Activation of Arene Carbon–Hydrogen Bonds. Direct Electrophilic Aromatic Metallation with a Rhodium–Porphyrin Complex

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Anion exchange of octaethylporphyrinatorhodium(III) chloride with $AgClO_4$ or $AgBF_4$ results in the formation of a highly electrophilic Rh^{III}–porphyrin capable of direct metallation of arenes.

The homogeneous activation of arene carbon–hydrogen bonds by metal complexes involves either oxidative or electrophilic addition of the metal to an arene C–H bond.[1] The great majority of successful arene C–H bond activations by transition metal species, in particular those of group 8 metals, involve an oxidative-addition mechanism.[2] A few possible examples of electrophilic aromatic metallation with transition metal species have also been reported.[3] We report a clear example of the direct metallation of arenes with a rhodium(III)-porphyrin complex under mild conditions.

The dropwise addition of a solution of octaethylporphyrinatorhodium(III) chloride $[(OEP)Rh^{III}(Cl)]$ (**1**) (0.58 mM in C_6H_6) to a solution of $AgClO_4$ or $AgBF_4$ (slight molar excess in C_6H_6) at 50 °C for 2 h followed by further stirring of the resulting mixture at 25 °C for 48 h resulted in the formation of the phenyl-rhodium(III) derivative (**2a**) in yields of 40 (with $AgClO_4$) and 70% (with $AgBF_4$) after purification (Scheme 1). The product was unambiguously identified by comparison with authentic (**2a**) obtained by reaction (1) ($X = H$).[4]

$$[(OEP)Rh^{III}(Cl)] + p\text{-}X\text{-}C_6H_4Li \rightarrow [(OEP)Rh^{III}(p\text{-}C_6H_4X)] \quad (1)$$

The presence of a silver salt was essential for our reaction, and the formation of (**2a**) was completely inhibited by the presence of potentially donor co-solvents such as methanol, tetrahydrofuran, and pyridine, but not by dioxygen. Treatment of (**1**) with $AgClO_4$ in CH_2Cl_2 afforded the unstable perchlorate species in *ca.* 30% yield.† In an independent experiment, it was found that an isolated perchlorate species

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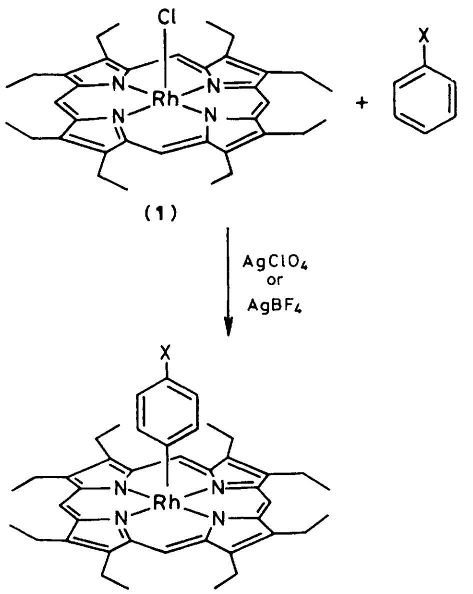
† The electronic spectrum is similar (λ_{max} 396, 513, and 548 nm) to that of (**1**) (λ_{max} 403, 520, and 554 nm) and the i.r. spectrum also is almost identical with that of (**1**) except for strong absorptions assignable to ClO_4^- in the range 1050—1160 cm^{-1}.



(2) a; X = H
b, X = OMe
c; X = Me
d; X = Cl

Scheme 1

attacks benzene to form (**2a**) without the participation of a silver salt.

Anisole, toluene, and chlorobenzene reacted similarly with (**1**) in the presence of $AgClO_4$ to give the corresponding aryl-rhodium(III) derivatives (**2b**—**d**) in yields of 46, 46, and 18%, respectively. Exclusive metallation at the *para*-positions of substituted arenes was evident from a comparison of the ^{1}H n.m.r. spectra of (**2b**—**d**) with those of (**2b**) and (**2c**) prepared by an alternative method [reaction (1)].‡

Competitive metallation reactions of X-C_6H_5 (X = H, OMe, Me, and Cl) show relative rate increases with increasing electron-donating abilities of the substituents: X (relative rate); OMe (1, standard), Me (0.15), H (0.014 after statistical correction for 6H), and Cl (0.0020). The logarithmic relative rates are correlated in the Hammett equation (r = 0.985) and give a ρ value of −5.32. Interestingly, the observed ρ value is comparable to that for the nitration of monosubstituted benzenes with the nitronium ion,[5] a typical example of electrophilic aromatic substitutions.

The large negative ρ value, coupled with the highly regioselective *para*-metallation,§ may characterize the present reaction as an (ionic) electrophilic aromatic metallation with an electrophilic intermediate generated from the reaction of (**1**) with silver salts. Similarly, mechanisms involving radical species can be ruled out. In particular, there is no evidence of isomers resulting from reaction at the *meta*-position, or of cleavage of potentially reactive methyl C–H bonds of toluene and anisole. The lack of an inhibitory effect by dioxygen provides additional evidence for the exclusion of radical mechanisms.

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‡ ^{1}H N.m.r. chemical shifts (δ/p.p.m. from Me_4Si in $CDCl_3$) for aromatic protons *ortho* and *meta* to rhodium: (**2b**), −0.44 (*o*) and *ca.* 4.1 (*m*, overlapping with CH_2CH_3); (**2c**), −0.43 (*o*) and 4.31 (*m*); (**2d**), −0.49 (*o*) and 4.43 (*m*).

§ The absence of an *ortho*-attack may be due to a steric effect.