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Activation of Arene Carbon–Hydrogen Bonds. Highly Regioselective, Electrophilic Aromatic Metalation with Rhodium(III) Porphyrin and Subsequent Cleavage of Carbon–Rhodium Bond[1]

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(Octaethylporphyrinato)rhodium(III) chloride, (OEP)$Rh^{III}Cl$, reacts with benzene in the presence of $AgClO_4$ or $AgBF_4$ to give the phenyl–rhodium(III) complex. Anisole, toluene, and chlorobenzene are similarly metalated exclusively at the para positions. The metalation of methyl benzoate, on the other hand, gives a 92:8 mixture of meta- and para-metalated isomers. The reactivities of arenes follow the Hammett equation with the ρ value of −5.43. The observed substituent effects both on reactivity and orientation unambiguously characterize the present reaction as an electrophilic aromatic metalation with a $[(OEP)Rh^{III}]^+$ intermediate generated from the anion exchange of (OEP)$Rh^{III}Cl$ with silver salts. The slow step in the reaction is coordination of arene to form $[(OEP)Rh(arene)]^+$, which subsequently loses a proton. Arenes thus activated with rhodium undergo photochemical homolysis of the C–Rh bond as well as its halogen-induced heterolysis. The photolysis in benzene leads to 4-substituted biphenyls and the halogenolysis gives *p*-haloarenes with extremely high regioselectivities (>99%).

The activation of chemically inert carbon–hydrogen bonds under mild conditions constitutes a rapidly growing research area in recent years.[2,3] The homogeneous activation of arene C–H bonds by metal complexes involves either oxidative or electrophilic addition of the metal to an arene C–H bond.[2] The great majority of intramolecular or intermolecular arene C–H bond activations by transition-metal species in lower oxidation states involves oxidative addition mechanisms.[3-15] Some non-transition-metal ions such as Hg^{2+}, Tl^{3+}, and Pb^{4+} are known to act as electrophiles capable of metalation of arenes.[16-18] A number of reactions of arenes are catalyzed by transition-metal ions, where arylmetal complexes are often proposed as plausible intermediates. In some cases, transition-metal *electrophiles* lead to isolable arylmetal complexes as is seen in many organic electrophilic substitution reactions; examples include intramolecular ortho metalations[14b,19,20] and intermolecular aromatic platination.[21] In the latter reaction, the observed substituent effects are different from those in classical electrophilic aromatic substitution. While the interaction of olefins with electrophilic transition-metal centers is well understood,[22,23]

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Table I. Microanalyses and Yields of $(\mathrm{OEP})\mathrm{Rh^{III}C_6H_4X}$

				calcd			found		
compd	X	yield, %	formula	C	H	N	C	H	N
2	p-OCH$_3$	46	$\mathrm{C_{43}H_{51}N_4ORh}$	69.53	6.92	7.54	69.08	6.84	7.42
4	p-Cl	18	$\mathrm{C_{42}H_{48}N_4ClRh}$	67.51	6.48	7.50	67.36	6.50	7.44
5	m-CO$_2$CH$_3$	22	$\mathrm{C_{44}H_{51}N_4O_2Rh}$	68.56	6.67	7.27	68.19	6.74	6.93

it still remains to be clarified how transition-metal electrophiles compare with such electrophiles as $\mathrm{NO_2^+}$ used in usual electrophilic aromatic substitution. In this study we have investigated the activation of arenes by a $\mathrm{Rh^{III}}$ electrophile and subsequent functionalization of the coordinated arenes.

Results

Metalation of Benzene. In the presence of a slightly greater than molar amount of $\mathrm{AgClO_4}$ or $\mathrm{AgBF_4}$, (octaethylporphyrinato)rhodium(III) chloride, $(\mathrm{OEP})\mathrm{Rh^{III}Cl}$, readily reacted with benzene under mild conditions (≤50 °C) to give the σ-bonded phenyl–rhodium(III) complex 1 (eq 1) in yields of 40 (with $\mathrm{AgClO_4}$) and 70% (with $\mathrm{AgBF_4}$)

$$(\mathrm{OEP})\mathrm{Rh^{III}Cl} + \mathrm{C_6H_5X} \xrightarrow[\mathrm{AgBF_4}]{\mathrm{AgClO_4\ or}} (\mathrm{OEP})\mathrm{Rh^{III}C_6H_4}\text{-}p\text{-X}$$

1, X = H
2, X = OCH$_3$
3, X = CH$_3$
4, X = Cl
(1)

after purification.[24] The product was unambiguously identified by comparison with authentic 1 obtained by the published procedure (eq 2, X = H).[25] In the absence of

$$(\mathrm{OEP})\mathrm{Rh^{III}Cl} + \mathrm{X}\text{-}p\text{-}\mathrm{C_6H_4Li} \rightarrow (\mathrm{OEP})\mathrm{Rh^{III}C_6H_4}\text{-}p\text{-X} \quad (2)$$

a silver salt no reaction took place. The formation of 1 was completely inhibited by the presence of potential donor cosolvents such as methanol, tetrahydrofuran, and pyridine, but not by dioxygen. The TLC monitoring of the reaction indicated a facile exchange of $\mathrm{Cl^-}$ of $(\mathrm{OEP})\mathrm{Rh^{III}Cl}$ with $\mathrm{ClO_4^-}$ or $\mathrm{BF_4^-}$ of the silver salt followed by the gradual conversion of the thus formed intermediate complex to 1. The only noticeable side reaction was decomposition of the intermediate to some extent as independently confirmed. Treatment of $(\mathrm{OEP})\mathrm{Rh^{III}Cl}$ with a silver salt in dichloromethane afforded relatively unstable and hygroscopic complexes $(\mathrm{OEP})\mathrm{Rh^{III}(ClO_4)}$ and $(\mathrm{OEP})\mathrm{Rh^{III}(BF_4)}$ in yields of 56 and 51%, respectively, with concomitant precipitation of AgCl. The isolated perchlorate and tetrafluoroborate species were independently shown to undergo reaction with benzene to generate 1 without the participation of a silver salt. The silver ion assisted phenylation of $(\mathrm{OEP})\mathrm{Rh^{III}Cl}$ with a 1:1 mixture of benzene and benzene-d_6 gave rise to 1 and 1-d_5 in nearly the same amounts determined from comparison of the integrated intensities of the axial phenyl and the meso protons in NMR spectrum. The present result indicates essentially no kinetic deuterium isotope effect ($k_\mathrm{H}/k_\mathrm{D} \simeq 1$).

Metalation of Substituted Benzenes. Anisole, toluene, and chlorobenzene reacted similarly with $(\mathrm{OEP})\mathrm{Rh^{III}Cl}$ in the presence of $\mathrm{AgClO_4}$ to give the corresponding aryl–rhodium(III) complexes 2–4 (eq 1). The tolyl complex 3, obtained in 46% yield, was identified by NMR spectral comparison with authentic 3 prepared according to eq 2 (X = CH$_3$).[25] The yields and analytical data of new aryl–rhodium(III) complexes are shown in Table I. The highly regioselective para metalation of substituted benzenes was demonstrated by the ^{1}H NMR spectra of 2–4, in which the aromatic proton resonances appeared as a pair of doublets in 1:1 integrated ratio for two types of protons, one being highly and the other moderately shielded due to the porphyrin ring current effect. (Table II). These were readily assigned to the ortho and meta protons respectively to rhodium on the basis of their geometrical parameters and the isoshielding map of organorhodium porphyrins.[25] Exclusive para metalation was always observed when the reaction conditions (time and temperature) were altered. Furthermore, the aryl–rhodium complexes were found to be quite stable under the present reaction conditions even in the presence of aqueous HCl or $\mathrm{HClO_4}$. These facts are indicative of an essentially irreversible electrophilic metalation of arenes.

Table II. ^{1}H NMR Spectral Data for Aryl Ligands in $(\mathrm{OEP})\mathrm{Rh^{III}C_6H_4X}$ (δ from Me$_4$Si)[a,b]

complex	ortho H	meta H	para H	CH$_3$
1	−0.39 (d)	4.49 (t)	5.11 (t)	
2	−0.44 (d)	~4.1[c]		2.57 (s)
3	−0.43 (d)	4.31 (d)		0.88 (s)
4	−0.49 (d)	4.43 (d)		
5	−0.19[d] (dq), 0.26[d] (q)	4.54 (t)	5.70 (dq)[d]	3.20 (s)
6	−0.26 (d)	5.18 (d)		3.13 (s)

[a] Spectra were obtained for CDCl$_3$ solutions with tetramethylsilane as standard using either 200- (for 1, 2, 3, 4, and 6) or 270-MHz machine (for 5): s, singlet; d, doublet; t, triplet; q, quartet; dq, double quartet. Ortho, meta, and para are in reference to rhodium. [b] J_ortho = 7–8 Hz. [c] Overlapping with CH_2CH$_3$. [d] J_meta = 1.7 and 2.8 Hz.

The metalation of methyl benzoate required more drastic conditions than those used for the substituted benzenes above. At 90 °C in the presence of a silver salt, the ester reacted with $(\mathrm{OEP})\mathrm{Rh^{III}Cl}$ and afforded in 24% total yield a chromatography-separable mixture of two aryl–rhodium(III) complexes in a ratio of 92:8 (eq 3). The

$$(\mathrm{OEP})\mathrm{Rh^{III}Cl} + \mathrm{C_6H_5CO_2CH_3} \xrightarrow[\mathrm{AgBF_4}]{\mathrm{AgClO_4\ or}}$$

$$\underset{5\ (92\%)}{(\mathrm{OEP})\mathrm{Rh^{III}C_6H_4}\text{-}m\text{-}\mathrm{CO_2CH_3}} + \underset{6\ (8\%)}{(\mathrm{OEP})\mathrm{Rh^{III}C_6H_4}\text{-}p\text{-}\mathrm{CO_2CH_3}} \quad (3)$$

minor one 6 was readily assigned as the para-metalated isomer from the NMR spectrum which showed an A$_2$B$_2$ aromatic proton resonance. The NMR spectrum of the major isomer 5 showed two highly shielded ortho (to rhodium) proton resonances and the two remaining proton resonances at lower field. The observed splitting and coupling patterns (Table II) were consistent with the structure in which the position meta to the methoxycarbonyl group was metalated. In Table I the analytical data are shown.

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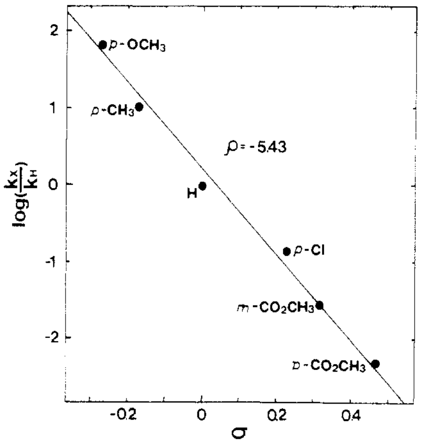

Figure 1. Hammett plots for reactivities of arenes in the Ag^+-assisted metalation with $(OEP)Rh^{III}Cl$: k_X and k_H stand respectively for the statistically corrected reactivity of an arene and benzene.

The competitive metalation reactions of C_6H_5X (X = H, OCH_3, CH_3, Cl, and CO_2CH_3) show relative rate increases with increasing electron-donating abilities of the substituents X (relative rate): OCH_3 (71.4), CH_3 (10.7), H (1 after statistical correction for 6 H), Cl (0.143), and CO_2CH_3 (0.062, statistically not corrected). The isomer distribution in eq 3 allows the respective reactivities of meta and para hydrogens of methyl benzoate to be evaluated; meta H (0.029 after statistical correction for 2 H) and para H (0.005). The logarithmic relative rates are correlated with substituent constants σ or σ^+ in the Hammett-type equations. Use of σ results in a better correlation (correlation coefficient 0.995) and gives a ρ value of −5.43 (Figure 1). Interestingly, this ρ value is comparable to that for the nitration of monosubstituted benzenes with NO_2^+,[26] a typical example of electrophilic aromatic substitution.

Cleavage of Aryl–Rhodium(III) Bonds. The present aryl–rhodium(III) complexes underwent facile cleavage of the C–Rh bond induced by halogen. Treatment of complex 1 with iodine at room temperature gave iodobenzene in nearly quantitative yield together with $(OEP)Rh^{III}I$ (eq 4).

$$(OEP)Rh^{III}C_6H_5 + I_2 \rightarrow (OEP)Rh^{III}I + C_6H_5I \quad (4)$$

Bromine and chlorine reacted similarly with 1 to afford bromobenzene and chlorobenzene in ~100 and 94% yields, respectively. Iodination and bromination of the tolyl complex 3 derived from the present metalation (eq 1) gave the corresponding p-halotoluenes in nearly quantitative chemical yields and with extremely high regioselectivities (>99%). This trend is also found for the bromination of the anisyl complex 2. The regioselective para metalation shown by the analysis of ^1H NMR spectra of 2 and 3 has thus been put on a more quantitative level.

Complex 1, like homologous organocobalt derivatives,[27-32] underwent photolysis of the carbon–metal bond. Irradiation of a degassed benzene solution of 1 led to the formation of biphenyl in 85% yield. Photolysis of 2 and 3 gave 4-methoxy- and 4-methylbiphenyl, respectively, arising from homolytic aromatic substitution[33] of the solvent benzene with the photogenerated para-substituted phenyl radicals. In neither case was 4,4′-disubstituted biphenyl detected, a product which may result from radical coupling.

Discussion

Electrophilic Aromatic Metalation. Substituent effects in electrophilic aromatic substitution have been thoroughly investigated.[34] The substituents employed in this study cover the three categories; OCH_3 and CH_3 (ortho and para orienting with activation), Cl (ortho and para orienting with deactivation), and CO_2CH_3 (meta orienting with deactivation). The observed substituent effects on both reactivity (Figure 1) and orientation (eq 1 and 3) clearly characterize the present reaction as an (ionic) electrophilic aromatic metalation with a cationic intermediate, $[(OEP)Rh^{III}]^+$, generated from the anion exchange of $(OEP)Rh^{III}Cl$ with silver salts. As in the recent catalytic transformations of olefins by $[Pd(CH_3CN)_4](BF_4)_2$,[23] the role of ClO_4^- or BF_4^- would be that of noncoordinating counteranions, thus accommodating vacant coordination sites and enhancing the electrophilicity of the central metal. This explanation is compatible with the observed inhibition of the reaction by coordinating cosolvents. The absence of an ortho attack may be due to a steric effect. Mechanisms involving radical species are not consistent with the observed large negative ρ value and regioselectivity.[35] Furthermore, there is no evidence of cleavage of potentially reactive methyl C–H bonds of toluene and anisole. The lack of an inhibitory effect by dioxygen provides further evidence for the exclusion of radical mechanisms. The substituent effects observed here are in marked contrast to those found in oxidative addition processes of lower valent transition metals to the arene C–H bonds: these reactions are facilitated by electron-withdrawing groups[5a,c] and usually give nonregioselective isomer mixtures (vide infra); in some cases metalation of alkyl side chains takes place.[4c,e,f]

An interesting comparison can be made between the present aromatic metalation and aromatic nitration with NO_2^+. Both reactions give rise to comparable Hammett ρ values and are free from kinetic deuterium isotope effects.[34] An indication of this is that $[(OEP)Rh^{III}]^+$ of a similar electrophilicity as NO_2^+ attacks the arene in the rate-determining step to form $[(OEP)Rh^{III}(arene)]^+$, which subsequently undergoes rapid loss of a proton as in nitration (eq 5). Relevant to the deprotonation step is the

$$[(OEP)Rh^{III}]^+ + C_6H_6 \xrightarrow{\text{slow}} [(OEP)Rh^{III}(C_6H_6)]^+ \xrightarrow[-H^+]{\text{fast}} 1 \quad (5)$$

recent report of the protonation–deprotonation interconversion of σ-aryl and η^2-arene complexes of $[(\eta\text{-}C_5H_5)Re$-

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Table III. Isomer Distribution in Aromatic Substitution

entry	reaction	substrate C_6H_5X, X =	reagent	isomer distributn, % ortho	meta	para	ref
1	bromination	CH_3	$[(OEP)Rh^{III}]^+$, Br_2	0	<1	>99	this work
2	iodination	CH_3	$[(OEP)Rh^{III}]^+$, I_2	0	<1	>99	this work
3	bromination	OCH_3	$[(OEP)Rh^{III}]^+$, Br_2	0	<1	>99	this work
4	nitration	CH_3	NO_2^+	56.5	3.5	40	*a*
5	metalation (Hg)	CH_3	$Hg(CH_3CO_2)_2$[b]	~20	~10	~70[c]	16
6	metalation (Tl)	CH_3	$Tl(CF_3CO_2)_3$	9	4	87[d]	17
7	metalation (Pt)	CH_3	H_2PtCl_6	0	ca. 50	ca. 50	21c
8	chlorination	Cl	$PtCl_6^{2-}$	1	61–62	38–39	37
9	metalation (Fe)[e]	CH_3	$Fe(dmpe)_2$[f]	0	62	38	5c
10	metalation (Rh)[g]	CH_3	$Rh[C_5(CH_3)_5][P(CH_3)_3]$	0	67	33	6
11	metalation (Re)[h]	CH_3	$[(C_5H_5)Re(NO)(CO)]^+$	0	6	94	36
12	metalation (Re)[h]	CF_3	$[(C_5H_5)Re(NO)(CO)]^+$	0	84	16	36
13	chlorination	OCH_3	HOCl, α-CD[i]	4	0	96	*j*
14	metalation (Rh)	CO_2CH_3	$[(OEP)Rh^{III}]^+$	~0	92	8	this work
15	nitration	$CO_2CH_2CH_3$	NO_2^+	28.3	68.4	3.3	*a*
16	metalation (W)	CO_2CH_3	$(C_5H_5)_2W$[k]	0	26	74	4f

[a] Reference 26, p 568. [b] Under perchloric acid catalysis. [c] Isomer distribution extraporated to zero reaction time. The distribution changes with reaction time to approach a statistical distribution of the three. [d] At 22 °C. At higher temperatures, thermally induced reorientation results in predominant meta substitution: Taylor, E. C.; Kienzle, F.; Robey, R. L.; McKillop, A.; Hunt, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 4845. [e] Isomer distribution from exchange reaction of $HFe(C_{10}H_7)(dmpe)_2 + C_6H_5CH_3 \rightleftharpoons HFe(C_6H_5CH_3)(dmpe)_2 + C_{10}H_8$. [f] dmpe = $(CH_3)_2PCH_2CH_2P(CH_3)_2$. [g] Isomer distribution from oxidative addition to coordinated toluene in a η^2 fashion. [h] Isomer distribution from deprotonation of η^2-arene complex of $[(C_5H_5)Re(NO)(CO)]^+$. [i] α-Cyclodextrin (9.39×10^{-3} M). [j] Breslow, R.; Campbell, P. *J. Am. Chem. Soc.* **1969**, *91*, 3085. [k] Photochemically generated from $(C_5H_5)_2WH_2$.

$(NO)(CO)]^+$.[36] Such a formulation of a cationic η^2-arene complex, rather than an η^1-arenium cation, may apply to the present intermediate in eq 5, and this might also explain, at least partially, a better correlation of reactivities with substituent constants σ ($r = 0.995$) than with σ^+ ($r = 0.979$), in contrast to usual electrophilic aromatic substitution.

Electrophilic interactions of transition-metal ions may be involved in a number of reactions of arenes[2j] including metal-catalyzed hydrogen isotope exchange[37–39] and oxidation of arenes.[37] A class of facile, intramolecular aromatic metalations is known as ortho metalation or cyclometalation.[14b,19,20] However, these intramolecular reactions preclude a systematic study on the substituent effects as presented here, and in most of metal-catalyzed reactions aryl–metal complexes only have been proposed as intermediates. In some cases, reductive elimination follows initial oxidative addition so that the metal retains its original formal valency.[14b] When simple transition-metal salts or complexes are used, further complexities arise from facile ligand exchanges; this may lead to many species usually not readily identified unambiguously and may leave many mechanistic possibilities.[37] In this respect the rigid porphyrin ligand has a great significance.

Regioselectivity. In Table III are summarized the isomer distributions in aromatic substitutions. The crucial factors in the extremely regioselective (>99%) para substitution (metalation and subsequent halogenation) of toluene and anisole (entries 1–3) are (1) the electrophilic attack of the central metal and (2) the planar and bulky porphyrin ligand which effectively prevents otherwise facile ortho substitution (entry 4). A steric inhibition of ortho attack due to inclusion complex formation has been noted (entry 13). The mercuration and thallation are predominantly para orienting (entry 5 and 6) (but see footnotes *c* and *d* of Table III). The platination of arenes with $H_2Pt^{IV}Cl_6$ may involve an electrophilic mechanism on the basis of reactivity correlation:[21d] $\rho = -3.6$ which should be compared with the present ρ of -5.43. Aromatic auration might proceed through a similar mechanism.[40] However, the observed meta/para ratio in the platination of toluene (entry 7) is apparently not consistent with the electrophilic mechanism. A similar trend has been reported for the aromatic chlorination with $PtCl_6^{2-}$ (entry 8), where aryl–platinum complexes are intermediates.[21h,37] In fact the latter reaction gives the meta/para ratio very close to the statistical one (meta/para = 2:1), and this is also characteristic of the oxidative addition processes of lower valent transition metals (entries 9 and 10). The platination might also involve similar mechanisms.[41] Furthermore, it is interesting to compare the isomer distributions in the case of meta-directing alkoxycarbonyl substituents (entries 14–16). This brief survey of the substituent effects is intended to show that the hitherto known metalation reactions of arenes with transition-metal species are rather nonregioselective, irrespective of the mechanisms involved. There is, however, at least one clear example of electrophilic aromatic metalation that follows the directive effects of electrophilic aromatic substitution (entries 11 and 12), as in the present case.

A significance of homogeneous C–H bond activation by transition metals lies in further conversion of the resulting C–M bonds.[42,43] The present system provides a way to the functionalization of arenes via activation by transition metals. For simple arenes, there is no precedent for such a high regioselectivity as observed here for the halogenation of toluene and anisole. The present halogenolysis of the carbon–rhodium bond probably takes place in a similar

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(41) In the isotope exchange and oxidation reactions of arenes with Pt^{IV} halides, the active catalyst is shown to be a Pt^{II} species which forms aryl-Pt^{II} complexes as intermediates.[37] Furthermore, the aryl–Pt^{II} complexes formed from reactions of arenes with Na_2PtCl_4 undergo oxidation with H_2PtCl_6 to give aryl-Pt^{IV} complexes.[21h]

(42) The formation of aryl–metal complexes was proposed in a number of reactions of arenes with palladium salts such as oxidative coupling, arene–olefin coupling, and carboxylation. See, for example: (a) Moritani, I.; Fujiwara, Y. *Synthesis* **1973**, 524. (b) Fujiwara, Y.; Kawauchi, T.; Taniguchi, M. *J. Chem. Soc., Chem. Commun.* **1980**, 220.

(43) For organic syntheses via arylthallium complexes, see: Taylor, E. C.; McKillop, A. *Acc. Chem. Res.* **1970**, *3*, 338.

manner as reported for the electrophilic cleavage of the carbon–cobalt bond with halogen.[44,45] In fact, a close similarity of the electronic spectra of (OEP)Rh^{III}aryl and (OEP)Rh^{III}Cl indicates a significant carbanion character of the coordinated aryl ligands.

In principle it seems to be possible to carry out the present functionalization of arenes in a catalytic manner with respect to rhodium porphyrin. Various functionalizations of the C–Rh bond other than halogenation also seem promising, since rhodium is homologous to cobalt and there is a rich chemistry in organocobalt complexes.

Concluding Remarks

From the mechanistic viewpoint, this work provides an unambiguous example of intermolecular electrophilic aromatic metalations with transition metals in a single step. On all the criteria we stand on, except for a rather minor difference in the reactivity correlation with σ vs. σ^+, the present Rh^{III} electrophile behaves quite similarly to NO_2^+, a typical electrophile in classical electrophilic aromatic substitution; there is no special metal effect. From the synthetic viewpoint, the arenes thus activated by Rh^{III} indeed undergo extremely regioselective functionalization.

Experimental Section

General Analyses. IR spectra were obtained by using KBr disks on a Hitachi 260-10 spectrophotometer. ^{1}H NMR spectra were taken on a JEOL JNM-PMX 60, JNM-FX 200, or JNM-GX 270 spectrometer using tetramethylsilane as internal reference. Electronic spectra were recorded on a Hitachi 200-10 or 320 spectrophotometer. Elemental analyses were performed at the Microanalysis Center of Kyoto University. Gas chromatographic analyses were made with a Shimadzu GC-4C gas chromatograph using helium as a carrier gas. Identification of the reaction products was performed by coinjection with authentic samples on columns of poly(ethylene glycol) 60M, silicone SE-30, and azoxydianisole SG. Column chromatographic separations were carried out with silica gel (Wakogel C-200) and alumina (Merck 90, activity II-III). Silica gel 60 F$_{254}$ (Merck) was used for analytical and preparative thin-layer chromatography (TLC).

Materials. (Octaethylporphyrinato)rhodium(III) chloride [(OEP)Rh^{III}Cl] was prepared by a slight modification of the published procedure.[25] A mixture of octaethylporphyrin (1 g) and $[Rh(CO)_2Cl]_2$ (1.2 g) in benzene (1 L) was stirred at room temperature for 6 h. About 700 mL of the solvent was removed, and the concentrated solution left was refluxed for 2 h. Usual workup and chromatographic (silica gel) purification followed by recrystallization from dichloromethane–hexane afforded the rhodium porphyrin in yields of 75–80%. Silver salts ($AgClO_4$ and $AgBF_4$) were dried at 80 °C in vacuo for 1–2 h just before use. Thiophene-free benzene was crystallized three times; one-fourth was discarded each time as unfrozen liquid. It was then dried over calcium hydride and finally distilled through a 35-cm Vigreux column. Toluene, anisole, chlorobenzene, and methyl benzoate were also purified by standard procedures.

Metalation of Arenes. A dried 200-mL three-necked flask equipped with a reflux condenser, N_2 inlet, addition funnel, and a magnetic stirring bar was charged with a solution of $AgClO_4$ or $AgBF_4$ (10 mg) in an arene (50 mL). To this was added a solution of (OEP)Rh^{III}Cl (20 mg) in the arene (50 mL) over a period of 2 h at 50 °C (for benzene, toluene, anisole, and chlorobenzene) or 90 °C (for methyl benzoate). The mixture was further stirred at room temperature for 48 h. The solvent was removed in vacuo, and the residue was chromatographed first on alumina and then on silica gel. The reddish orange fraction eluted with benzene–hexane (4:1 by volume) (for **1**, **3**, and **4**) or with benzene (for **2** and mixture of **5** and **6**) was evaporated to dryness. The residue was further purified by recrystallization from dichloromethane–methanol to give reddish orange needles of phenyl- (**1**, 8.5 mg (40%) with $AgClO_4$ and 14.9 mg (70%) with $AgBF_4$), *p*-anisyl- (**2**, 10.2 mg (46%) with $AgClO_4$), *p*-tolyl- (**3**, 10.0 mg (46%) with $AgClO_4$), and *p*-chlorophenyl-Rh^{III} (**4**, 4.0 mg (18%) with $AgClO_4$) complexes. The isomeric mixture of (methoxycarbonyl)phenyl-Rh^{III} complexes **5** and **6** was separated by means of preparative TLC using benzene–hexane (85:15 by volume) as eluant: **5** (R_f 0.23; 5.1 mg (22%) with $AgClO_4$) and **6** (R_f 0.15; 0.5 mg (2%) with $AgClO_4$). The electronic spectra for solutions in CH_2Cl_2 showed λ_{max} (log ϵ) as follows: **1**, 394 nm (5.00), 509 (3.96), 542 (4.58); **2**, 393 nm (5.09), 510 (4.08), 542 (4.66); **3**, 394 nm (5.11), 508 (4.12), 542 (4.70); **4**, 394 nm (5.09), 509 (4.06), 544 (4.69); **5**, 394 nm (5.22), 510 (4.16), 543 (4.69).

Competition Reactions. A 1:1 molar mixture of anisole (standard) and C_6H_5X (X = H, CH_3, or Cl) was subjected to $AgClO_4$-assisted metalation with (OEP)Rh^{III}Cl as above. After the workup as described above, the product mixture was chromatographed on silica gel. (OEP)Rh$^{III}C_6H_4$-*p*-X (**1**, **3**, or **4**) was eluted with benzene–hexane (1:1 by volume) and (OEP)Rh$^{III}C_6H_4$-*p*-OCH_3 (**2**) with benzene–hexane (4:1 by volume); the separation was complete in every case. Since the reactivity of methyl benzoate was too low to compete with anisole, chlorobenzene was taken as a second standard. The competitive metalation of a 1:1 mixture of chlorobenzene and methyl benzoate was carried out under the conditions required for that of methyl benzoate. Chlorophenyl (**4**) and (methoxycarbonyl)phenyl (**5** and **6**) derivatives were separated by TLC. The relative reactivities of arenes were based on the amounts (determined by electronic spectroscopy) of the isolated aryl-Rh^{III} complexes in respective competition runs. The molar extinction coefficients of **6** were assumed to be the same as those of its isomer (**5**). Independent experiments indicated that all of aryl-Rh^{III} complexes are stable under the condition of metalation reaction and chromatographic manipulation.

The competitive metalation of benzene and benzene-d_6 (Merck, minimum 99%) was carried out similarly. The ratio of light and heavy phenyl complexes was determined from the ^{1}H NMR spectrum. An integrated ratio of 4:1 of the meso-proton signal to that of phenyl meta protons to rhodium indicated that (OEP)Rh$^{III}C_6H_5$ and (OEP)Rh$^{III}C_6D_5$ had been formed in approximately equal amounts.

(OEP)Rh^{III}(ClO_4) and (OEP)Rh^{III}(BF_4). A solution of (OEP)Rh^{III}Cl (20 mg) and $AgClO_4$ or $AgBF_4$ (10 mg) in 100 mL of dichloromethane dried with CaH_2 was stirred at room temperature under nitrogen for 2 days. Deposition of microprecipitates of AgCl was observed. The solvent was removed, and the residue was chromatographed on silica gel. Elution with a mixed solvent of dichloromethane and ethyl acetate (9:1 by volume) followed by recrystallization from dichloromethane–hexane afforded (OEP)Rh^{III}(ClO_4) (12.9 mg, 56%) or (OEP)Rh^{III}(BF_4) (11.5 mg, 51%) as the dihydrated form. These complexes are hygroscopic, and they pick up water during manipulation of chromatography on silica gel.

For the perchlorate complex: IR 1155, 1115, 1092 cm^{-1} (ν_{ClO});[46] ^{1}H NMR (CD_2Cl_2) δ 10.49 (br s, 4 H, meso H), 4.19 (m, 16 H, CH_2), 1.92 (t, 24 H, CH_3); electronic spectrum in CH_2Cl_2, λ_{max} (log ϵ) 396 nm (5.00), 516 (4.20), 549 (4.54). Anal. Calcd for $C_{36}H_{54}ClN_4O_4Rh\cdot 2H_2O$: C, 56.07; H, 6.27; N, 7.26. Found: C, 56.25; H, 6.44; N, 7.20.

For the tetrafluoroborate complex: IR 1115, 1089, 1070, 1060 cm^{-1} (ν_{BF});[46] ^{1}H NMR (CD_2Cl_2) δ 10.46 (br s, 4 H, meso H), 4.22 (m, 16 H, CH_2), 1.97 (t, 24 H, CH_3); electronic spectrum in CH_2Cl_2, λ_{max} (log ϵ) 396 nm (5.26), 514 (4.20), 548 (4.51). Anal. Calcd for $C_{36}H_{54}BF_4N_4Rh\cdot 2H_2O$: C, 57.01; H, 6.37; N, 7.38. Found: C, 57.35; H, 6.42; N, 7.42.

A solution of the purified perchlorate or tetrafluoroborate complex in benzene was stirred at room temperature. The gradual formation of **1** was ascertained by TLC and absorption spectroscopy.

Halogenation. A solution of **1** (20 mg) in dichloromethane–benzene (10:1 by volume, 30 mL) containing iodine (50-molar

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excess) was stirred at room temperature under nitrogen for 3 days. The solution was washed three times with aqueous $Na_2S_2O_4$ or $NaHSO_3$ solution. The organic layer was dried (Na_2SO_4), and the solvent was carefully removed in vacuo. The residue was chromatographed on silica gel. Elution with benzene afforded iodobenzene and (OEP)Rh^{III}I. These products were identified by comparison of their chromatographic and spectral behavior with those of authentic samples.[47] Similarly, the iodination of **3** and bromination of **1**, **2**, and **3** with a 50-molar excess of bromine in benzene (30 mL) were carried out. In the chlorination of **1**, chlorine gas was introduced with a stream of nitrogen into a solution of **1** in benzene (30 mL) for 30 min, and the mixture was worked up as described above. Gas chromatography was applied to determine the analytical yields of haloarenes and isomer distributions therein, on columns of azoxydianisole SG (for halotoluenes) and poly(ethylene glycol) 60M (for haloanisoles) with durene as an internal standard.

Photolysis. A solution of **1** (5 mg) in benzene (25 mL) in a Pyrex flask was irradiated with a 100-W high-pressure mercury lamp for 12 h. The solution was analyzed by gas chromatography. The photolyses of **2** and **3** were carried out similarly. The organic products, isolated by column chromatography on silica gel using benzene–hexane (4:1 by volume), showed ^1H NMR spectra identical with those of 4-methoxy- and 4-methylbiphenyl, respectively.

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Communications

Silicon-Containing Carbene Complexes. 6.[1] Stable 16-Electron Carbonyl Carbene Complexes of Tungsten(0), Molybdenum(0), and Chromium(0)

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Summary: On warming $(CO)_5W{=}C(NR_2)SiPh_3$ (NR_2 = NMe_2, **1a**, NC_5H_{10}, **1b**) under vacuum, a CO ligand is eliminated and 16-electron carbene complexes $(CO)_4W{=}C(NR_2)SiPh_3$ (**2a**,**b**) are formed as stable compounds. Analogous chromium and molybdenum complexes $(CO)_4M{=}C(NC_5H_{10})SiPh_3$ (M = Mo, **2c**, Cr, **2d**) are already formed during the preparation of $(CO)_5M{=}C(NC_5H_{10})SiPh_3$ (**1c**,**d**). The reaction is readily reversed on bubbling CO through solutions of **2**. X-ray structure determination of $(CO)_4W{=}C(NC_5H_{10})SiPh_3$ (**2b**) shows that the vacant coordination site at the metal is capped by a phenyl group of the $SiPh_3$ substituent. However, the long W–C(phenyl) distances exclude strong bonding interaction. The driving force for the conversion of **1** to give **2** seems to be relaxation of the steric strain within the carbene ligand.

The dissociative loss of a carbonyl ligand is the initial step in many reactions of Fischer-type carbene complexes $(CO)_5M{=}C(YR)R'$ (M = Cr, Mo, W; YR = OR, SR, NR_2, etc.), cis CO's being particularly labile.[2] Some $(CO)_5Cr{=}C(NEt_2)X$ complexes (X = Cl, Br, I, SeR, TeR, $SnPh_3$, $PbPh_3$) rearrange spontaneously to give *trans*-X-$(CO)_4Cr{\equiv}CNEt_2$ by an intramolecular process probably involving concerted dissociation of a CO ligand and C,-Cr-migration of the group X.[3] In the synthetically important reactions of $(CO)_5M{=}C(OR)R'$ with alkenes or alkynes, CO dissociation is the rate-determining first step, which is followed by addition of the unsaturated molecule to the vacant coordination site.[4] In no case have the 16-electron $(CO)_4M{=}C(YR)R'$ intermediates been observed directly.

We have now been able to isolate such complexes. If solid $(CO)_5W{=}C(NMe_2)SiPh_3$ (**1a**)[5,6] or $(CO)_5W{=}C(NC_5H_{10})SiPh_3$ (**1b**)[6] (but not $(CO)_5W{=}C(NEt_2)SiPh_3$[7]) are warmed to 110 °C at 0.1–0.2 torr in a Schlenk tube, the color changes from yellow to orange-red and the 16-electron complexes $(CO)_4W{=}C(NMe_2)SiPh_3$ (**2a**) or $(CO)_4W{=}C(NC_5H_{10})SiPh_3$ (**2b**) are obtained as major products.[8] They can be separated from byproducts and unreacted **1a**,**b** by column chromatography on silica at −20 °C (pentane/ether, 25:1). Contrary to **2a** and **2b** the

$$\underset{\textbf{1a–d}}{(CO)_5M{=}C(NR_2)SiPh_3} \rightleftharpoons CO + \underset{\textbf{2a–d}}{(CO)_4M{=}C(NR_2)SiPh_3} \qquad (1)$$

a, M = W, NR_2 = NMe_2; **b**, M = W, NR_2 = NC_5H_{10}; **c**, M = Mo, NR_2 = NC_5H_{10}; **d**, M = Cr, NR_2 = NC_5H_{10}

analogous complexes of molybdenum (**2c**) and chromium

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(8) Anal. Calcd for $C_{25}H_{21}NO_4SiW$ (**2a**): C, 49.11; H, 3.46; N, 2.29. Found: C, 49.35; H, 3.43; N, 1.87. Anal. Calcd for $C_{28}H_{25}NO_4SiW$ (**2b**): C, 51.62; H, 3.87; N, 2.15. Found: C, 51.62; H, 3.73; N, 1.72. Mass spectrum of **2b** (70 eV): *m/e* (relative intensity) 651 (1, M^+), 595 (25, M − 2CO), 567 (18, M − 3CO), 539 (31, M − 4CO), 507 (36), 446 (24), 259 (51, $SiPh_3$), 182 (100, $SiPh_2$), 105 (66, SiPh).

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