

CH₂ bonded to ¹⁰³Rh (I = 1/2) and a singlet for CH₃ at higher magnetic fields due to the porphyrin ring-current effect.⁷ The silver salt assisted reactions of (OEP)Rh^{III}(Cl) with acetylacetone and ethyl acetoacetate were complete in 2-3 min and gave the corresponding metallation products (1 (R = COCH₃) and 1 (R = CO₂CH₂CH₃), eq 1) in 70 and 65% yields, respectively. ¹H NMR spectra indicated that the internal CH₂ was the site of metallation (Table I).

Table I. Yields and ¹H NMR Data for (OEP)Rh^{III}-CHRCOCH₃^a

R in <u>1</u>	yield (%)	¹ H NMR chemical shift ^b (integration)			
		Rh-CH	COCH ₃	CO ₂ CH ₂ CH ₃	CO ₂ CH ₂ CH ₃
H	50	-5.40 ^c (2H)	-2.31 (3H)		
COCH ₃	70	-4.50 ^c (1H)	-1.93 (6H)		
CO ₂ CH ₂ CH ₃	65	-4.50 ^c (1H)	-1.80 (3H)	0.89 (2H)	-0.16 (3H)

^a Spectra were taken for CDCl₃ solutions. ^b δ ppm. ^c d (J = 4 Hz).

The silver salt was essential for the present metallation of acetone. The role of ClO₄⁻ is that of a noncoordinating counteranion, thus accomodating vacant coordination sites and enhancing the electrophilicity of the central metal, as in the aromatic metallation with the same Rh(III) complex.⁵ It was confirmed independently that (OEP)Rh^{III}(ClO₄) or (OEP)Rh^{III}(BF₄), isolated from the reaction of (OEP)Rh^{III}(Cl) with AgClO₄ or AgBF₄,⁵ attacks acetone to form 1 (R = H) without the participation of a silver salt (eq 1).

REFERENCES AND NOTES

- (a) J. J. Doney, R. G. Bergman, and C. H. Heathlock, *J. Am. Chem. Soc.*, **107**, 3724 (1985); (b) Y. Ito, H. Aoyama, T. Hirao, A. Mochizuki, and T. Saegusa, *ibid.*, **101**, 494 (1979).
- R. Silverman and D. Dolphin, *J. Am. Chem. Soc.*, **98**, 4626, 4633 (1976).
- H. Ogoshi, J. Setsune, Y. Nanbo, and Z. Yoshida, *J. Organometal. Chem.*, **159**, 329 (1978).
- (a) A. Bigotto, G. Costa, G. Mestroni, G. Pellizer, A. Puxeddu, E. Reisenhofer, L. Stefani, and G. Tauzher, *Inorg. Chim. Acta Rev.*, **4**, 41 (1970); (b) M. E. Kastner and W. R. Scheidt, *J. Organometal. Chem.*, **157**, 109 (1978).
- (a) Y. Aoyama, T. Yoshida, K. Sakurai, and H. Ogoshi, *J. Chem. Soc., Chem. Commun.*, 478 (1983); (b) *idem.*, *Organometallics*, in press.
- The oxidative-addition reaction of bisdicarbonylrhodium(I) complex of porphyrin to a ketone C-H bond is known; A. M. Abeysekera, R. Grigg, J. Trocha-Grimshaw, and V. viswanatha, *J. Chem. Soc., Perkin I*, 1395 (1977).
- H. Ogoshi, J. Setsune, T. Omura, and Z. Yoshida, *J. Am. Chem. Soc.*, **97**, 6461 (1975).

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