153(2)	Ir(1)-C(1)	2.140(3)
Ir(1)-C(2)	2.134(3)	Ir(1)-C(3)	2.142(3)
Ir(1)-C(4)	2.131(3)	Ir(1)-C(5)	2.125(3)
C(1)-C(2)	1.450(4)	C(2)-C(3)	1.449(4)
C(3)-C(4)	1.434(4)	C(4)-C(5)	1.462(4)
C(1)-C(5)	1.440(4)		
O(1)-Ir(1)-O(2)	81.13(7)	O(1)-Ir(1)-O(3)	87.15(8)
O(1)-Ir(1)-C(1)	152.05(9)	O(1)-Ir(1)-C(2)	112.90(10)
O(1)-Ir(1)-C(3)	95.24(10)	O(1)-Ir(1)-C(4)	112.78(9)
O(1)-Ir(1)-C(5)	152.36(9)	O(2)-Ir(1)-O(3)	74.75(7)
O(2)-Ir(1)-C(1)	126.72(9)	O(2)-Ir(1)-C(2)	165.22(10)
O(2)-Ir(1)-C(3)	138.56(8)	O(2)-Ir(1)-C(4)	104.43(8)
O(2)-Ir(1)-C(5)	98.64(9)	O(3)-Ir(1)-C(1)	97.45(10)
O(3)-Ir(1)-C(2)	109.38(9)	O(3)-Ir(1)-C(3)	146.62(9)
O(3)-Ir(1)-C(4)	159.86(10)	O(3)-Ir(1)-C(5)	119.68(10)

4. Acknowledgment

This work was partially supported by a Grant-in-Aid for Science Research and from the Ministry of Education, Science, Culture, Sports and Technology in Japan. We thank to Mr. Y. Deguchi and Mr. N. Gunjima for their assistance.

5. References

1. J. D. Atwood, ”*Comprehensive Organometallic Chemistry II*”, Pergamon Press, Oxford, 1992, Vol. 8, ch. 3, pp.303-417.
2. ”*Metallocenes*”, ed. by A. Togni and R.L. Halterman, Wiley-VCH, Weinheim, Germany, **1998**.
3. M. Maekawa, Y. Suenaga, T. Kuroda-Sowa and M. Munakata, *Inorg. Chim. Acta,* **2004**, *357*, 331.
4. M. Maekawa, N. Hashimoto, T. Kuroda-Sowa Y. Suenaga and M. Munakata, *Inorg. Chim. Acta,* **2002**, *328*, 254.
5. M. Maekawa, N. Hashimoto, K. Sugimoto, T. Kuroda-Sowa, Y. Suenaga and M. Munakata, *Inorg. Chim. Acta,* **2003**, *344*, 143.
6. H. Amouri, C. Guyard-Duhayon and J. Vaissermann, *Inorg. Chem.,* **2002**, *41*, 1397.
7. *PATTY*: P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel and J. M. M. Smits, 1994. The *DIRDIF-94* program system, Technical report of the crystallography Laboratory, University of Nijmegen, The Netherlands.
8. ”*International Tables for X-ray Crystallography*”, Vol. IV, The Kynoch Press, Birmingham, England, **1974**.
9. ”*teXsan*”, Crystal Structure Analysis Package, Molecular Structure Corporation **1985** and **1999**.
10. S. M. Contakes, M. Schmidt and T. B. Rauchfuss, *Chem. Commum.,* **1999**, 1183.
11. M. Valderrama, R. Contreras and D. Boys, *Polyhedron,* **1997**, *16*, 1811.
12. R. H. Crabtree, G. G. Hlatky, C. P. Parnell, B. E. Segmuller and R. J. Uriarte, *Inorg. Chem.,* **1984**, *23*, 354.