Facile  $\alpha$ -Metallation of Ketone with a Rhodium Porphyrin Complex Under Mild Conditions

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Abstract: Acetone, acetylacetone, and ethyl acetoacetate undergo facile and direct metallation at the  $\alpha$ -positions of carbonyl groups with a cationic rhodium(III) porphyrin complex under mild conditions.

The organo-transition-metal species having an  $\alpha$ -metallocarbonyl or its tautomeric oxo- $\pi$ -allylmetal structure are important intermediates in synthetic reactions<sup>1</sup> and the biological dehydration of 1,2-diols catalyzed by vitamin  $B_{12}$  dependent dehydrases. A typical procedure for the preparation of this type of compounds involves the nucleophilic interaction of low-valent metal centers with  $\alpha$ -halo ketones.<sup>1a</sup> An alternative general method utilizes the electrophilic interaction of M(III) complexes (M = Co, Rh) with alkyl<sup>2,3</sup> or silyl enol ethers<sup>1b</sup> as activated ketone derivatives. The direct metallation of ketone, on the other hand, is a rather rare phenomenon; an example is the slow metallation of ketone with some cobalt complexes with one strongly basic axial ligand or under basic conditions.<sup>4</sup> We have been investigating the C-H activation under mild conditions.<sup>5</sup> We report here the facile and direct  $\alpha$ -metallation of ketone with a cationic rhodium(III) porphyrin complex.<sup>6</sup>

A solution of octaethylporphyrinatorhodium(III) chloride [(OEP)Rh<sup>III</sup>(Cl)] (0.6 mM) and AgClO<sub>4</sub> (0.8 mM) in dry acetone (50 ml) was stirred under nitrogen at 50°C for 20 min until no further change was observed in the visible spectra. Work-up and chromatography on alumina afforded the acetylmethyl-Rh(III) complex (1 (R = H), eq 1) in a yield of 50%. Its electronic spectrum (CH<sub>2</sub>Cl<sub>2</sub>) having  $\lambda_{max}$  at 391, 513, and 543 nm was typical of organorhodium OEP complexes<sup>7</sup> and its IR spectrum (KBr) showed  $v_{C=0}$  at 1675 cm<sup>-1</sup>. The convincing evidence for the structure came from the <sup>1</sup>H NMR spectrum showing a doublet (J = 4 Hz) for

$$(OEP) Rh^{III} (C1) \xrightarrow{AgClO_4} (OEP) Rh^{III} (ClO_4) \xrightarrow{RCH_2 - C - CH_3} (OEP) Rh^{III} - CH - C - CH_3 (1)$$

 $CH_2$  bonded to  ${}^{103}$ Rh (I = 1/2) and a singlet for  $CH_3$  at higher magnetic fields due to the porphyrin ring-current effect.<sup>7</sup> The silver salt assisted reactions of (OEP)Rh<sup>III</sup>(Cl) with acetylacetone and ethyl acetoacetate were complete in 2-3 min and gave the corresponding metallation products (<u>1</u> (R = COCH<sub>3</sub>) and <u>1</u> (R = CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), eq 1) in 70 and 65% yields, respectively. <sup>1</sup>H NMR spectra indicated that the internal CH<sub>2</sub> was the site of metallation (Table I).

R in <u>1</u>	yield (%)	<sup>1</sup> H NMR chemical shift <sup>b</sup> (integration)			
		Rh-CH	соснз	со <sub>2</sub> с <u>н</u> 2сн <sub>3</sub>	<sup>со</sup> 2 <sup>сн</sup> 2 <sup>сн</sup> 3
н	50	-5.40 <sup>C</sup> (2H)	-2.31 (3H)	<u>, ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,</u>	
COCH	70	-4.50 <sup>°</sup> (1H)	-1.93 (6Н)		
CO2CH2CH3	65	-4.50 <sup>°</sup> (1H)	-1.80 (3H)	0.89 (2H)	-0.16 (3H)
<sup>a</sup> Spectra	were taken	for CDCl, sol	utions. <sup>b</sup> δ	ppm. <sup>c</sup> d (J	J = 4 Hz).

Table I.	Yields and	<sup>⊥</sup> H NMR	Data for	(OEP) Rh <sup>III</sup> -CHRCOCH <sub>2</sub> <sup>a</sup>
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The silver salt was essential for the present metallation of acetone. The role of  $\text{ClO}_4$  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.<sup>5</sup> It was confirmed independently that (OEP)Rh<sup>III</sup>(ClO<sub>4</sub>) or (OEP)Rh<sup>III</sup>(BF<sub>4</sub>), isolated from the reaction of (OEP)Rh<sup>III</sup>(Cl) with AgClO<sub>4</sub> or AgBF<sub>4</sub>,<sup>5</sup> attacks acetone to form 1 (R = H) without the participation of a silver salt (eq 1).

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