Synthesis of Ruthenium Pentamethyl[60]fullerene Complexes Bearing Monodentate Diphenylphosphino-methane, -ferrocene, and -butane Ligands[†]

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Incorporation of fullerene-based ligands and transition metal atoms has attracted the interest of organic, inorganic, and organometallic chemists,[1] because of the possibility that dπ-conjugative synergy may lead to the creation of new properties that are not the same as those of individual systems.[2] The family of metal-penta(organo)[60]fullerene complexes and relatives[1c] has attracted much attention because of its unique electrochemical, photoelectrochemical,[3] and steric[4] properties. These metal-organic π-electron hybrids have been utilized for ultra-fast charge separation systems,[5] photocurrent conversion cells,[6] liquid crystalline materials,[7] molecular device motifs,[8] and catalysts for asymmetric C-C bond formation reactions.[9]
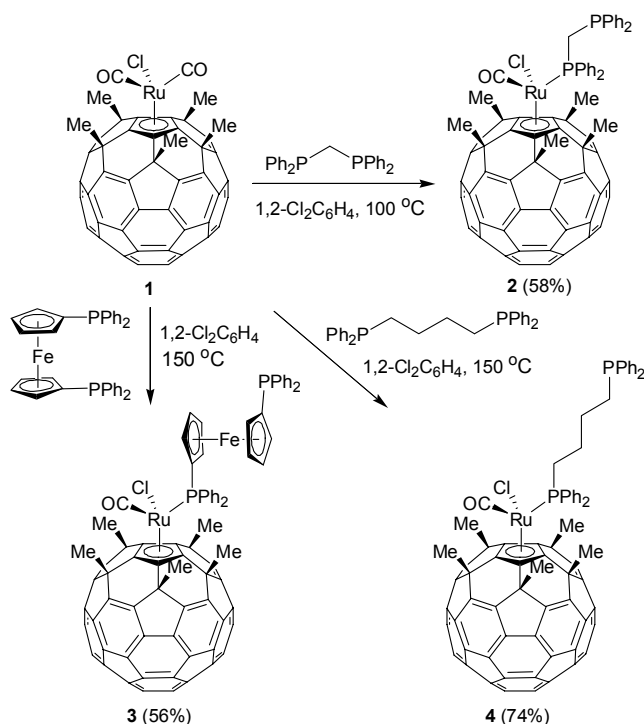
Ruthenium-pentamethyl[60]fullerene complexes, such as Ru(C$_{60}$Me$_5$)Cl(CO)$_2$ (**1**),[10] are useful metal-fullerene complexes. Carbon monoxide and chloride ligands can be replaced with various other ligands to obtain phosphine, isocyanide, alkyl, alkynyl,[11] π-allyl,[12] and cyclopentadienyl[13] complexes. From the organometallic chemistry point of view, it is found that bidentate bis(diphenylphosphino)ethane (abbr. dppe) complexes[9] of ruthenium-pentamethyl[60]fullerene are the most attractive complexes; these complexes have been derivatized into chiral, cationic, and carbene (i.e., vinylidene and allenylidene complexes) complexes (Figure 1).[14]

During course of the synthetic studies to obtain such diphosphine complexes, we obtained monodentate diphosphine complexes, which attract another interest owing to the existence of a coordination-free phosphine site, potentially available for further complexation to give multi-metal complex systems. Herein we report syntheses of monodentate bis(diphenylphosphino)methane (abbr. dppm), bis(diphenylphosphino)ferrocene (abbr. dppf), and bis(diphenylphosphino)butane (abbr. dppb) complexes of the ruthenium-pentamethyl[60]fullerene. The results of this study have provided us insight into how the steric property of the penta(organo)[60]fullerene ligand affects on their complexation.

We first tried to synthesize the dppm complexes, because dppm is a compact diphosphine ligand, which is expected to yield a bidentate complex. However, contrary to our expecta-
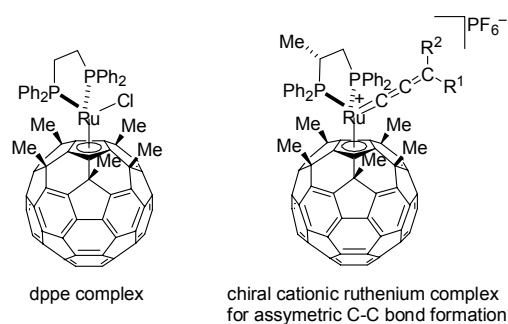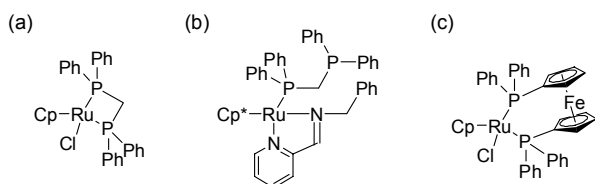
Figure 1. Bidentate phosphine complexes of the ruthenium-pentamethyl[60]fullerene.

Scheme 1. Synthesis of monodentate phosphine complexes of the ruthenium-pentamethyl[60]fullerene.

Figure 2. Examples of reported cyclopentadienyl ruthenium dppm and dppf complexes.

tions, the treatment of ruthenium complex **1** with dppm in 1,2-dichlorobenzene at 100 °C produced a monodentate complex, Ru(η^5-C$_{60}$Me$_5$)Cl(dppm)(CO) (**2**) (Scheme 1). This complex **2** is air-stable, and it can be purified by silica gel column chromatography using a toluene/hexane mixed eluent. Coordination of the diphosphine ligand in a monodentate fashion was confirmed by ^{31}P NMR and IR measurements. In the ^{31}P NMR spectrum of **2** exhibited signals due to the phosphorus atom attaching to the metal center at lower magnetic field (δ 30.52) and free phosphine at upper magnetic field (δ −28.08). These two signals were coupled each other with a coupling constant of $^2J_{\text{P-P}}$ = 35 Hz. The IR spectrum of **2** showed a strong absorption peak attributed to the stretching vibration of the remaining carbonyl ligand at 1940 cm^{-1}. The reason for the monodentate coordination in **2** is the rigidity of the dppm ligand. The inflexible nature of the ligand backbone causes incompatibility between the sterically congested bidentate coordination of the dppm ligand and the large pentamethyl[60]fullerene ligand. Cyclopendadienyl ruthenium monodentate dppm complex has been seldom reported in the literatures.[15] Usually the dppm ligand coordinates to the cyclopentadienyl ruthenium center in a bidentate fashion (Figure 2a).[16] An exception is a pentamethyl-cyclopentadienyl iminopyridine complex with a monodentate dppm ligand (Figure 2b).[17] Complex **2** thus represents a rare example of the cyclopentadienyl monodentate dppm complex.

Next, we investigated the synthesis of the dppf complex, since the dppf ligand is regarded as a rigid diphosphine ligand that bears an inflexible backbone. As expected, we obtained a monodentate dppf complex, Ru(η^5-C$_{60}$Me$_5$)Cl(dppf)(CO) (**3**), as air-stable orange powder *via* the similar reaction with dppf (Scheme 1). Room-temperature ^{1}H NMR measurement gave a complex spectrum due to fluctionality of the dppf ligand. At −60 °C, the ^{1}H NMR spectrum became clear because of hindered rotation of the ferrocene group giving a dissymmetric pattern for the signals due to the C$_5$H$_4$ moieties. In the case of the ordinary cyclopentadienyl ruthenium chloro complex, the dppf ligand has been known to coordinate to the ruthenium atom in a bidentate fashion (Figure 2c).[18] Compound **3** is a unique class of the monodentate dppf complex.

We finally tested the dppb ligand, whose backbone is flexible. The reaction of **1** with dppb under the same condition produced a monodentate dppb complex, Ru(η^5-C$_{60}$Me$_5$)Cl(dppb)(CO) (**4**), in 74% yield. We were unable to detect a corresponding bidentate complex at all for any reaction condition.[19] Even though the dppb ligand is a flexible ligand because of the aliphatic butylene moiety, bidentate coordination of this ligand requires large bite angle and bulky coordination space. These requirements are not suitable for the coordination in a bidentate

fashion to the metal center bearing sterically bulky pentamethyl-[60]fullerene ligand. We ascribe better yield of **4** than other complexes to sterically less bulkiness of the monodentate dppb ligand in which two phenyl groups and one butyl group attach to the phosphorus atom coordinating to the metal center.

In summary, we synthesized three monodentate diphosphine (dppm, dppf, and dppb) complexes of the ruthenium penta-methyl[60]fullerene. Whereas the dppe ligand has coordinated to this complex in a bidentate fashion,[9] we think that the ruthenium pentamethyl[60]fullerene complex prefers monodentate coordination as shown in this paper. This fact indicates that the thermodynamic barrier for coordination of the second phosphine part is high because of the sterically demanding pentamethyl[60]fullerene ligand. Coordination-free phosphine parts in these complexes **2-4** are expected to be utilized into formation of dimetallic complexes. This project is currently underway.

Experimental Section

General. Syntheses were carried out under nitrogen or argon atmosphere with standard Schlenk techniques. The water contents of the solvents were determined, using Karl-Fischer moisture titration (MK-210, Kyoto Electronics Co.), to be less than 30 ppm. All the reactions were monitored by HPLC (column, Cosmosil-Buckyprep, 4.6 × 250 mm, Nacalai Tesque; flow rate, 2.0 mL/min; eluent, toluene/isopropanol; detector, Shimadzu SPD-M10Avp). Preparative HPLC was performed on a Buckyprep column (20 × 250 mm) using toluene/isopropanol as the eluent (detected at 350 nm with an UV spectrophotometric detector, Shimadzu SPD-6A). The isolated yields were calculated on the basis of the starting fullerene compounds. The NMR spectra were measured with JEOL ECA-500 (500 MHz) instruments. Spectra are reported in parts per million from the internal tetramethylsilane (δ 0.00 ppm) or residual protons of the deuterated solvent for ^{1}H NMR, and from solvent carbon (e.g. δ 77.00 ppm for chloroform) for ^{13}C NMR. IR spectra were recorded on Applied Systems Inc. React-IR 1000. The starting compound, Ru(η^5-C$_{60}$Me$_5$)Cl(CO)$_2$ (**1**), was synthesized according to the procedure described in our previous report.[10] Phosphine compounds were purchased and used as received.

Synthesis of Ru(η^5-C$_{60}$Me$_5$)Cl(Ph$_2$PCH$_2$PPh$_2$)(CO) (2). Bis-(diphenylphosphino)methane (80 mg, 0.21 mmol) was added to the solution of **1** (30 mg, 0.030 mmol) in 1,2-dichlorobenzene (3.0 mL). The mixture was heated at 100 °C for 20 h. Purification with silica gel column chromatography using a toluene/hexane mixed eluent (1:1) afforded **2** (23 mg, 0.017 mmol, 58%). ^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ 2.10 (s, 15H, C$_{60}$Me$_5$), 3.34 (dd, $J_{\text{P-H}}$ = 10.5 Hz, $J_{\text{H-H}}$ = 5 Hz, 1H, PCH$_2$P), 4.18 (dd, $J_{\text{P-H}}$ = 15.5 Hz, $J_{\text{H-H}}$ = 7 Hz 1H, PCH$_2$P), 6.97-7.42 (m, 16H, PPh$_2$), 8.00-8.04 (m, 2H, PPh$_2$), 8.49-8.52 (m, 2H, PPh$_2$). ^{13}C NMR (125 MHz, CDCl$_3$, 298 K) δ 27.89 (s, 5C, C$_{60}$Me$_5$), 29.84 (t, $J_{\text{C-P}}$ = 32.5 Hz, 1C, PCH$_2$P), 51.19 (s, 5C, C$_{60}$Me$_5$), 108.77 (d, J = 2.4 Hz, 5C, C$_{60}$), 127.70-135.15 (m, 24C, PPh$_2$), 143.26 (s, 10C, C$_{60}$), 143.47 (s, 10C, C$_{60}$), 146.78 (s, 5C, C$_{60}$), 147.94 (s, 10C, C$_{60}$), 148.12 (s, 5C, C$_{60}$), 152.26 (d, $J_{\text{C-P}}$ = 25 Hz, 10C, C$_{60}$), 205.25 (d, $J_{\text{C-P}}$ = 23.8 Hz, 1C, CO). ^{31}P NMR (200 MHz, CDCl$_3$, 298 K) δ −28.08 (d, $J_{\text{P-P}}$ = 35 Hz,

1P, CH_2PPh_2), 30.52 (d, J_{P-P} = 35 Hz, 1P, $RuPPh_2CH_2$). IR (diamond probe): v (CO)/cm^{-1} 1940 (s).

Synthesis of Ru(η^5-C$_{60}$Me$_5$)Cl(Ph$_2$PC$_5$H$_4$FeC$_5$H$_4$PPh$_2$)(CO) (3). Bis(diphenylphosphino)ferrocene (116 mg, 0.21 mmol) was added to the solution of **1** (30 mg, 0.030 mmol) in 1,2-dichlorobenzene (3.0 mL). The mixture was heated at 150 °C for 24 h. Purification with silica gel column chromatography using a toluene/hexane mixed eluent (1:1) afforded **3** (22 mg, 0.014 mmol, 47%). ^{1}H NMR (400 MHz, CDCl$_3$, 233 K) δ 2.15 (s, 15H, C$_{60}$Me$_5$), 3.33 (s, 1H, C$_5H_4$PPh$_2$Ru), 3.56 (s, 1H, C$_5H_4$PPh$_2$Ru), 3.94 (s, 1H, C$_5H_4$PPh$_2$), 4.06 (s, 1H, C$_5H_4$PPh$_2$), 4.31 (s, 1H, C$_5H_4$PPh$_2$Ru), 4.34 (s, 1H, C$_5H_4$PPh$_2$), 4.36 (s, 1H, C$_5H_4$PPh$_2$), 4.62 (s, 1H, C$_5H_4$PPh$_2$Ru), 7.21-7.62 (m, 16H, PPh$_2$), 7.91 (m, 2H, PPh$_2$), 8.69 (m, 2H, PPh$_2$). ^{31}P NMR (160 MHz, CDCl$_3$, 298 K) δ −18.11 (s, 1P, C$_5H_4$PPh$_2$), 30.98 (br s, 1P, PPh$_2$Ru). IR (diamond probe): v (CO)/cm^{-1} 1958 (s).

Synthesis of Ru(η^5-C$_{60}$Me$_5$)Cl(Ph$_2$PCH$_2$CH$_2$CH$_2$CH$_2$PPh$_2$) (CO) (4). Bis(diphenylphosphino)butane (102 mg, 0.24 mmol) was added to the solution of **1** (30 mg, 0.030 mmol) in 1,2-dichlorobenzene (6.0 mL). The mixture was heated at 150 °C for 15 h. Purification with silica gel column chromatography using an eluent (toluene:hexane = 1:1) afforded **4** (31 mg, 0.022 mmol, 74%). ^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ 1.31 (m, 1H, CH_2CH$_2$PPh$_2$), 1.47 (m, 3H, CH_2CH$_2$CH$_2$PPh$_2$), 1.95 (m, 2H, CH_2PPh$_2$), 2.17 (s, 15H, C$_{60}$Me$_5$), 2.85 (m, 1H, RuPPh$_2$CH_2), 2.99 (m, 1H, RuPPh$_2$CH_2), 7.17 (m, 2H, PPh_2), 7.32 (m, 8H, PPh_2), 7.55 (m, 6H, PPh_2), 8.09 (t, J = 9.15 Hz, 2H, PPh_2), 8.34 (t, J = 8.87 Hz, 2H, PPh_2). ^{13}C NMR (125 MHz, CDCl$_3$, 298 K) δ 25.92 (1C, dppb), 27.50 (1C, dppb), 28.08 (5C, C$_{60}$Me$_5$), 29.71 (1C, dppb), 30.98 (1C, dppb), 51.50 (5C, C$_{60}$Me$_5$), 109.07 (5C, C$_{60}$), 125.27-138.59 (PPh_2), 143.52 (10C, C$_{60}$), 143.60 (10C, C$_{60}$), 147.04 (5C, C$_{60}$), 148.17 (10C, C$_{60}$), 148.33 (5C, C$_{60}$), 152.47 (5C, C$_{60}$), 152.65 (5C, C$_{60}$), 205.60 (d, $^2J_{P-C}$ = 23.84 Hz). ^{31}P{^{1}H} NMR (125 MHz, CDCl$_3$, 298 K) δ −16.04 (s, 1P, free); 29.20 (s, 1P, coordinated).

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19. Diphenylphosphinopropane (dppp) was examined for this reaction with **1**, but the bidentate complex was not obtained (data not shown).