Synthesis of Novel Zerovalent Ruthenium η^6-Arene Complexes via Direct Displacement of a 1,3,5-Cyclooctatriene Ligand by Arenes

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Novel zerovalent arene complexes bearing two dimethyl fumarate ligands, Ru(η^6-arene)-(dimethyl fumarate)$_2$ (arene = benzene (**2a**), toluene (**2b**), *p*-xylene (**2c**), mesitylene (**2d**), hexamethylbenzene (**2e**), *tert*-butylbenzene (**2f**), anisole (**2g**), *N*,*N*-dimethylaniline (**2h**), biphenyl (**2i**), methyl benzoate (**2j**), naphthalene (**2k**)), were synthesized via the direct ligand exchange reaction of Ru(η^6-cot)(dimethyl fumarate)$_2$ (**1**; cot = 1,3,5-cyclooctatriene) with arenes. The detailed structures of **2g**,**h** were determined by X-ray crystallography, which revealed that the coordination geometry can be represented by a highly distorted trigonal bipyramid.

Introduction

Many ruthenium η^6-arene complexes have been synthesized and investigated so far, since these complexes are of great interest in catalysis.[1,2] Most of them are divalent complexes, and there are comparatively few examples of *zerovalent* arene complexes. There are three well-known methods for the practical preparation of zerovalent ruthenium η^6-arene complexes. One is the cyclotrimerization of alkynes on a metal center.[3−5] This procedure can use various alkynes, although a mixture of regioisomers is formed with unsymmetrical alkynes.[4,5] The second method is the reduction of divalent ruthenium arene complexes.[6−29] Divalent arene complexes are reduced by appropriate reagents such as alkali metal,[6−9] sodium naphthalenide,[10−12] sodium borohydride,[13−15] carbonate/alcohol,[16−18] Grignard reagent,[19] zinc,[20] etc., which efficiently generates zerovalent arene complexes. However, this method has been established only for a limited number of divalent ruthenium arene complexes. The third method is the ligand exchange reaction of zerovalent ruthenium complexes with arenes. Pertici and co-workers found that Ru(η^4-cod)(η^6-arene) complexes could be obtained by reacting Ru(η^4-cod)(η^6-cot) (cod = 1,5-cyclooctadiene, cot = 1,3,5-cyclooctatriene) with arenes under a hydrogen atmosphere.[30] They also found that the same complexes could be obtained via

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the exchange of a naphthalene moiety of Ru(η^4-cod)(η^6-naphthalene) with arenes in the presence of acetonitrile.[31] In these reactions, the additives are essential, and there has been no previous report of a simple and direct ligand exchange reaction of zerovalent ruthenium complexes with arenes.

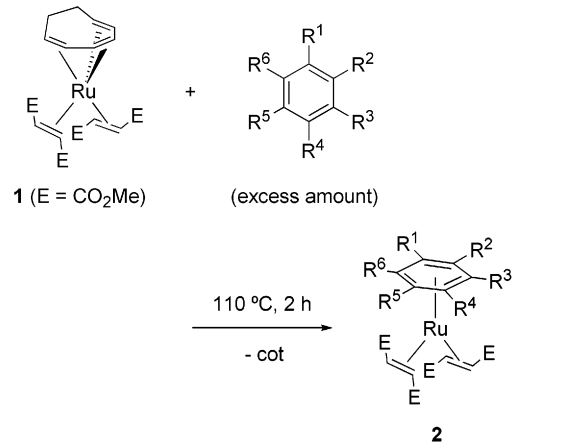
Recently, we reported the novel zerovalent ruthenium complex Ru(η^6-cot)(dmfm)$_2$ (**1**; dmfm = dimethyl fumarate). Complex **1** shows very high catalytic activity in a unique dimerization of 2,5-norbornadiene to afford a novel half-cage compound.[32] During our investigation of the reactivity of complex **1**,[33−35] we found that reactions of **1** with arenes gave novel *zerovalent* arene complexes via the direct displacement of cyclooctatriene with arenes. We report here the synthesis and structures of these complexes bearing two olefinic π-acceptor ligands; i.e., dimethyl fumarate.

Results and Discussion

Complex **1** reacted with various aromatic compounds to give a series of novel zerovalent ruthenium η^6-arene complexes, Ru(η^6-arene)(dmfm)$_2$ (**2**), in good yields by ligand exchange between the tridentate ligands 1,3,5-cyclooctatriene and arene (Table 1). Arenes were used as solvents in all the reactions except in the case of complex **2e**. Benzene (entry 1), alkyl-substituted arenes (entries 2−6), and arenes with an electron-donating or electron-withdrawing group such as anisole (entry 7), *N*,*N*-dimethylaniline (entry 8), and biphenyl (entry 9) were efficient. In the case of biphenyl, only a mononuclear Ru η^6-biphenyl complex was obtained and no binuclear complex was formed. The reaction with methyl benzoate gave the desired complex **2j** in low yield (entry 10). The use of naphthalene also gave a naphthalene complex in an η^6 fashion (entry 11).

The structures of **2a**−**k** were deduced on the basis of ^{1}H and ^{13}C NMR spectroscopic analyses (Tables 2 and 3). The signals for the aromatic protons of the coordinated arenes in **2a**−**k** appear at 4.6−6.8 ppm in the ^{1}H NMR spectra, which are shifted to a higher magnetic field by around 1−2 ppm compared to those of free arenes. These values are similar to those of reported zerovalent Ru(η^6-arene) complexes.[3−31] One of the signals for the olefinic protons of dimethyl fumarate in **2a**−**k** consistently appears at around 2.0 ppm as a doublet, and another doublet signal is observed at 3.0−4.5 ppm. This chemical shift value strongly depends on the substituents on the coordinated aromatic ring. In particular, as far as **2a**−**e** are concerned, the olefinic proton signal shifts to higher field, i.e., δ 4.27 (**2a**), 4.07 (**2b**), 3.85 (**2c**), 3.71 (**2d**), and 2.98 (**2e**), respectively, as the number of the methyl substituents on the aromatic ring increases. This higher shift may be attributable to shielding by the methyl groups.

Table 1. Reactions of 1 with Arenes



entry	arene	compd	yield (%)[a]
1[b]	benzene	**2a**	66
2	toluene	**2b**	64
3	*p*-xylene	**2c**	67
4	mesitylene	**2d**	40
5[c]	hexamethylbenzene	**2e**	31
6	*tert*-butylbenzene	**2f**	61
7	anisole	**2g**	59
8	*N*,*N*-dimethylaniline	**2h**	77
9	biphenyl	**2i**	61
10	methyl benzoate	**2j**	13
11	naphthalene	**2k**	60

[a] Isolated yield. [b] The reaction was carried out in an autoclave. [c] Hexamethylbenzene (1.2 equiv) and diglyme (as a solvent) were used.

As for the ^{13}C NMR signals for aromatic carbons in **2b**,**f**−**j** (monosubstituted arene complexes), six nonequivalent peaks appear within the range of 70−142 ppm. This suggests that no symmetry plane exists in these complexes, and thus, the two dimethyl fumarate ligands coordinate to the ruthenium center through the same enantiofaces, as in complex **1**.[32] The two signals for the olefinic carbons of dimethyl fumarates in **2a**−**k** are shifted to a higher field (40−44 and 47−50 ppm), and both of the chemical shift values are almost constant, in contrast to the signals of the olefinic protons in the ^{1}H NMR spectra described above.

The structures of **2g**,**h** were confirmed by X-ray crystallography, and their ORTEP drawings are shown in Figures 1 and 2, respectively. The crystal data and experimental details for **2g**,**h** are summarized in Table 4. The coordination geometry of these complexes can be represented by a highly distorted trigonal bipyramid. In complex **2g**, one of the dimethyl fumarate ligands (C1−C2) and an aromatic olefin moiety (C17−C18) occupy the axial positions, while the other dimethyl fumarate (C7−C8) and two residual aromatic olefin moieties (C13−C14, C15−C16) are located at the three equatorial positions. As mentioned above, two dimethyl fumarates coordinate to ruthenium C_2 symmetrically to avoid steric hindrance. The bond lengths between ruthenium and the four olefinic carbons of dimethyl fumarates in **2g** (Ru−C1, −C2, −C7, and −C8) are in the range 2.138(4)−2.162(3) Å and are thus slightly shorter than those of the corresponding bonds in **1** (2.155(5)−2.204(5) Å).[32] The C−C double-bond lengths of the

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Table 2. ^{1}H NMR Data of 2a−k (δ, ppm)[a]

	dimethyl fumarate		aromatic ligand	
complex	=CH	Me	aromatic	others
2a[b]	4.27 (d, 9.9, 2H), 2.02 (d, 9.9, 2H)	3.72 (s, 6H), 3.60 (s, 6H)	5.72 (s, 6H)	
2b	4.07 (d, 9.8, 2H), 2.04 (d, 9.8, 2H)	3.72 (s, 6H), 3.60 (s, 6H)	6.16 (m, 1H), 5.40−5.37 (m, 3H), 5.17 (d, 5.9, 1H)	2.41 (s, 3H)
2c[b]	3.85 (d, 9.7, 2H), 2.03 (d, 9.7, 2H)	3.71 (s, 6H), 3.60 (s, 6H)	5.24 (d, 5.9, 2H), 5.14 (d, 5.9, 2H)	2.42 (s, 6H)
2d	3.71 (d, 9.8, 2H), 2.04 (d, 9.8, 2H)	3.70 (s, 6H), 3.58 (s, 6H)	5.24 (s, 3H)	2.17 (s, 9H)
2e	2.98 (d, 9.8, 2H), 2.07 (d, 9.8, 2H)	3.66 (s, 6H), 3.56 (s, 6H)		2.00 (s, 18H)
2f	4.34 (d, 9.8, 2H), 1.99 (d, 9.8, 2H)	3.71 (s, 6H), 3.59 (s, 6H)	6.58 (vt, 5.7, 1H), 5.39 (d, 6.4, 1H), 5.27 (d, 6.4, 1H), 5.21 (vt, 6.2, 1H), 5.16 (vt, 6.0, 1H)	1.45 (s, 9H)
2g	3.98 (d, 9.7, 2H), 2.08 (d, 9.7, 2H)	3.97 (s, 6H), 3.75 (s, 6H)	6.10 (t, 5.8, 1H), 5.65 (t, 5.8, 1H), 5.34 (dd, 6.4, 2.0, 1H), 5.06 (dd, 6.4, 2.0, 1H), 4.94 (t, 5.8, 1H)	3.97 (s, 3H)
2h	3.96 (d, 9.8, 2H), 2.03 (d, 9.8, 2H)	3.70 (s, 6H), 3.58 (s, 6H)	5.99 (t, 5.8, 1H), 5.74 (ddd, 6.6, 5.4, 1.2, 1H), 5.07 (dd, 6.6, 2.2, 1H), 4.71 (dd, 6.6, 2.2, 1H), 4.62 (ddd, 6.6, 5.4, 1.2, 1H)	3.18 (s, 6H)
2i	4.21 (d, 10.3, 2H), 2.06 (d, 10.3, 2H)	3.71 (s, 6H), 3.20 (s, 6H)	7.63−7.61 (m, 2H), 7.45−7.40 (m, 3H), 6.45 (d, 6.9, 1H), 6.23 (t, 6.2, 1H), 6.00 (t, 6.6, 1H), 5.32 (d, 6.9, 1H), 4.94 (t, 5.9, 1H)	
2j	4.30 (d, 9.8, 2H), 2.04 (d, 9.8, 2H)	3.72 (s, 6H), 3.63 (s, 6H)	6.75 (t, 5.7, 1H), 6.08 (d, 5.9, 1H), 5.73 (d, 6.3, 1H), 5.51 (t, 5.9, 1H), 5.28 (t, 6.1, 1H)	4.06 (s, 3H)
2k	4.46 (d, 9.9, 2H), 1.84 (d, 9.9, 2H)	3.56 (s, 6H), 3.55 (s, 6H)	7.81 (br, 2H), 7.61 (br, 1H), 7.60 (br, 1H), 6.77 (t, 5.9, 1H), 5.74 (d, 5.9, 1H), 5.68 (t, 5.9, 1H), 5.54 (d, 6.3, 1H)	

[a] Measured in $CDCl_3$ at room temperature and 400 MHz. Abbreviations: s = singlet, d = doublet, t = triplet, vt = virtual triplet, m = multiplet, br = broad. Figures in parentheses are the values of the coupling constants J_{H-H} (in Hz). [b] 300 MHz.

Table 3. ^{13}C NMR Data of 2a−k (δ, ppm)[a]

	dimethyl fumarate			aromatic ligand	
complex	C=O	=CH	Me	aromatic	others
2a[b]	177.1, 173.1	47.6, 41.4	51.3, 51.2	96.4	
2b	176.7, 173.1	48.1, 42.5	51.4, 51.2	112.7, 97.1, 97.0, 95.9, 95.8, 94.4	19.0
2c[b]	177.0, 173.4	48.3, 43.8	51.2, 51.0	111.0, 97.8, 95.5	18.7
2d	176.3, 173.8	47.3, 41.3	51.2, 51.0	109.5, 96.6	18.1
2e	175.3, 174.4	47.4, 41.4	51.1, 50.9	106.0	15.2
2f	177.5, 173.3	47.0, 40.0	51.3, 51.2	126.8, 103.4, 100.3, 92.5, 92.2, 88.8	35.3, 30.6
2g	176.9, 173.4	48.6, 43.5	51.4, 51.2	142.1, 94.9, 94.8, 92.7, 85.6, 77.9	56.5
2h	177.6, 174.3	46.5, 39.7	51.1, 51.0	136.3, 94.5, 92.2, 92.1, 78.8, 69.6	39.5
2i	175.2, 172.7	48.8, 42.3	51.2, 50.8	133.2, 129.2, 128.7, 128.5, 128.4, 127.9, 112.2, 97.5, 96.4, 95.0, 95.0, 92.7	
2j	176.5, 172.3	50.2, 44.1	51.7, 51.5	104.1, 103.3, 94.9, 94.5, 92.3, 91.4	164.6, 53.3
2k	176.7, 172.7	48.7, 44.2	51.1, 50.9	131.8, 130.8, 128.7, 127.5, 105.7, 104.7, 98.5, 97.2, 91.5, 90.7	

[a] Measured in $CDCl_3$ at room temperature and 100 MHz. [b] 75 MHz.

dimethyl fumarates in **2g** (1.409(5) and 1.413(5) Å) are almost as long as those in **1** (1.408(8) and 1.431(7) Å).[32]

As a displacement mechanism, two pathways can be considered (Scheme 1). Path A shows a straightforward exchange mechanism between cyclooctatriene and arene without dissociation of dimethyl fumarate. On the other hand, in path B, the release of a dimethyl fumarate ligand is followed by displacement of the cyclooctatriene ligand with arene and the recoordination of dimethyl fumarate to give complex **2**. While the intermediates **3**−**7** have not yet been detected, monodentate amine- and phosphine-ligated analogues of **5**, i.e., Ru(η^6-cot)(dmfm)(NR_3)[33b] and Ru(η^6-cot)(dmfm)(PR_3),[34] have been obtained by reacting **1** with corresponding ligands. Analogues of **6**, Ru(η^4-cot)(dmfm)(N⁀N)[33a] (N⁀N = 2,2′-bipyridyl, 1,10-phenanthroline) and Ru(η^4-cot)(dmfm)(dppm)[35] (dppm = bis(diphenylphosphino)methane), have also been synthesized in a similar manner. Thus, one of the two dimethyl fumarate ligands in **1** was found to be labile. In addition, the recoordination of dimethyl fumarate has been demonstrated. The reaction of **1** with excess pyridine (py) first gave Ru(η^6-cot)(dmfm)(py) at room temperature, which was then converted into Ru(dmfm)$_2$(py)$_3$ at 115 °C.[33c] The reaction of **1** with tridentate nitrogen ligands (N⁀N⁀N) gave a mixture of stereoisomers of Ru(dmfm)$_2$(N⁀N⁀N) via ligand ex-

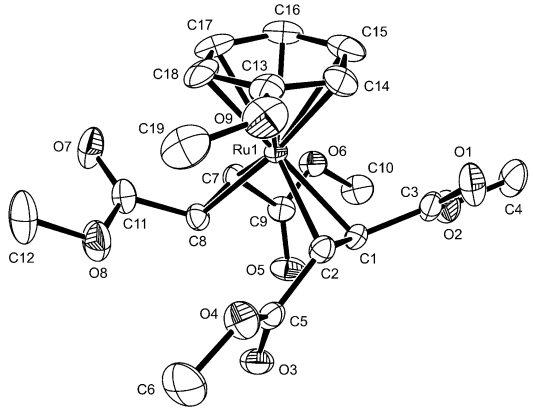


Figure 1. ORTEP drawing of **2g**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ru1−C1 = 2.151(3), Ru1−C2 = 2.158(3), Ru1−C7 = 2.162(3), Ru1−C8 = 2.138(4), Ru1−C13 = 2.318(4), Ru1−C14 = 2.213(4), Ru1−C15 = 2.271(5), Ru1−C16 = 2.277(4), Ru1−C17 = 2.224(3), Ru1−C18 = 2.291(4), C1−C2 = 1.413(5), C7−C8 = 1.409(5).

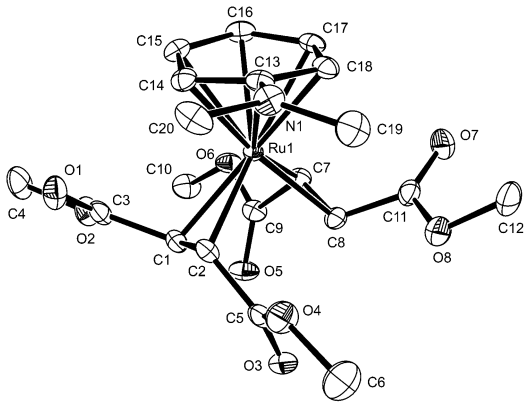


Figure 2. ORTEP drawing of **2h**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ru1−C1 = 2.144(2), Ru1−C2 = 2.172(2), Ru1−C7 = 2.164(2), Ru1−C8 = 2.139(2), Ru1−C13 = 2.391(2), Ru1−C14 = 2.224(2), Ru1−C15 = 2.265(2), Ru1−C16 = 2.282(2), Ru1−C17 = 2.218(2), Ru1−C18 = 2.288(2), C1−C2 = 1.420(3), C7−C8 = 1.415(3).

change from cyclooctatriene to a tridentate nitrogen ligand. The stereoisomers are different from each other at the coordinated enantiofaces of one of the dimethyl fumarate ligands, which means that the cyclooctatriene ligand is not directly substituted by a tridentate nitrogen ligand.[33c]

Furthermore, the reaction of **1** with toluene-d_8 in the presence of dimethyl fumarate was investigated (Table 5). Significantly, the addition of dimethyl fumarate decelerated the displacement of 1,3,5-cyclooctatriene with toluene-d_8. This result also strongly supports path B, which involves the dissociation step of a dimethyl fumarate ligand.

Conclusion

A novel additive-free displacement of cyclooctatriene by arenes on zerovalent ruthenium was achieved and was found to be applicable to several arenes. X-ray crystallography of Ru(η^6-anisole)(dmfm)$_2$ and Ru(η^6-*N*,*N*-dimethylaniline)(dmfm)$_2$ revealed that the coordination geometry of both complexes can be represented by a highly distorted trigonal bipyramid. Further studies on the stoichiometric and catalytic reactivity of these complexes are expected.

Table 4. Summary of Crystal Data, Collection Data, and Refinement of 2g,h

	2g	**2h**
formula	$C_{19}H_{24}O_9Ru$	$C_{20}H_{27}NO_8Ru$
fw	497.46	510.51
cryst color	yellow	yellow
cryst habit	platelet	platelet
cryst size, mm	0.30 × 0.20 × 0.10	0.30 × 0.30 × 0.30
cryst syst	monoclinic	monoclinic
space group	$P2_1$	$P2_1$
a, Å	7.7075(8)	7.6613(4)
b, Å	16.088(1)	15.9060(5)
c, Å	8.1884(6)	8.6199(5)
β, deg	96.341(6)	96.612(2)
V, Å^3	1009.1(1)	1043.44(9)
Z	2	2
D(calcd), g cm^{-3}	1.637	1.625
data collecn temp, °C	−180	−180
μ(Mo Kα), cm^{-1}	8.26	7.99
$2\theta_{max}$, deg	54.6	54.9
no. of measd rflns	8451	9976
no. of unique rflns	3778 (R_{int} = 0.044)	4596 (R_{int} = 0.034)
no. of obsd rflns ($I > -10.00\sigma(I)$)	3768	4593
no. of variables	263	272
R^a ($I > 2.00\sigma(I)$)	0.031	0.024
$R_w{}^a$ ($I > -10.00\sigma(I)$)	0.076	0.062
GOF	1.09	1.04

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

Table 5. Effect of the Addition of Dimethyl Fumarate on Reaction of 1 with Toluene-d_8[a]

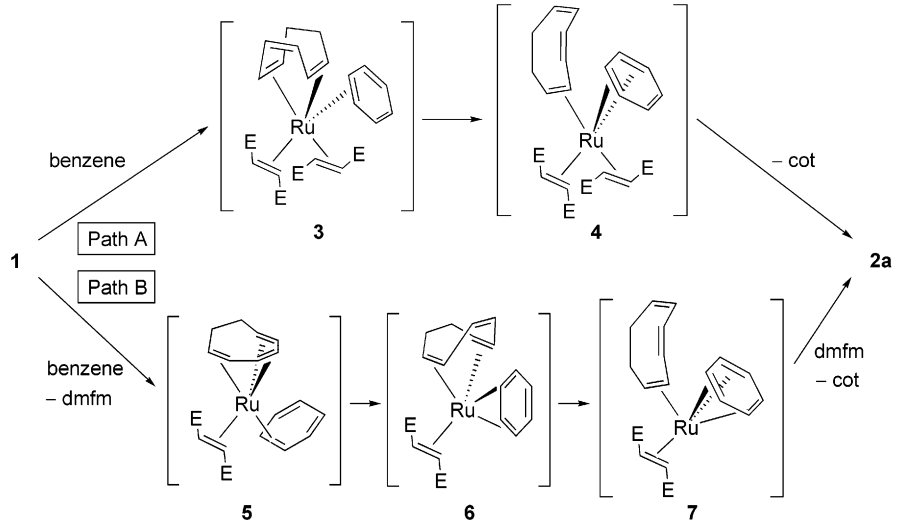
amt of dimethyl fumarate (equiv)[b]	conversn of **1** (%)[c]	yield of **2b**-d_8 (%)[c]
	91	44
2.0	76	27
5.0	51	23

[a] Reactions of **1** with toluene-d_8 were done in the absence/presence of dimethyl fumarate at 100 °C for 3 h in an NMR sample tube. [b] Based on **1**. [c] Determined by ^{1}H NMR.

Experimental Section

Materials and Methods. All manipulations were performed under an argon atmosphere using standard Schlenk

Scheme 1. Possible Displacement Mechanisms



techniques. Ru(cot)(dmfm)$_2$ (**1**) was synthesized as we reported previously.[32] All solvents were distilled under argon over appropriate drying reagents (sodium, calcium hydride, sodium−benzophenone, and calcium chloride).

Physical and Analytical Measurements. NMR spectra were recorded on JEOL EX-400 (FT, 400 MHz (^{1}H), 100 MHz (^{13}C)) and AL-300 (FT, 300 MHz (^{1}H), 75 MHz (^{13}C)) spectrometers. Chemical shift values (δ) for ^{1}H and ^{13}C are referenced to internal solvent resonances and reported relative to $SiMe_4$. NMR data for **2a**−**k** are summarized in Tables 2 (^{1}H) and 3 (^{13}C). IR spectra were recorded on a Nicolet Impact 410 FT-IR spectrometer. Melting points were determined under argon on a Yanagimoto micro melting point apparatus. HR-MS spectra were recorded on JEOL SX102A spectrometers with *m*-nitrobenzyl alcohol (*m*-NBA) as the matrix. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

Synthesis of Ru(η^6-benzene)(dmfm)$_2$ (2a). A mixture of 0.30 g (0.61 mmol) of Ru(cot)(dmfm)$_2$ (**1**) and 5.0 mL of benzene was placed in a 50 mL stainless steel autoclave equipped with a glass liner and a magnetic stirring bar. The mixture was stirred at 110 °C for 2 h and then chromatographed on alumina. Elution with $CHCl_3$ gave a yellow solution, from which the solvent was evaporated to give complex **2a** (0.19 g). It was recrystallized from Et_2O to give pale yellow microcrystals.

Complex **2a**: mp 185−187 °C dec. IR (KBr disk): 1702, 1696 cm^{-1}. HR-MS (FAB-*m*NBA): *m*/*z* 469.0420 (M + H)$^+$, calcd for $C_{18}H_{23}O_8Ru$ 469.0436.

Synthesis of Ru(η^6-toluene)(dmfm)$_2$ (2b). A suspension of 0.50 g (1.0 mmol) of Ru(cot)(dmfm)$_2$ (**1**) in 5.0 mL of toluene was stirred at 110 °C for 2 h and then chromatographed on alumina. Elution with $CHCl_3$ gave a yellow solution, from which the solvent was evaporated to give complex **2b** (0.31 g). It was recrystallized from Et_2O to give pale yellow microcrystals. Complexes **2c**−**k** were also synthesized in a similar manner except in the case of **2e**, where 1.2 equiv of hexamethylbenzene and diglyme as a solvent were used.

Complex **2b**: mp 156−159 °C dec. IR (KBr disk): 1707, 1692 cm^{-1}. HR-MS (FAB-*m*NBA): *m*/*z* 483.0630 (M + H)$^+$, calcd for $C_{19}H_{25}O_8Ru$ 483.0593.

Ru(η^6-*p*-xylene)(dmfm)$_2$ (2c): pale yellow microcrystals, mp 152−153 °C dec. IR (KBr disk): 1710, 1691 cm^{-1}. HR-MS (FAB-*m*NBA): *m*/*z* 497.0735 (M + H)$^+$, calcd for $C_{20}H_{27}O_8Ru$ 497.0749.

Ru(η^6-mesitylene)(dmfm)$_2$ (2d): pale yellow microcrystals, mp 114−116 °C dec. IR (KBr disk): 1706, 1698 cm^{-1}. Anal. Calcd for $C_{21}H_{28}O_8Ru$: C, 49.50; H, 5.54. Found: C, 49.30; H, 5.54.

Ru(η^6-hexamethylbenzene)(dmfm)$_2$ (2e): brown microcrystals, mp 231−233 °C dec. IR (KBr disk): 1708, 1691 cm^{-1}. HR-MS (FAB-*m*NBA): *m*/*z* 553.1371 (M + H)$^+$, calcd for $C_{24}H_{35}O_8Ru$ 553.1375.

Ru(η^6-*tert*-butylbenzene)(dmfm)$_2$ (2f): pale yellow microcrystals, mp 125−126 °C dec. IR (KBr disk): 1713, 1697 cm^{-1}. HR-MS (FAB-*m*NBA): *m*/*z* 525.1053 (M + H)$^+$, calcd for $C_{22}H_{31}O_8Ru$ 525.1062.

Ru(η^6-anisole)(dmfm)$_2$ (2g): pale yellow microcrystals, mp 204−206 °C dec. IR (KBr disk): 1708, 1688 cm^{-1}. HR-MS (FAB-*m*NBA): *m*/*z* 499.0564 (M + H)$^+$, calcd for $C_{19}H_{25}O_9Ru$ 499.0542.

Ru(η^6-*N*,*N*-dimethylaniline)(dmfm)$_2$ (2h): pale yellow microcrystals, mp 166−168 °C dec. IR (KBr disk): 1704, 1697 cm^{-1}. HR-MS (FAB-*m*NBA): *m*/*z* 512.0850 (M + H)$^+$, calcd for $C_{20}H_{28}NO_8Ru$ 512.0858.

Ru(η^6-biphenyl)(dmfm)$_2$ (2i): pale yellow microcrystals, mp 162−163 °C dec. IR (KBr disk): 1714, 1691 cm^{-1}. HR-MS (FAB-*m*NBA): *m*/*z* 545.0772 (M + H)$^+$, calcd for $C_{24}H_{27}O_8Ru$ 545.0749.

Ru(η^6-methyl benzoate)(dmfm)$_2$ (2j): pale yellow microcrystals, mp 203−205 °C dec. IR (KBr disk): 1728, 1708, 1685 cm^{-1}. HR-MS (FAB-*m*NBA): *m*/*z* 527.0508 (M + H)$^+$, calcd for $C_{20}H_{25}O_{10}Ru$ 527.0491.

Ru(η^6-naphthalene)(dmfm)$_2$ (2k): brown microcrystals, mp 183−185 °C dec. IR (KBr disk): 1702, 1691 cm^{-1}. HR-MS (FAB-*m*NBA): *m*/*z* 519.0604 (M + H)$^+$, calcd for $C_{22}H_{25}O_8Ru$ 519.0593.

Crystallographic Study of Complexes 2g,h. Single crystals of complexes **2g**,**h** obtained by recrystallization from $CHCl_3$/pentane were subjected to X-ray crystallographic analyses. The crystal data and experimental details for **2g**,**h** are summarized in Table 4. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). The structure of **2g** was solved by heavy-atom Patterson methods,[36] and the structure of **2h** was solved by direct methods using SIR92,[37] and both of them were expanded using Fourier techniques (DIRDIF99).[38] The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically. The absolute structures of **2g**,**h** were determined on the basis of the Flack parameters[39] 0.01(4) and −0.03(2), respectively, refined by least-squares techniques. Neutral atom scattering factors were taken from Cromer and Waber.[40] Anomalous dispersion effects were included in F_c;[41] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[42] The values for the mass attenuation coefficients were those of Creagh and Hubbell.[43] All calculations were performed using the CrystalStructure[44,45] crystallographic software package.

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Supporting Information Available: Text giving a description of the X-ray procedures, tables of X-ray data, positional and thermal parameters, and bond lengths and angles, and ORTEP diagrams for complexes **2g**,**h**. This material is available free of charge via the Internet at http://pubs.acs.org.

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