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^{13}C-CP-MAS NMR Spectroscopic Study of the Reaction Products of Osmocene with Lewis Acids

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The adducts of osmocene derivatives with Lewis acids were studied by means of ^{13}C-CP-NMR spectroscopy and other physicochemical techniques. The large low-field shifts found through ^{13}C-CP-MAS NMR and ^{1}H NMR spectroscopy and the organotin(IV) species found in the ^{119}Sn-Mössbauer spectroscopic data suggest the presence of direct chemical bonds between the osmium atoms and the Lewis acids in the adducts.

It is well-known that [2]ferrocenophane and ruthenocene derivatives react with appropriate Lewis acids such as $HgCl_2$, $SnCl_4$, and I_2, giving diamagnetic stable adducts with a direct chemical bond between the central metal atom in the metallocene (Fe, Ru) and the Lewis acid, based on the results of ^{57}Fe- and ^{119}Sn-Mössbauer and ^{13}C-CP-MAS NMR spectroscopic studies.[1-6] Osmocene was first prepared more than 30 years ago by the reaction of osmium tetrachloride and a large excess amount of sodium cyclopentadienide in THF.[7] However, its chemical properties have been investigated less because of the lack of a high-yield synthetic route of osmocene. Osmocene is expected to react with Lewis acids, giving more stable adducts than [2]ferrocenophane and ruthenocene, because osmocene has a smaller steric hindrance in donating e_{2g}-electrons (5d) than do [2]ferrocenophane and ruthenocene. However, few studies have been reported on the osmocene-Lewis acid adducts. The present studies were designed to find a high-yield synthetic route of osmocene and to provide information about the structure of some osmocene-Lewis acids adducts ($HgCl_2$, $SnCl_4$, I_2, Br_2 etc.) by means of ^{13}C-CP-MAS NMR, ^{1}H NMR, ^{119}Sn-Mössbauer spectroscopy and other physicochemical measurements.

Experimental

Materials: In the present study, osmocene was first prepared in high yield by mixing osmium trichloride and cyclopentadiene with zinc dust in ethanol under conditions similar to those used for ruthenocene.[8] Freshly distilled cyclopentadiene (100 cm^3) and zinc dust (5 g) were added to a solution of hydrated $OsCl_3$ (5.0 g, 0.015 mol) in ethanol (200 cm^3). The mixture was stirred for 10 h at room temperature and refluxed for 1 h. The solution was extracted with hexane mixed with benzene, washed with water, dried over $MgSO_4$ and separated by column chromatography on alumina. Hexane was used to elute dicyclopentadiene and a mixed solvent with hexane and benzene (1:1) to elute osmocene, which was obtained as pale-yellow precipitates. Osmocene was purified by recrystallization from hexane mixed with benzene (3.5 g, 0.011 mol; yield, 73%). ^{1}H NMR ($CDCl_3$) δ=4.71 and (CD_3CN) δ=5.52 (lit(CCl_4)[9] δ=4.57). ^{13}C NMR ($CDCl_3$) δ=63.6 and (CD_3CN) δ=63.4 (lit(C_6D_6)[9] δ=63.9. Infrared spectrum data(KBr) 3083.5, 1399.5, 1096.6, 997.3, 988.6, 876.7, 830.4, 821.7, and 429.2 cm^{-1}, (lit[10] 3108, 1400, 1098, 998, 989, 831, and 823 cm^{-1}). Found: C, 37.54; H, 3.22%. Calcd for $C_{10}H_{10}Os$:C, 37.49; H, 3.15%.

Adducts of $HgCl_2$ and $SnCl_4$ with osmocene were prepared by mixing a large excess amount of $HgCl_2$ and $SnCl_4$ with osmocene in an ether and hexane solution, respectively. Pale-yellow diamagnetic precipitates were filtered, washed with ether and dried in vacuo. Found: C, 13.98; H, 1.35%. Calcd for $C_{10}H_{10}OsHg_2Cl_4$: C, 13.91; H, 1.17%. Found: C, 18.93; H, 1.82%. Calcd for $C_{10}H_{10}OsSn_{1.5}Cl_6H_2O$: C, 19.28; H, 1.94%. $[OsCp_2]_2Hg(BF_4)_2$ and $[RuCp_2]_2Hg(BF_4)_2$ adducts were prepared by the method described previously.[11] Found: C, 23.68; H, 2.01%. Calcd for $C_{20}H_{20}Os_2HgB_2F_8$: C, 23.66; H 1.99%. Found: C, 28.83; H, 2.45%. Calcd for $C_{20}H_{20}Ru_2HgB_2F_8$: C, 28.71; H, 2.41%. Adducts of $AgBF_4$ with osmocene and ruthenocene were prepared under the same conditions as those used for their $HgCl_2$ adducts. Diamagnetic white precipitates were immediately formed. Found: C, 17.01; H, 1.79%. Calcd for $C_{10}H_{10}OsAg_2B_2F_8$: C 16.99; H, 1.42%. Found: C, 23.62; H, 2.31%. Calcd for $C_{10}H_{20}RuAg_{1.5}B_{1.5}F_6$: C, 22.95; H, 1.93%. An adduct of $Pd(BF_4)_2$ with osmocene was prepared by mixing a large excess amount of $Pd(BF_4)_2(CH_3CN)_4$ with osmocene in acetonitrile. The solution was stirred for 1 h at room temperature and refluxed for 3 h and cooled. To the solution, a small amount of ethyl ether was added; yellow crystals were formed. Found: N, 4.63; C, 24.16; H, 2.42%. Calcd for $C_{10}H_{10}OsPd(BF_4)_2(CH_3CN)_2$: N, 4.10; C, 24.64; H, 2.36%. The reaction products of iodine with osmocene were prepared by mixing iodine and osmocene in dry CCl_4. Black diamagnetic precipitates were filtered. The products were well soluble in acetonitrile. The well-formed needle crystals were obtained by recrystallization from the solution. Found: C, 14.61; H, 1.18%. Calcd for $C_{10}H_{10}OsI_4$: C, 14.49; H, 1.21%. Reaction products of bromine with osmocene and ruthenocene were prepared under the same conditions used for the I_2 adduct of osmocene. Diamagnetic yellow-green precipitates were also formed. Found:C, 18.53; H, 1.56%. Calcd for $C_{10}H_{10}OsBr_4$:C, 18.76; H, 1.57%. Found: C, 22.20; H, 1.89%. Calcd for $C_{10}H_{10}RuBr_4$: C, 21.80; H, 1.83%.

[RuthenoceniumCl]$^+$$PF_6^-$ salt was prepared by a previously reported method.[12] Found: C, 23.88; H, 2.04%. Calcd for $C_{10}H_{10}RuClPF_6$; C, 23.98; H, 2.01%. [Osmocenium Cl]$^+$$PF_6^-$ salt was prepared in a condition similar to that used for [ruthenoceniumCl]$^+$$PF_6^-$ salt. Found: C, 23.88; H, 2.04%. Calcd for $C_{10}H_{10}OsClPF_6$; C, 23,98; H, 2.01%. [OsmoceniumBr]$^+$$PF_6^-$ and [ruthenoceniumBr]$^+$$PF_6^-$ salts were prepared by a method similar to that used for the [ruthenoceniumCl]$^+$PF$_6^-$ salt, except for the use of FeBr$_3$ and HBr. Found: C, 22.19; H, 1.82%. Calcd for $C_{10}H_{10}OsBrPF_6$; C, 22.02; H, 1.85%. Found: C, 26.33; H, 2.14%. Calcd for $C_{10}H_{10}RuBrPF_6$; C, 26.33; H, 2.21%.

Osmocenium$^+$PF$_6^-$ salt was prepared by a previously reported method.[13] Found: C, 26.58; H, 2.33%. Calcd for $C_{10}H_{10}RuPF_6$; C, 25.81; H, 2.17%.

Measurements: ^{119}Sn-Mössbauer spectra were measured against a Ca^{119}SnO$_3$ source. The velocity calibration was by determining the resonance line of an ^{57}Fe-enriched metallic-iron absorber aginst a ^{57}Co(Rh) source. The isomer shift (I.S.) for ^{119}Sn was described with respect to a BaSnO$_3$ absorber. The experimental error of the I. S. value was estimated to be within ±0.02 mm s^{-1}.

The ^{13}C-CP-MAS NMR spectra were obtained at a frequency of 50.18 MHz using a JEOL FX-200 Fourier Transform NMR Spectrometer. Four thousand data points were collected by following a spin-locking cross-polarization sequence. The ^{13}C frequency spread was 20 kHz. Magic-angle sample spinning rates of 3 to 3.5 kHz were achieved by using Kel-F rotors. The chemical shifts (δ) were measured with respect to external adamantane and then converted to the shifts from TMS. The ^{1}H and ^{13}C NMR spectra were measured in solution with the same spectrometer at 199.56 and 50.18 MHz, respectively, using TMS as a standard.

Cyclic voltammograms were obtained by the same method as in the case of a previous report.[2] A working electrode of platinum button and an Ag/AgCl reference electrode were connected via a salt bridge of CH$_3$CN containing (0.1 mol dm^{-3}) [(C$_4$H$_9$)$_4$N]ClO$_4$. The scanning rate was 200 mV s^{-1}. Ir spectra were obtained using a JASCO FT/IR-5MP spectrometer at a resolution of 2 cm^{-1} by 128 scans.

Results and Discussion

Osmocene-SnCl$_4$ Adduct. Most ferrocene derivatives react with SnCl$_4$ merely giving paramagnetic ferrocenium salts,[5] while [2]ferrocenophane, ruthenocene and osmocene react with a large excess amount of SnCl$_4$, giving diamagnetic adducts. [2]Ferrocenophane- and ruthenocene–SnCl$_4$ adducts, however, are so unstable that the red–orange and yellow color of the adducts gradually changes into green-yellow upon standing at room temperature for a few hours or several days in air after preparation, respectively.[14–16] The pale-yellow osmocene–SnCl$_4$ adduct is much more stable than the [2]ferrocenophane- and ruthenocene–SnCl$_4$ adducts on standing for a long time, showing no color change.

The ^{119}Sn-Mössbauer parameters of the osmocene–SnCl$_4$ adduct and related compounds are listed in Table 1 and typical ^{119}Sn–Mössbauer spectra of the adducts are shown in Fig. 1. Two kinds of chemical shifts of the tin(IV) species (I. S, 0.50 and 2.13 mm s^{-1} at 78 K, as shown in Fig. 1-a) are observed in the spectra of the osmocene–SnCl$_4$ adduct. The component with a higher I. S value is ascribed to tin(IV) in [Cp$_2$Os–SnCl$_2$–OsCp$_2$]$^{2+}$ species and the other one to an ionic SnCl$_5^-$ species, based on the results of the

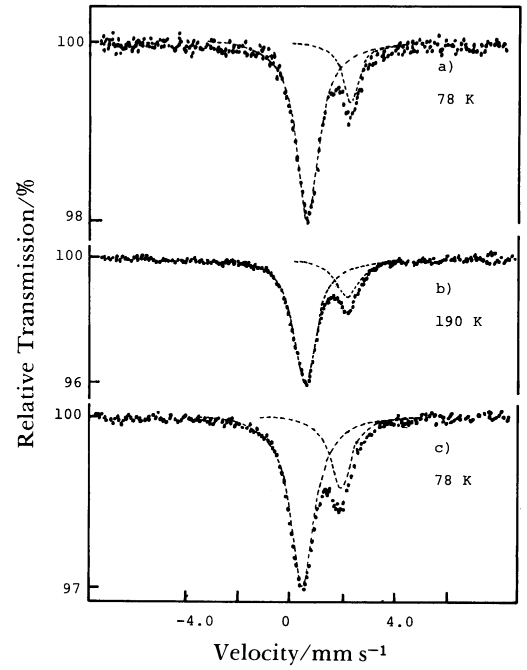

Fig. 1. ^{119}Sn-Mössbauer spectra of osmocene–1.5SnCl$_4$(H$_2$O) (a,b) and ruthenocene–1.5SnCl$_4$ adducts (c), at indicated temperatures.

Table 1. ^{119}Sn-Mössbauer Parameters of Osmocene–Tin Cloride Adduct and Related Compounds

Compound	Temperature/K	I.S./mm s^{-1}	Area ratio/%
Osmocene–1.5SnCl$_4$(H$_2$O)	78	0.50	0.75
		2.13	0.25
	140	0.52	0.79
		2.18	0.21
	190	0.53	0.80
		2.16	0.20
Ruthenocene–1.5SnCl$_4$	78	0.56	0.72
		2.08	0.28
[2]Ferrocenophane–1.5SnCl$_4$(H$_2$O)	4.2	0.54	0.68
		2.11	0.32
	78	0.54	0.78
		2.14	0.22

studies of similar adducts of ruthenocene with $SnCl_4$ (0.56 and 2.08 mm s^{-1} at 78 K, as shown in Fig. 1-c) and [2]ferrocenophane with $SnCl_4$ (0.54 and 2.14 mm s^{-1} at 78 K).[5]

Figure 2 shows the FT–IR spectra of osmocene (a) and its $SnCl_4$ adduct (b). The sharp singlet assigned to an antisymmetric C–C stretching mode of the cyclopentadienyl rings[10] is observed at 1399.5 cm^{-1} in osmocene. It has been reported that the C–C stretching mode is split when the cyclopentadienyl rings are tilited by the bond formation between the Lewis acids and the central metal atoms of metallocene; i. e., Ru-Hg, Ru-I and Ru–Hg.[11,14,17,18] Therefore, the splitting of the band (ν; 1426.5 and 1401.4 cm^{-1} and $\Delta\nu$; 25.1 cm^{-1}, as shown in Fig. 2-b and Table 2) can be used for an indication of the bond formation between the Sn and Os atoms in the $SnCl_4$ adduct of osmocene.

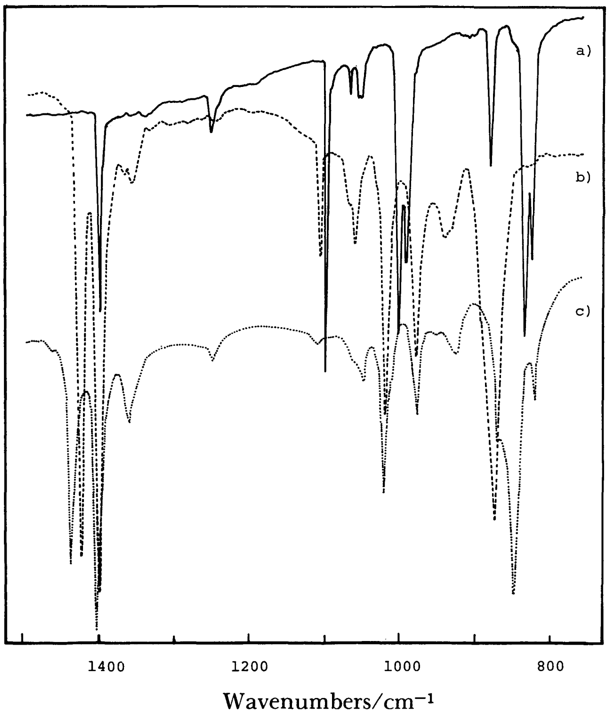

Fig. 2. IR spectra of osmocene (a), osmocene-1.5$SnCl_4(H_2O)$ (b), and (osmoceniumBr)$^+Br_3^-$ salt (c).

Although osmocene is well-soluble and stable in most organic solvents, some of the Lewis acid adducts of osmocene are less soluble and unstable in solvents, as in the cases of the adducts of ruthenocene and [2]ferrocenophane.[14–16] Applications of ^{13}C-CP-MAS NMR spectroscopy to the reaction products of osmocene have made it possible to obtain a high-resolution ^{13}C NMR spectrum, even in the solid state. Figure 3 shows the ^{13}C-CP-MAS NMR spectra of the osmocene (a) and its $SnCl_4$ adduct (b). Their ^{13}C chemical shift values are listed in Table 3. The chemical shift (δ_C) values of the cyclopentadienyl ring carbon in osmocene was found to be 67.4 ppm, which is smaller than the value of ferrocene (69.8 ppm) and ruthenocene (73.2 ppm).

The large low-field shift found for the $SnCl_4$ adduct ($\Delta\delta_C$; 15.5 ppm) compared with the chemical shift value of osmocene is very similar to the value of the ruthenocene–$SnCl_4$ adduct (15.9 ppm),[2] suggesting that the effect of $SnCl_4$ on the Os atoms in osmocene is similar to that on the Ru atoms in ruthenocene. By analogy to the structure of the ruthenocene-$SnCl_4$ adduct,[14] it may be reasonable to conclude that the osmocene–$SnCl_4$ adducts can be expressed as $[Cp_2Os–SnCl_2–OsCp_2]^{2+}$ $(SnCl_5^-)_2(H_2O)_2$, based on the results of ^{119}Sn-Mössbauer, ^{13}C-CP-MAS NMR, and IR spectroscopic studies as well as elemental analysis.

Figure 4 shows the ^{1}H NMR spectra of osmocene (a),

Table 2. Comparison of the Infrared Spectra Assigned as Antisymmetric C–C Stretching Mode of Osmocene or Ruthenocene and Their Reaction Products with Lewis Acids

Compound	ν/cm^{-1}	$\Delta\nu$/cm^{-1}
Osmocene	1399.5	—
Osmocene–2$AgBF_4$	1399.5	—
Osmocene–2$HgCl_2$	1400.4, 1417.0	16.6
(Osmocene)$_2$–$Hg(BF_4)_2$	1404.3, 1417.0	12.7
Osmocene–1.5$SnCl_4(H_2O)$	1401.4, 1426.5	25.1
(OsmoceniumI)$^+I_3^-$	1400.4, 1431.3	30.9
(OsmoceniumBr)$^+Br_3^-$	1402.4, 1436.1	33.7
(OsmoceniumCl)$^+PF_6^-$	1407.2, 1441.0	33.8
(OsmoceniumBr)$^+PF_6^-$	1408.2, 1440.5	32.3
(Osmocenium$^+$)$_2(PF_6^-)_2$	1407.2, 1429.4	22.2
Ruthenocene	1405.3	—
Ruthenocene–1.5$AgBF_4$	1406.2	—
Ruthenocene–2$HgCl_2$	1405.3, 147.2, 1416.8, 1421.7	16.4
Ruthenocene–$Hg(BF_4)_2$	1407.2, 1421.7	14.5
Ruthenocene–1.5$SnCl_4$	1531.0, 1406.0	25.0
(RuthenoceniumI)$^+I_3^-$	1403.3, 1436.1	32.8
(RuthenoceniumBr)$^+Br_3^-$	1405.3, 1441.0	35.7
(RuthenoceniumCl)$^+PF_6^-$	1411.1, 1446.7	35.6
(RuthenoceniumBr)$^+PF_6^-$	1411.1, 1445.0	33.9

Table 3. ^{13}C and ^{1}H Chemical Shifts of Osmocene and Ruthenocene and Related Compounds in the Solid State and in a Solution, Respectively

Compound	^{13}C Chemical shift δ_C/ppm	^{13}C Chemical shift $\Delta\delta_C$/ppm	^{1}H Chemical shift δ_H/ppm	^{1}H Chemical shift $\Delta\delta_H$/ppm
Osmocene	67.4	—	5.52	—
Osmocene–$2AgBF_4$	67.5	0.1	5.58	0.06
Osmocene–$Pd(BF_4)_2(CH_3CN)_2$	75.4	8.0	6.59	1.07
Osmocene–$2HgCl_2$	76.1	8.7	6.42	0.90
(Osmocene)$_2$–$Hg(BF_4)_2$	74.3	6.9	6.58	1.06
Osmocene–$1.5SnCl_4(H_2O)$	82.9	15.5	6.68	1.16
(OsmoceniumI)$^+I_3^-$	88.2	20.8	6.78	1.26
(OsmoceniumBr)$^+Br_3^-$	90.3	22.9	6.70	1.18
(OsmoceniumCl)$^+PF_6^-$	90.5	23.1	6.65	1.13
(OsmoceniumBr)$^+PF_6^-$	89.2	21.8	6.69	1.17
(Osmocenium$^+$)$_2$(PF_6^-)$_2$	80.4	13.0	6.53	1.01
Ruthenocene[a)]	73.2	—	5.37	—
Ruthenocene–$1.5AgBF_4$	74.0	0.8	5.38	0.01
Ruthenocene–$2HgCl_2$[a)]	81.2	8.0	6.21	0.84
Ruthenocene–$Hg(BF_4)_2$	79.7	6.5	6.38	1.01
Ruthenocene–$1.5SnCl_4$[a)]	89.1	15.9	5.35	0.02
(RuthenoceniumI)$^+I_3^-$[a)]	93.4	20.2	6.87	1.50
(RuthenoceniumBr)$^+Br_3^-$	96.9	23.7	6.84	1.47
(RuthenoceniumCl)$^+PF_6^-$	97.1	23.9	6.79	1.42
(RuthenoceniumBr)$^+PF_6^-$	95.3	22.1	6.79	1.42

a) Chemical shift values are cited from Ref. 2.

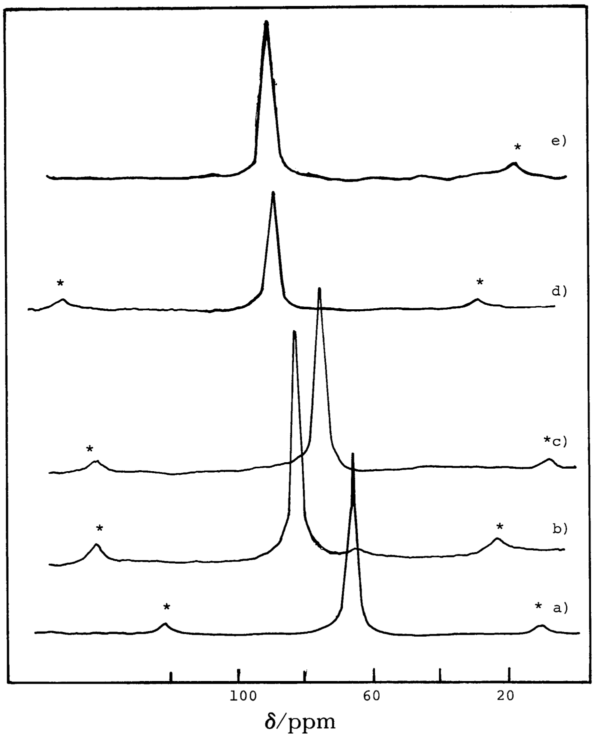

Fig. 3. ^{13}C-CP-MAS NMR spectra of the osmocene (a), osmocene–$1.5SnCl_4(H_2O)$ (b), osmocene–$2HgCl_2$ (c), (osmoceniumI)$^+I_3^-$ (d), and (osmoceniumCl)$^+PF_6^-$ (e). The sample spinning side band (SSB) is represented by * in the Figure.

its $SnCl_4$ adduct (b—e), ruthenocene (f), and its $SnCl_4$ adduct (g) all dissolved in acetonitrile. Although no peaks are observed in the ^{1}H- and ^{13}C NMR spectra of [2]ferrocenophane–SnX_4 (X; Cl, Br) adducts dissolved in acetonitrile (because [2]ferocenophane is oxidized by SnX_4 giving paramagnetic [2]ferrocenophanium cations in acetonitrile), a sharp line is observed for $SnCl_4$ adducts of ruthenocene and osmocene. A negligible low-field shift found in the ruthenocene–$SnCl_4$ adduct ($\Delta\delta_H$; 0.02 ppm) suggests a rapid dissociation of the adduct into ruthenocene and $SnCl_4$. However, a large low-field shift ($\Delta\delta_H$; 1.16 ppm) is observede for the osmocene–$SnCl_4$ adduct, although a new peak assigned to osmocene grows with a several hours in acetontrile, as shown in Fig. 4 (c—e). These facts indicate that the Os–Sn bond in the osmocene–$SnCl_4$ adduct is more stable than the Fe–Sn and Ru–Sn bonds in the [2]ferrocenophane and ruthenocene–$SnCl_4$ adducts, respectively, even in acetonitrile. The stability of the Os–Sn bond may be ascribed to the greater softness of osmium atoms in osmocene.

Osmocene $HgCl_2$ and $Hg(BF_4)_2$ adducts. Osmocene reacts with a large excess amount of $HgCl_2$ in ether, giving a pale-yellow diamagnetic stable adduct, expressed as Cp_2Os–$2HgCl_2$. As in the case of the $SnCl_4$ adduct of osmocene, splitting of the 1400 cm^{-1} region is also observed for the $HgCl_2$ adduct in the IR spectrum, although the splitting value of the $HgCl_2$ adduct ($\Delta\delta$; 16.6 cm^{-1}) is not as large as that of the $SnCl_4$ adduct ($\Delta\delta$; 25.1 cm^{-1}).

Figure 3 shows ^{13}C-CP-MAS NMR spectra of the osmocene-$2HgCl_2$ (c) adduct. A higher ^{13}C chemical shift value ($\Delta\delta_C$; 8.7 ppm) is found for the $HgCl_2$ adduct and the $\Delta\delta_C$ value well corresponds to the values of the $HgCl_2$ adducts with ferrocene ($\Delta\delta_C$; 8.9 ppm)[6)] and ruthenocene ($\Delta\delta_C$; 8.0 ppm)[2)] which

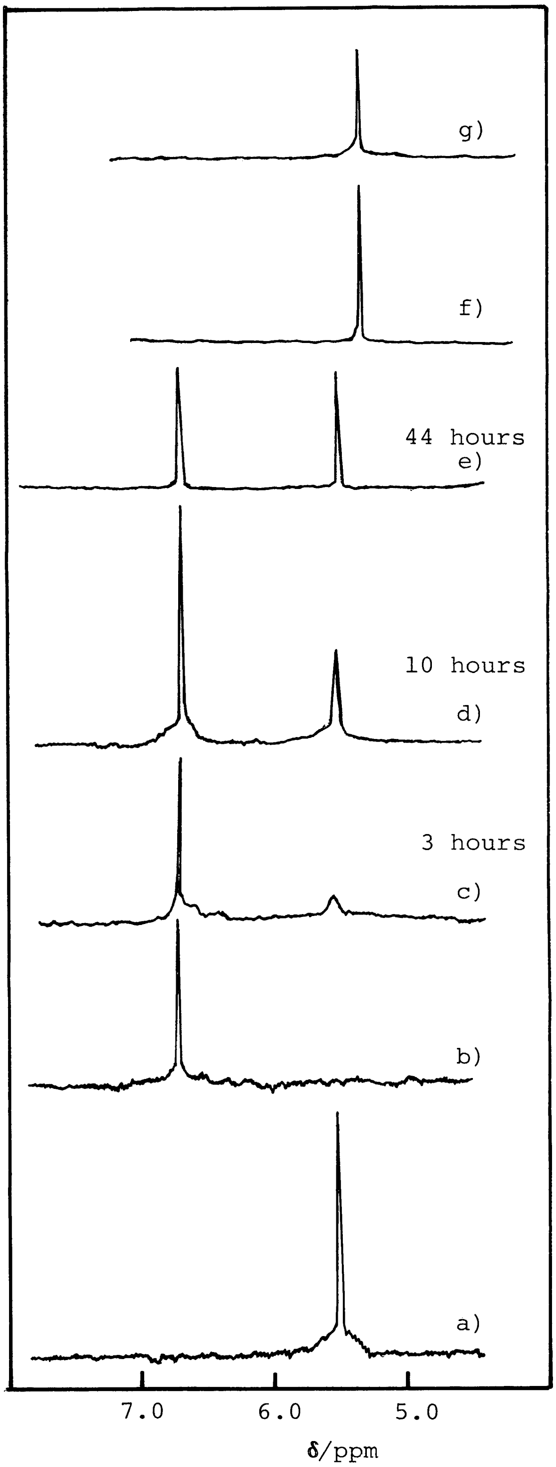

Fig. 4. ^{1}H NMR spectra of osmocene (a), osmocene–1.5SnCl$_4$(H$_2$O) adduct (b—e), ruthenocene (f), and ruthenocene–1.5SnCl$_4$ (g) adduct at the indicated time after the preparation of acetonitrile solution.

have an Fe–Hg and a Ru–Hg bond, respectively.

Similar large low-field shifts ($\Delta\delta_H$; 0.90 ppm) are also observed for the ^{1}H NMR spectra of the osmocene–HgCl$_2$ adduct in CD$_3$CN, as shown in Table 3. These facts clearly suggest the presence of an Os–Hg bond in a solid, or even in acetonitrile. The smaller values of $\Delta\delta_C$ and $\Delta\delta_H$ than the values of the SnCl$_4$ adduct (15.5 and 1.16 ppm, respectively), suggest that osmium atoms interact more weekly with HgCl$_2$ than with SnCl$_4$. Actually, the osmocene–HgCl$_2$ adduct is not as stable as the SnCl$_4$ adduct. After standing in air for a few days after preparation of the osmocene–HgCl$_2$ adduct, the pale-yellow color of the adduct gradually changes into yellow-green. The Cp-ring proton signals of the yellow-green HgCl$_2$ adduct appear at δ=6.42 and 6.80 in acetonitrile; former value well corresponds to the pale-yellow HgCl$_2$ adduct, but the latter to an osmocenium salt.

Osmocene and ruthenocene react with Hg(CN)$_2$ and HBF$_4$ in ethanol, giving yellow-colored adducts; determined as [osmocene]$_2$Hg(BF$_4$)$_2$ and [ruthenocene]$_2$Hg(BF$_4$)$_2$,[11] respectively. Splittings in the 1400 cm^{-1} region are observed for both the mercury(II) adducts of osmocene ($\Delta\nu$; 12.7 cm^{-1}) and ruthenocene ($\Delta\nu$; 14.5 cm^{-1}), as shown in Table 2. The large $\Delta\delta_C$ value of the [osmocene]$_2$Hg(BF$_4$)$_2$ adducts is found to be 6.9 ppm, although the $\Delta\nu$ and $\Delta\delta_C$ values of [osmocene]$_2$Hg(BF$_4$)$_2$ adduct are a little smaller than the values of the HgCl$_2$ adduct (16.6 cm^{-1} and 8.7 ppm, respectively). Similar results are found for the ruthenocen–2HgCl$_2$ (16.4 cm^{-1} and 8.0 ppm respectively) and [ruthenocene]$_2$Hg(BF$_4$)$_2$ adducts (14.5 cm^{-1} and 6.5 ppm, respectively). The structure of the latter adduct is determined as [Cp$_2$Ru–Hg–RuCp$_2$]$^{2+}$(BF$_4^-$)$_2$ by Hendrickson et al., on the basis of the IR and Raman-spectroscopic studies.[11] Considering of the smaller $\Delta\nu$ and $\Delta\delta_C$ values of the [Cp$_2$Os]$_2$Hg(BF$_4$)$_2$ adduct than those values of the osmocene–2HgCl$_2$, it may be reasonable to conclude that the [osmocene]$_2$Hg(BF$_4$)$_2$ adduct is expressed as [Cp$_2$Os–Hg–OsCp$_2$]$^{2+}$(BF$_4^-$)$_2$ in a solid.

Osmocene Pd(BF$_4$)$_2$ and AgBF$_4$ Adducts. Osmocene reacts with Pd(BF$_4$)$_2$(CH$_3$CN)$_4$ in acetonitrile, giving pale yellow diamagnetic precipitates expressed as osmocene–Pd(BF$_4$)$_2$(CH$_3$CN)$_2$, whereas ruthenocene does not react with Pd(BF$_4$)$_2$(CH$_3$CN)$_4$. As in the case of the SnCl$_4$ and HgCl$_2$ adducts, higher ^{13}C ($\Delta\delta_C$; 8.0 ppm) and ^{1}H chemical shift values ($\Delta\delta_H$; 1.07 ppm) are observed. The $\Delta\delta_C$ values of Pd(BF$_4$)$_2$ adduct is, however, a little smaller than the value of the HgCl$_2$ adduct ($\Delta\delta_C$; 8.7 ppm), suggesting the Os–Pd bond is not as stable as the Os–Hg bond. Actually, the color of the Pd(BF$_4$)$_2$ adduct changes into brown after being allowed to stand in air for a several hours. The Cp-ring proton signals of the pale-yellow Pb(BF$_4$)$_2$ adduct appear at δ=6.59 and 5.50 in acetonitrile for several minutes after the preparation of the solution, suggesting a rapid dissociation of the adduct in acetonitrile, because the latter value well corresponds to that of osmocene itself (5.52 ppm).

Osmocene and ruthenocene react with AgBF$_4$ in ether, giving diamagnetic precipitates determined as osmocene–2$AgBF_4$ and ruthenocene–1.5$AgBF_4$, respectively, based on elemental analysis. Although the colors of the $HgCl_2$ and $SnCl_4$ adducts of osmocene and ruthenocene are yellow or pale-yellow, respectively, the color of the $AgBF_4$ adducts of osmocene and ruthenocene is white. Much smaller low-field shifts ($\Delta\delta_C$, 0.1 and $\Delta\delta_H$, 0.06 ppm) and no splitting for the 1400 cm^{-1} mode are observed in the osmocene–2$AgBF_4$ adduct in the ^{13}C-CP-MAS, ^{1}H NMR, and IR spectroscopic studies, respectively. Such smaller low-field shifts are also found for the ruthenocene–1.5$AgBF_4$ adduct ($\Delta\delta_C$, 0.8 and $\Delta\delta_H$, 0.01 ppm). Therefore, it can be concluded that reaction products with $AgBF_4$ and metallocene are neither mixtures nor adducts with a metal–metal (Os–Ag or Ru–Ag) bond, but molecular complexes with a weak interaction between the metallocene and $AgBF_4$.

Reaction Products of I_2, Br_2, HX, and FeX_3 (X; Cl and Br) with Osmocene. Studies of the cyclic voltammography of osmocene show two irreversible one-electron oxidation peaks (Eox; 0.50 and 0.85 V; as illustrated in Fig. 5-a), whereas ruthenocene gives one irreversible two-electons oxidation peak (E_{ox}; 0.72 V). The potential of the first oxidation step is similar to that of ferrocene (E_{ox}, 0.44 V), suggesting that osmocene is oxidized more easily than ruthenocene.

Osmocene is oxidized by a large excess amount of I_2 and Br_2 in CCl_4, giving diamagnetic precipitates expressed as osmocene–2I_2 and osmocene–2Br_2, respectively. The reaction products with halogen are more stable than any other products of osmocene in a solid, or even in acetonitrile, without showing any change of color. The larger splittings of the 1400 cm^{-1} band ($\Delta\nu$, 30.9 and 33.7 cm^{-1} for the I_2 and Br_2 products, respectively, as shown in Table 2 and Fig. 2-c) are observed for both products than for the osmocene–$HgCl_2$ and –$SnCl_4$ adducts.

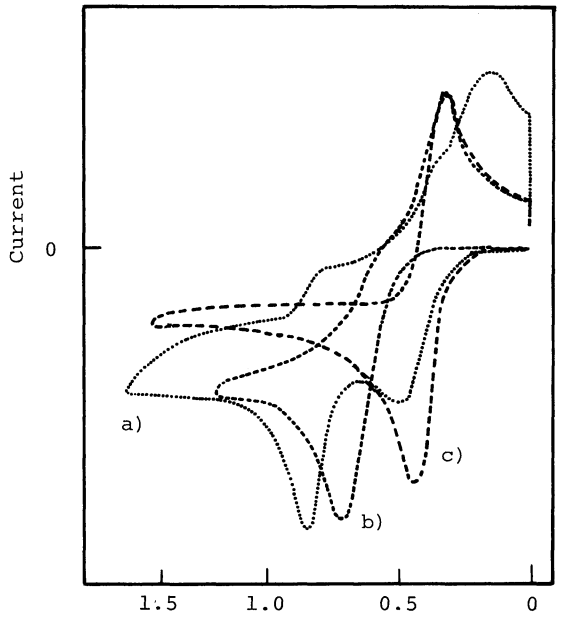

Fig. 5. Cyclic voltammograms of osmocene (a), ferrocene (c), and ruthenocene (b) in acetonitrile solution. (Sweep rate; 200 mV s^{-1}).

The ^{13}C-CP-MAS NMR parameters of the products are listed in Table 3 and a typical spectrum of the I_2 product is shown in Fig. 3-d. Much larger $\Delta\delta_C$ and $\Delta\delta_H$ values (20.8 and 1.26 ppm for the I_2 product and 22.9 and 1.18 ppm for the Br_2 product) are observed in the halogen products than the values found in the $HgCl_2$ and $SnCl_4$ adducts. This suggests that the effect of the halogen on the osmium atoms in osmocene is stronger than that of the other Lewis acids ($SnCl_4$ and $HgCl_2$). Similar large $\Delta\delta_C$ and $\Delta\delta_H$ values are also observed for the ruthenocene-halogen products (20.2 and 1.5 ppm for the I_2 product and 23.7 and 1.47 ppm for the Br_2 product, respectively),[2] which have structures expressed as $[Cp_2Ru(IV)\text{-}X]^+X_3^-$ (X; I and Br) on the basis of X-ray analysis.[17] By analogy to the ruthenocene-halogen products, the structure of the osmocene-halogen products may be expressed as $[Cp_2Os(IV)\text{-}X]^+X_3^-$(X; I and Br).

A benzene solution of osmocene reacts with a large excess amount of HX and FeX_3 (X; Cl and Br) in an aqueous solution of NH_4PF_6, giving diamagnetic brown precipitates determined as Cp_2OsXPF_6. The largest $\Delta\nu$ (33.8 cm^{-1}) and $\Delta\delta_C$ values (23.1 ppm) in all the products of osmocene and a large $\Delta\delta_H$ (1.13 ppm) value are observed for the $Cp_2OsClPF_6$ product. Similar large $\Delta\nu$, $\Delta\delta_C$, and $\Delta\delta_H$ values (32.3 cm^{-1}, 21.8 ppm, and 1.17 ppm, respectively) are also observed for the $Cp_2OsBrPF_6$ products. These values correspond to the values of $[Cp_2Os(IV)\text{-}Br]^+Br_3^-$ salt (33.7 cm^{-1}, 22.9 ppm, and 1.18 ppm, respectively). This fact clearly suggests the presence of a bond between the Os(IV) and halogen atoms (Cl, Br), both in the Cp_2OsXPF_6 products; it can be concluded that the reaction products are expressed as $[Cp_2Os(IV)\text{-}X^-]^+PF_6^-$ (X; Cl and Br). The increasing values of $\Delta\nu$ and $\Delta\delta_C$ in the products of osmocene with halogen suggest that the interaction between the osmocene and the halogen increases in the order $I^- < Br^- < Cl^-$.

Raction Products of $Ce(NO_3)_2(NH_4)_6$ with Osmocene. Though osmocene is oxidized $Ce(NO_3)_6(NH_4)_2$ in an aqueous solution of NH_4PF_6, giving a green osmocenium salt analyzed as Cp_2OsPF_6, ruthenocene is not oxidized by the same treatment, since ruthenocene is oxidized less easily than osmocene. Droege et al. determined the crystal structure of the PF_6^- salt of osmocenium using X-ray analysis, concluding that two osmocenium cations are joined by an antiferromagnetic Os(III)–Os(III) bond in the salt; $[Cp_2Os\text{-}OsCp_2]^{2+}(PF_6^-)_2$.[13] A splitting in the 1400 cm^{-1} region is found to be 22.2 cm^{-1}. This value is much smaller than that of the halogen products of osmocene (30—34 cm^{-1}) and a little smaller than the

$SnCl_4$ adduct (25.1 cm^{-1}). In the ^{13}C-CP-MAS NMR and ^{1}H NMR spectroscopy of the salt, large low-field shifts ($\Delta\delta_C$; 13.0 and $\Delta\delta_H$; 1.01 ppm) are observed; the values of low-field shift of the dimer cation, however, are much smaller than the values of the I_2 and Br_2 products, suggesting that the Os(III)–Os(III) bond is not as stable as the Os(IV)–I^- and Os(IV)–Br^- bonds. Actually, the PF_6^- salt is not stable in acetonitrile; i.e., the green color of the PF_6^- salt in acetonitrile changes to brown upon standing at room temperature for a several minutes, whereas the I_2 and Br_2 products are stable and show no change in color and NMR spectra. Droege et al. have reported that the dimer cations react with acetonitrile, giving pale-yellow and red-brown precipitates which are determined as $[Cp_2(C_5H_4)_2Os_2]^{2+}(PF_6^-)_2$ and $[Cp_2OsNCCH_3]^{2+}(PF_6^-)_2$, respectively, based on the results of X-ray analysis and elemental analysis data.[13)]

Conclusion

Figure 6 shows the correlation between the $\Delta\delta_C$ and $\Delta\nu$ values of osmocene- and ruthenocene–Lewis acid products. A remarkable dependence of the $\Delta\delta_C$ value on the $\Delta\nu$ value is observed for both the products. The large $\Delta\delta_C$ and $\Delta\nu$ values found in the osmocene–Lewis acids products indicate that the enhanced interaction between the metal in metallocene (Os, Ru) and the Lewis acids ($AgBF_4 \ll Hg(BF_4)_2 < HgCl_2 < SnCl_4 < I_2 < Br_2$) should result in a decrease in the electron density around the Cp-ring carbon and an increase in the distortion of the molecular structure of metallocene unit.

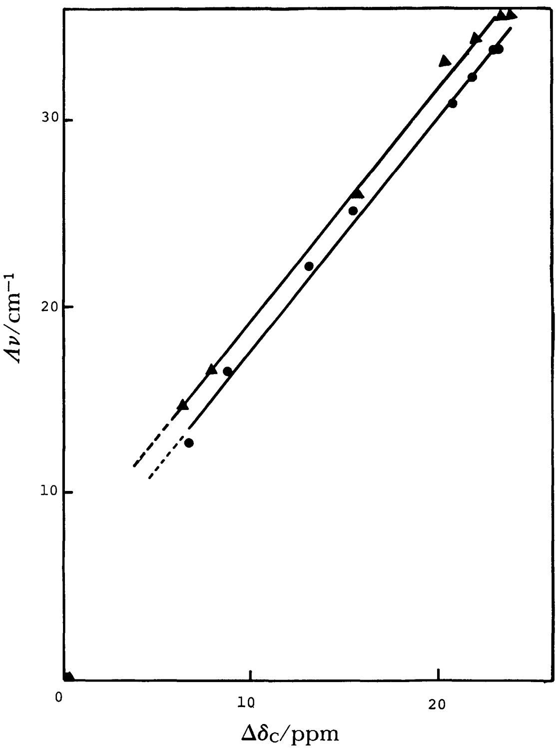

Fig. 6. The correlation between the $\Delta\nu$ and $\Delta\delta_C$ values for osmocene- (●) and ruthenocene–Lewis acid products (▲).

The $\Delta\delta_C$ values of osmocene–Lewis acids products agree with the values of corresponding ruthenocene–Lewis acids products and the $\Delta\nu$ values of osmocene–Lewis acid products are a little smaller (2—3 cm^{-1}) than the values of the corresponding ruthenocene–Lewis acid products. The results show that the two five-membered rings of the osmocene-Lewis acid products are less titled than those of the ruthenocene–Lewis acid products, giving more stable osmocene products with Lewis acids compared with ruthenocene products. Further studies must be conducted in order to provide direct evidence for proving the conclusion, by using X-ray analysis of osmocene–Lewis acid products.

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