# Oxidative Addition of CH<sub>3</sub>I and CO Migratory Insertion in a Series of Ferrocene-Containing Carbonyl Phosphine β-Diketonato Rhodium(I) Complexes

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A kinetic study of the oxidative addition reaction between CH<sub>3</sub>I and a series of ferrocene-containing  $\beta$ -diketonato carbonyl phosphine rhodium(I) complexes [Rh(FcCOCHCOR)(CO)(PPh\_3)], with R = CF\_3 (1),  $CH_3$  (2), Ph = phenyl (3), and Fc = ferrocenyl (4), showed that the mechanism consists of three definite sets of reactions involving isomers of at least two distinctly different classes of Rh<sup>III</sup>-alkyl and two different classes of Rh<sup>III</sup>-acvl species. The first reaction set involves oxidative addition itself, while the second and third reaction sets lead to different isomerization products involving carbonyl insertion or deinsertion in the Rh-CH<sub>3</sub> or Rh-COCH<sub>3</sub> bond. Second-order rate constants for the first oxidative addition step in CHCl<sub>3</sub> at 25 °C were  $k_i = 0.0061(1), 0.065(1), 0.077(2), \text{ and } 0.16(1) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for 1, 2, 3, and 4, respectively. The latter is the fastest reaction of this type reported to date for any  $[Rh(\beta$ diketonato)(CO)(PPh<sub>3</sub>)] complex. Activation parameters for all reactions from a variable temperature kinetic study resulted in 29  $\leq \Delta H^{\#} \leq 45$  kJ mol<sup>-1</sup> and  $-188 \leq \Delta S^{\#} \leq -116$  J mol<sup>-1</sup> K<sup>-1</sup>. Utilizing kinetic results from this and several previously reported studies involving 13 different [Rh( $\beta$ diketonato)(CO)(PPh<sub>3</sub>)] complexes, it was possible to quantify the relationship between  $[Rh(R^1COCHCOR^2)(CO)(PPh_3)]$  reactivity toward oxidative addition and the propensity of  $\beta$ -diketonato ligands to donate electrons to the Rh center as  $\ln k_1 = -3.14(\chi_{R1} + \chi_{R2}) + 10.0$ , where  $\chi_R$  is the group electronegativity on the Gordy scale of  $\beta$ -diketonato R groups. The pK<sub>a</sub> of the free  $\beta$ -diketone may be estimated from the relationship  $pK_a = -3.484(\chi_{R1} + \chi_{R2}) + 24.6$ .

## Introduction

The oxidative addition of  $CH_3I$  to rhodium(I) carbonyl centers is a fundamental process in organometallic chemistry with significant implications in catalysis, especially when followed by carbonyl insertion in a Rh-CH<sub>3</sub> bond to generate an acyl derivative, Rh-COCH<sub>3</sub>. A classic example of such a system is the oxidative addition of  $CH_3I$  to the  $[Rh(CO)_2(I)_2]^-$  catalyst in the Monsanto process of converting methanol to acetic acid.<sup>1</sup>

We have focused our attention on oxidative addition studies of [Rh<sup>I</sup>(R<sup>1</sup>COCHCOR<sup>2</sup>)(CO)(PPh<sub>3</sub>)] complexes. It is wellknown that electron-rich Rh<sup>I</sup> complexes undergo faster oxidative addition than electron-poor complexes.<sup>2</sup> The electron density on the Rh<sup>I</sup> center of a [Rh(R<sup>1</sup>COCHCOR<sup>2</sup>)(CO)(PR<sub>3</sub>)] complex can be manipulated by selecting R, R<sup>1</sup>, and R<sup>2</sup> groups, which are either electron-withdrawing or electron-donating. The CF<sub>3</sub> group with group electronegativity  $\chi_{CF_3} = 3.01$  represents an example of a very powerful electron-withdrawing group, while the ferrocenyl group is one of the strongest electron-donating groups having  $\chi_{Fc} = 1.87$  as measured on the Gordy scale.<sup>3</sup> Gordy scale  $\chi_R$  values are empirical numbers that express the combined tendency of not only one atom but a group of atoms, like CF<sub>3</sub> in the present  $\beta$ -diketones, to attract electrons (including those in a covalent bond) as a function of the number of valence electrons, *n*, and the covalent radius, *r* (in Å), of groups, as discussed elsewhere.<sup>4</sup>

Much interest is now devoted to the effects of the ancillary ligands on the rates of oxidative addition and migratory carbonyl insertion steps. Previous studies have described in detail the effect of electron-withdrawing R<sup>1</sup> and R<sup>2</sup> groups on the rate of oxidative addition of CH<sub>3</sub>I to [Rh(R<sup>1</sup>COCHCOR<sup>2</sup>)(CO)(PPh<sub>3</sub>)].<sup>5</sup> Only one report<sup>6</sup> exists on the effect of the highly electron-donating ferrocenyl group on the rate of oxidative addition. There, a study of the reaction between CH<sub>3</sub>I and the rhodium(I) carbonyl complex [Rh(FcCOCHCOCF<sub>3</sub>)(CO)(PPh<sub>3</sub>)] led to the following reaction sequence for the oxidative addition of CH<sub>3</sub>I to any  $\beta$ -diketonato complex of the type [Rh( $\beta$ -diketonato)(CO)-(PPh<sub>3</sub>)].<sup>6</sup>

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This reaction sequence proved to be a completely general mechanism, with all previously reported mechanisms just being a simplification of eq 1 that is controlled by the size of  $k_i$ , where  $i = \pm 4, \pm 3, \pm 2$ , or  $\pm 1$ . The end scripts 1 and 2 in Rh<sup>III</sup>-alkyl1, Rh<sup>III</sup>-acyl1, Rh<sup>III</sup>-alkyl2, and Rh<sup>III</sup>-acyl2 denote the first- or second-formed alkyl or acyl species during the course of the reaction. In addition, two geometrical isomers of the Rh<sup>I</sup> and each of the four Rh<sup>III</sup> species were detected by <sup>1</sup>H NMR spectroscopy. The equilibrium between the two Rh<sup>I</sup> isomers has been discussed in detail;<sup>7</sup> the single-crystal X-ray-determined structures of [Rh<sup>I</sup>(FcCOCHCOCF<sub>3</sub>)(CO)(PPh<sub>3</sub>)]<sup>8</sup> and [Rh<sup>III</sup>-(FcCOCHCOCF<sub>3</sub>)(CO)(PPh<sub>3</sub>)(CH<sub>3</sub>)(I)], an isomer of a Rh<sup>III</sup>alkyl2 species,<sup>6</sup> have been reported; and the solution geometry of a Rh<sup>III</sup>-alkyl1 intermediate isomer, [Rh(PhCOCHCOTh)- $(CO)(PPh_3)(CH_3)(I)$ ] with Th = thienyl = C<sub>4</sub>H<sub>3</sub>S, has been determined by NMR techniques.9 Density functional theoretical (DFT) computations of the equilibrium geometry of the 12 possible [Rh<sup>III</sup>(RCOCHCOTh)(CO)(PPh<sub>3</sub>)(CH<sub>3</sub>)(I)]-alkyl reaction products ( $R = CF_3$ , Ph, or Th) revealed that the first alkyl1 product results from trans addition to Rh<sup>I</sup> and that the second thermodynamic stable alkyl2 product adopts an octahedral geometry with the PPh<sub>3</sub> group and the iodide above and below the square planar plane.  $^{10}$ 

We report here on the reactivity toward oxidative addition of a series of ferrocene-containing [Rh(FcCOCHCOR)(CO)(P-Ph<sub>3</sub>)] complexes where the R group on the  $\beta$ -diketonato ligand is successively replaced with more electron-donating groups CF<sub>3</sub>, CH<sub>3</sub>, Ph, and Fc. We also unify our own studies and that of previous studies for the first time in a mathematical model to predict the reactivity of [Rh(R<sup>1</sup>COCHCOR<sup>2</sup>)(CO)(PPh<sub>3</sub>)] complexes toward oxidative addition by relating electron density of the Rh<sup>I</sup> center expressed in terms of the sum of R<sup>1</sup> and R<sup>2</sup> group electronegativities,  $\chi_{R1} + \chi_{R2}$ , with kinetic rate constants irrespective of whether R<sup>1</sup> and R<sup>2</sup> are electron-withdrawing or electron-donating. Finally, utilizing present structural knowledge obtained from single-crystal X-ray structure determinations, structural NMR experiments, and density functional theory structure optimizations on related complexes, the geometry of intermediates in the complete reaction sequence is proposed.

#### **Results and Discussion**

To determine how different Rh<sup>I</sup> electron densities in mixedmetal ferrocene-containing  $\beta$ -diketonato complexes influence the rate of oxidative addition of CH<sub>3</sub>I to [Rh(FcCOCHCOR)-(CO)(PR<sub>3</sub>)] complexes, we focused our attention on the complexes shown in Figure 1. Rh<sup>I</sup> electron densities were manipulated by choosing  $\beta$ -diketonato R groups, which are highly electron-withdrawing (complex 1), highly electrondonating (4), or intermediate in electron-withdrawing nature (complexes 2 and 3). We have previously shown that a measure of the relative electron density on a molecule due to a ligand or a particular molecular side group on a molecule can be expressed as the sum of group the electronegativities  $\chi_R$  of the



**Figure 1.** Electron density of the Rh<sup>I</sup> nucleus is a function of R side groups on the  $\beta$ -diketonato ligand. The Rh<sup>I</sup> nucleus of **4** is much more electron-rich than that of any other complex studied herein by virtue of the smaller group electronegativity,  $\chi_{\rm R}$ , of the ferrocenyl group.

relevant R groups.<sup>3a,11</sup> When applied to the present series of complexes, the change in electron density of the Rh<sup>I</sup> center in 1–4 as a result of changes in the  $\beta$ -diketonato ligand should be a function of  $\chi_{\rm R} + \chi_{\rm Fc}$ , where R and Fc are the pendant side groups of the  $\beta$ -diketonato ligand. Should the Fc group be replaced by another group, say R<sup>2</sup>, then the change in the electron density of the Rh<sup>I</sup> center should be a function of  $\chi_{\rm R} + \chi_{\rm R2}$ .

The complete reaction between all of the [Rh(FcCOCHCOR)-(CO)(PPh<sub>3</sub>)] complexes 1-4 and CH<sub>3</sub>I proceeds via three sets of reactions according to eq 1. However, each individual complex exhibits small mechanistic variations due to the size of especially  $k_1$  and  $k_2$ . The first of the three sets of reactions for all four complexes involves the oxidative addition of CH<sub>3</sub>I to the Rh<sup>I</sup> center to form an easily observable intermediate Rh<sup>III</sup>alkyl1 complex followed by a near simultaneous CO migratory insertion to yield the corresponding Rh<sup>III</sup>-acyl1 complex according to eq 2.

First set of reactions
$$Rh^{I} + CH_{3}I$$
 $k_{1}$  $[Rh^{III}-alkyl1]$  $K_{2}, k_{2}$  $[Rh^{III}-acyl1]$ (2)oxidative  
additionCO insertion

The Rh<sup>III</sup>-alkyl and Rh<sup>III</sup>-acyl reaction products for the first set of reactions are distinguished from later-formed, second Rh<sup>III</sup>-alkyl and Rh<sup>III</sup>-acyl reaction products by the nomenclature Rh<sup>III</sup>-alkyl1 and Rh<sup>III</sup>-acyl1 as opposed to Rh<sup>III</sup>-alkyl2 and Rh<sup>III</sup>-acyl2. The Rh<sup>III</sup>-alkyl1 and Rh<sup>III</sup>-acyl1 complexes were identified by IR and NMR spectroscopy. IR spectroscopy can clearly differentiate the various species observed in these reactions. Thus, terminal Rh(I) carbonyls, terminal Rh(II) carbonyls, and Rh(III) acyl complexes reveal characteristic bands in the 1980–2000, 2050–2100, and 1700–1750 cm<sup>-1</sup> regions, respectively. IR spectroscopy is ideal to distinguish between CO groups that vibrate at ~1980–2000 cm<sup>-1</sup> in Rh<sup>II</sup>-carbonyl complexes, at ~2050–2100 cm<sup>-1</sup> for Rh<sup>III</sup>-alkyl-carbonyl complexes that resonate at ~1700–1750 cm<sup>-1</sup> for Rh<sup>III</sup>-COCH<sub>3</sub> complexes.

Figure 2a illustrates the course of the first set of reactions for the oxidative addition of CH<sub>3</sub>I to **2** in chloroform as monitored by IR spectroscopy in the range 1690–2140 cm<sup>-1</sup>. The disappearance of the Rh<sup>1</sup>-carbonyl complex [signal at 1983 cm<sup>-1</sup> in CHCl<sub>3</sub>; observed pseudo first-order rate constant  $k_{obs}$ = 0.0038(1) s<sup>-1</sup>] shows that the first step of the reaction leads to the formation of a Rh<sup>III</sup>-alkyl1 species [peak at 2077 cm<sup>-1</sup>,  $k_{obs}$  = 0.0056(2) s<sup>-1</sup>] followed by the near simultaneous

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**Figure 2.** Infrared monitoring of the oxidative addition of CH<sub>3</sub>I (0.0517 mol dm<sup>-3</sup>) to [Rh(FcCOCHCOCH<sub>3</sub>)(CO)(PPh<sub>3</sub>)] (0.0068 mol dm<sup>-3</sup>) in chloroform (T = 25.0 °C). The inserts give the absorbance vs time data of the indicated species. (a) The first set of reactions: Rh<sup>II</sup> + CH<sub>3</sub>I  $\Rightarrow$  {Rh<sup>III</sup>-alkyl1  $\Rightarrow$  Rh<sup>III</sup>-acyl1}. Here, the formation of the Rh<sup>III</sup>-alkyl1 species [ $k_1 = 0.100(3) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ] is followed by the formation of the Rh<sup>III</sup>-alkyl1 complex at a slower rate [ $k_1 = 0.032(1) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ]. The two products are actually in equilibrium with each other, although the equilibrium is too slow to be maintained on the time scale of the first reaction set. (b) The second set of reactions: {Rh<sup>III</sup>-alkyl1  $\Rightarrow$  Rh<sup>III</sup>-alkyl2  $\Rightarrow$  Rh<sup>III</sup>-alkyl3  $\Rightarrow$  Rh<sup>III</sup>-A

formation of the Rh<sup>III</sup>-acyl1 species at a slightly slower rate [peak at 1719 cm<sup>-1</sup>,  $k_{obs} = 0.0018(2) \text{ s}^{-1}$ ] as a result of CO insertion. The rate of formation of the Rh<sup>III</sup>-alkyl1 species at 2077 cm<sup>-1</sup> was slightly higher than the rate of disappearance of Rh<sup>I</sup>, but they are close enough to each other to be considered kinetically equivalent. The observed slower rate of Rh<sup>III</sup>-acyl1 appearance is considered to imply that the equilibrium involving the carbonyl insertion step, that is, the  $k_2$  and  $k_{-2}$  steps in eq 2, is too slow to be maintained during the oxidative addition of CH<sub>3</sub>I to Rh<sup>I</sup>. Compelling evidence that the carbonyl insertion step involves an equilibrium will be forthcoming from the discussion below involving the second general reaction step. Figure 2d illustrates  $k_{obs}$  for the first set of reactions involving 2 as a function of CH<sub>3</sub>I concentration. The Rh<sup>I</sup> disappearance represents the  $k_1$  step and the Rh<sup>III</sup>-acyl1 appearance the  $k_2$  step in eq 2. Because the graph of  $k_{obs}$  for the Rh<sup>I</sup> disappearance vs [CH<sub>3</sub>I] passes through the origin,  $k_{-1}$  is about 0 for **2**. Secondorder rate constants for the first oxidative addition step,  $k_1 =$  $k_{obs}$ /[CH<sub>3</sub>I], are summarized in Table 1.

The same reaction sequence for the first set of reactions for **2**, as observed by IR, was also observed by <sup>1</sup>H NMR and <sup>31</sup>P NMR spectroscopy. Rh<sup>III</sup>-alkyl complexes of the type [Rh( $\beta$ -diketonato)(CO)(PPh<sub>3</sub>)(CH<sub>3</sub>)(I)] can inter alia unambiguously be identified by the <sup>1</sup>H NMR resonance signal of the CH<sub>3</sub> group at ca. 1.4–1.7 ppm. This signal is a doublet of doublets due to coupling with Rh (spin 1/2) and P (spin 1/2). Rh<sup>III</sup>-acyl complexes of the type [Rh( $\beta$ -diketonato)(COCH<sub>3</sub>)(PPh<sub>3</sub>)(I)] can conveniently be identified by the sharp <sup>1</sup>H NMR resonance

signal of the acyl CH<sub>3</sub>-group at ca. 3 ppm.<sup>12</sup> By carefully comparing the positions and integrals of the different signals in the course of the reaction as followed by <sup>1</sup>H NMR, the spectral parameters of different reaction products could be identified, and their appearance and disappearance could be monitored as a function of time. The new feature introduced by the NMR study is the existence of two structural isomers for each reaction intermediate, referred to as A and B, for example, Rh<sup>III</sup>-alkyl1A and Rh<sup>III</sup>-alkyl1B in fast equilibrium with each other. The choice of the labels is arbitrary and has no significance. These isomers are expected, since the Rh<sup>1</sup> complexes also exist as two structural isomers in a fast equilibrium with each other.<sup>7</sup> The equilibria are labeled "fast" as compared to the half-life of each of the three reaction steps, but it is slow on the NMR time scale. This enabled us to observe them by  ${}^{1}H$ NMR. The ratio between the two structural isomers A and B of each reaction intermediate, the  $K_c$  values as indicated in the reaction scheme in Figure 3 and tabulated in Table 2, did not change during the course of each reaction step, implying that the two isomers of each reaction intermediate exist in a fast equilibrium with each other.

Figure 3 illustrates selected <sup>1</sup>H NMR signals of the reaction products of the reaction between  $CH_3I$  and **2**. The appearance and disappearance of these and other signals gave kinetic data in agreement with IR data; see Table 1 and Figure 2d for the combined IR and <sup>1</sup>H NMR data for the first set of reactions.

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			first set of reactions			second set of reactions		third set of n	eactions
complex	method	Rh <sup>I</sup> disappearance $k_1$ ( dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	Rh <sup>III</sup> -alkyl1 formation $k_1$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	$\frac{\text{Rh}^{\text{III}}\text{-acyll}}{\text{formation }k_2}$	Rh <sup>III</sup> -alkyl1 disappearance $10^4 k_3$ $(s^{-1})$	Rh <sup>III</sup> -acyl1 disappearance $10^4 k_3$ $(s^{-1})$	$\frac{\text{Rh}^{\text{III}}\text{-alkyl2}}{\text{formation 10}^4 k_3}$	Rh <sup>III</sup> -alkyl2 disappearance $10^{6} k_{4}$	$\frac{\text{Rh}^{\text{III}}\text{-acyl2}}{\text{formation 10}^6 k_4}$
$1: R = CF_{2}^{b}$	IR	0.0062(3)	0.0061(3) <sup>d</sup>	0.0061(5)	1.7(1)	1:7(1)	1.7(3)	4.9(5)	4.4(2)
	<sup>1</sup> H NMR	0.005(1)	0.007(1)	0.007(1)	1.2(1)	1.1(1)	1.2(1)	5.0(6)	
	<sup>31</sup> P NMR	0.0052(2)	0.0062(2)	0.0056(2)	1.2(1)	1.2(1)	1.4(1)	~	
	UV/vis	0.00611(1)			1.7(2)	n.		4.4(1)	
<b>2</b> : $\mathbf{R} = \mathbf{CH}_{3^g}$	IR	0.065(2)	0.100(3)	0.032(1)	1.0(1)	0.9(1)	0.8(1)	7(5)	4(1)
	<sup>1</sup> H NMR	0.061(3)	0.099(4)	0.030(2)	0.5(1)	0.6(1)	0.7(1)	5(1)	6(2)
	<sup>31</sup> P NMR			0.04(1)	0.8(2)	0.8(2)			
	UV/vis	0.065(1)			0.87(5)			7.7(5)	
3: $R = Ph^g$	IR	0.066(3)	0.130(3)	0.030(2)	1.0(1)	1.3(6)	1.2(4)	6(1)	5(2)
	<sup>1</sup> H NMR	0.07(2)			1.5(3)	1.5(3)	1.5(3)	8(2)	9(3)
	UV/vis	0.077(2)			1.2(1)			4.8(9)	
<b>4</b> : $\mathbf{R} = Fc^{g}$	IR	0.155(4)	0.252(4)	0.037(2)	1.4(3)	1.5(5)	1.4(3)	12(1)	10(4)
	<sup>1</sup> H NMR	0.16(1)	0.17(1)	0.038(4)					
	UV/vis	0.157(2)			1.3(1)			1.8(2)	

Oxidative addition of  $CH_3I$  to 1, 3, and 4 observed by <sup>1</sup>H NMR all followed the same reaction patterns as 2 given by eq 2, and the results are summarized in Table 1.

<sup>31</sup>P NMR of carbonyl phosphine rhodium complexes gives a doublet with  ${}^{1}J({}^{31}P-{}^{103}Rh) = ca. 170 \text{ ppm}$  (ca. 0.70 Hz) for Rh<sup>I</sup> complexes, ca. 120 ppm (ca. 0.50 Hz) for Rh<sup>III</sup>-alkyl complexes, and ca. 150 ppm (ca. 0.60 Hz) for Rh<sup>III</sup>-acyl complexes.<sup>9,12,13</sup> When following the oxidative addition reaction of CH<sub>3</sub>I to 2, two structural isomers of RhI and each RhIII reaction intermediate according to eq 2 are observed, giving kinetic data in agreement with <sup>1</sup>H NMR and IR data; see Figure 4 and Table 1.

Comparison of the influence of different side groups on the  $\beta$ -diketonato ligands of 1–4 showed that complex 4 reacted the fastest; Rh<sup>I</sup> disappeared ca. 30 times faster in 4 than in 1 (Table 1). Only **1** reacted slow enough that the equilibrium  $K_2$ (eq 2) could be maintained during Rh<sup>I</sup> disappearance, because only for 1 was the rate of Rh<sup>III</sup>-alkyl1 and Rh<sup>III</sup>-acyl1 formation equal. Rh<sup>1</sup> disappearance was ca. 10 times faster for 2 than for 1 and 12 times faster for 3 than for 1. It is clear from these results that the reactivity toward oxidative addition of the [Rh(FcCOCHCOR)(CO)(PPh<sub>3</sub>)] complexes is in the order (halflives in seconds of the first reaction with  $[CH_3I] = 1.000$  mol dm<sup>-3</sup> are given in brackets):

## $R = Fc(4) > Ph(9) \approx CH_3(11) > CF_3(114)$

The faster reaction rate of complexes 2-4 as compared to 1 resulted in the conclusion that in none of these three complexes could equilibrium  $K_2$  be maintained during Rh<sup>I</sup> disappearance because for all three of these complexes, Rh<sup>III</sup>-acyl1 formation was noticeably slower than Rh<sup>III</sup>-alkyl1 formation. For 4, the difference was the greatest with Rh<sup>III</sup>-acyl1 formation, almost seven times slower than Rh<sup>III</sup>-alkyl1 formation (IR data, Table 1). However, that Rh<sup>III</sup>-acyl1 and Rh<sup>III</sup>-alkyl1 is indeed involved in an equilibrium, stems clearly from the results involving the second reaction sequence that is described in the next paragraph.

The 30-fold variation in rate constants for the first reaction sequence is directly a consequence of the group electronegativity of the  $\beta$ -diketonato R groups influencing the electron density on the  $Rh^{I}$  nucleus of 1–4. To independently verify that the Rh<sup>I</sup> nucleus of 1–4 becomes more electron-rich as  $\chi_R$  decreases, we note from Table 2 that the decreasing  $\chi_R$  values<sup>3</sup> from 3.01 (complex 1) to 1.87 (complex 4) led to a decrease in [Rh(Fc-COCHCOR)(CO)(PPh<sub>3</sub>)] infrared carbonyl stretching wavenumber from v = 1986 till 1977 cm<sup>-1</sup>. This lowering in  $v_{co}$  is consistent with a more electron-rich Rh<sup>I</sup> center and explains the increase in oxidative addition reaction rate in moving from 1 to 4.

The second set of reactions as observed by IR and NMR spectroscopy involves a much slower ( $t_{1/2} \approx 4$  h for 2) CH<sub>3</sub>Iindependent CO deinsertion of the Rh<sup>III</sup>-acyl1 to yield a new Rh<sup>III</sup>-alkyl2 according to eq 3:

$$\left\{ [Rh^{III}-alky11] \underbrace{K_2, k_2}_{k_{-2}} [Rh^{III}-acy11] \right\} \underbrace{k_3}_{k_{-3}} [Rh^{III}-alky12]$$
(3)  
CO deinsertion

This second, slower set of reactions as observed by IR spectroscopy is illustrated in Figure 2b for 2. Here, the Rh<sup>III</sup>alkyl1 species at 2077 and the Rh<sup>III</sup>-acyl1 species at 1719 cm<sup>-1</sup> start to disappear at the same rate  $[k_3 = 4.4(2) \times 10^{-5} \text{ s}^{-1}$  and  $5(1) \times 10^{-5} \text{ s}^{-1}$ , respectively] with the simultaneous formation of a second alkyl product, the Rh<sup>III</sup>-alkyl2 species at 2059 cm<sup>-1</sup>—also at approximately the same rate  $[k_3 = 7.1(4) \times 10^{-5}]$ 



**Figure 3.** Selected  $\beta$ -diketonato methine (at ~5.8 ppm) and CH<sub>3</sub> <sup>1</sup>H NMR peaks in CDCl<sub>3</sub> of the indicated reactants and products during the three sets of reactions for the oxidative addition of 0.2034 mol dm<sup>-3</sup> CH<sub>3</sub>I to 0.01918 mol dm<sup>-3</sup> [Rh(FcCOCHCOCH<sub>3</sub>)(CO)(PPh<sub>3</sub>)] in CDCl<sub>3</sub> at 25.0 °C. Signals for two geometrical isomers for each reaction intermediate can be identified.

Table 2. Rate and Equilibrium Constants Applicable to the Equation in Figure 3 for the Oxidative Addition of CH<sub>3</sub>I to[Rh(FcCOCHCOR)(PPh\_3)(CO)] at 25 °C in Chloroform<sup>a</sup>

complex	χr	$v_{\rm co}({\rm cm}^{-1})$	$pK_a$ of $\beta$ -diketone <sup>b</sup>	$\frac{k_1 (\mathrm{dm}^3 }{\mathrm{mol}^{-1} \mathrm{s}^{-1}})$	$\frac{\Delta H^{\#}}{(k_1) \text{ (kJ mol}^{-1})}$	$\frac{\Delta S^{\#}}{(k_1) \text{ (J mol}^{-1} \text{ K}^{-1})}$	$10^4 k_3 (s^{-1})$	$\frac{10^6}{k_4 \ (s^{-1})}$	K <sub>c1</sub>	K <sub>c2</sub>	K <sub>c3</sub>	K <sub>c4</sub>	K <sub>c5</sub>
<b>1</b> : $R = CF_3^c$	3.01	1986	6.56	0.00611(1)	29(3)	-188(9)	1.7(2)	4.4(1)	0.68	2.57	1.00	4.56	d
<b>2</b> : $R = CH_3$	2.34	1980	10.01	0.065(1)	40(2)	-133(5)	0.87(5)	7.7(5)	0.22	0.52	2.13	0.82	1.50
<b>3</b> : R = Ph	2.21	1977	10.41	0.077(2)	45(1)	-116(4)	1.2(1)	4.8(9)	0.56	0.48	1.52	0.83	*
4: R = Fc	1.87	1977	13.10	0.157(2)	33.6(7)	-147(2)	1.3(1)	18(2)	е	е	е	е	е

<sup>*a*</sup> Experimentally,  $k_{-1} = k_{-3} = k_{-4} \approx 0$ , except for the CF<sub>3</sub> complex, where  $k_{-1} = 0.0005 \text{ s}^{-1}$ .  $K_{ci} = [\text{RhB species}]/[\text{RhA species}]$  with i = 1, 2, ..., 5 were determined from NMR data. <sup>*b*</sup> From ref 3a. <sup>*c*</sup> Data from ref 6. <sup>*d*</sup> Not determined. <sup>*e*</sup> Only one isomer.



**Figure 4.** <sup>31</sup>P NMR spectra illustrating doublet <sup>31</sup>P peaks of the indicated reactants and products during the three reaction sets for the oxidative addition of 0.500 mol dm<sup>-3</sup> CH<sub>3</sub>I to 0.018 mol dm<sup>-3</sup> [Rh(FcCOCHCOCH<sub>3</sub>)(CO)(PPh<sub>3</sub>)] in CDCl<sub>3</sub> at T = 25 °C and times (a) t = 0, (b) t = 1753 s (toward the end of the first reaction set), and (c) t = 7925 s (during the second reaction set).

s<sup>-1</sup>]. This observation, that the Rh<sup>III</sup>-alkyl1 species disappears at the same rate as the Rh<sup>III</sup>-acyl1 species, supplies strong evidence that an equilibrium exists between the Rh<sup>III</sup>-alkyl1 and the Rh<sup>III</sup>-acyl1 species. The equilibrium is clearly fast enough to be maintained on the time scale of the Rh<sup>III</sup>-alkyl2 formation but still slow enough on the NMR time scale to observe both species. Surprisingly, the second reaction sequence is almost independent of R group on the  $\beta$ -diketonato ligands of **1**–**4**. A variation of barely a factor of 2 was observed in the rate constants of this CH<sub>3</sub>I-independent reaction step; see Table 1.

Because of the long half-life of the second (and third,  $t_{1/2} \approx$  4 and 48 h for **2**, respectively) set of reactions in contrast to the

fast first set of reactions, the Rh<sup>III</sup>-alkyl2 products of 1-4 could be isolated and have previously been characterized.<sup>7</sup> X-ray crystallography revealed that the CF<sub>3</sub>-containing Rh<sup>III</sup>-alkyl2 product of **1** adopts an octahedral geometry with the PPh<sub>3</sub> group and the iodide above and below the square planar plane.<sup>6</sup> Theoretical DFT calculations of the equilibrium geometry of the possible reaction products of complexes of the type [Rh(ThCOCHCOR)(CO)(PPh<sub>3</sub>)] with Th = thionyl and R = Ph, CF<sub>3</sub>, or Th revealed that the Rh<sup>III</sup>-alkyl1 product results from

<sup>(13)</sup> Conradie, M.; Conradie, J. Inorg. Chim. Acta 2008, 361, 208.

trans CH<sub>3</sub>I addition to Rh<sup>I</sup>, that is, with the CH<sub>3</sub> group and the iodide above and below the square planar plane.<sup>10</sup>

The third set of reactions as observed by IR and NMR methods involves a very slow CO migratory insertion ( $t_{1/2} \approx$  48 h for **2**) to yield a new Rh<sup>III</sup>-acyl2 complex according to eq 4:

Third set of reactions
$$[Rh^{III}-alkyl2]$$
 $\overbrace{k_4}^{k_4}$  $[Rh^{III}-acyl2]$ CO insertion

(4)

This third, very slow set of reactions is illustrated in Figure 2c for the IR monitoring of **2** and demonstrates the slow disappearance of the Rh<sup>III</sup>-alkyl2 species  $[k_4 = 5(2) \times 10^{-6} \text{ s}^{-1}]$  at 2059 cm<sup>-1</sup> and the appearance at approximately the same rate of a new Rh<sup>III</sup>-acyl2 species at 1714 cm<sup>-1</sup>  $[k_4 = 3(1) \times 10^{-6} \text{ s}^{-1}]$ . The long half-life of this reaction implies that it could not be followed with great accuracy due to, for example, evaporation problems of the solvent.

As was found for reaction set 2, the variation in  $\beta$ -diketonato R groups had almost no influence on the isomerization rate constant  $k_4$  associated with reaction set 3 (Table 1). At most, in moving from 1 to 4,  $k_4$  increased 4-fold. This contrasts sharply with  $k_1$  of reaction set 1, which increased 30-fold in moving from 1 to 4.

UV/vis results of the oxidative addition of  $CH_3I$  to 1-4 also show all three general reaction steps with reaction rates in accordance with the IR and NMR results. Figure 5a illustrates the absorbance-time data of the oxidative addition of CH<sub>3</sub>I to complex 2. All three reactions could be followed at 493 nm. The second reaction, however, underwent a small change in absorbance at 493 nm (due to the influence of the third reaction) as opposed to the large change in absorbance at 410 nm. Reliable  $k_3$  values could be determined at 410 nm, because of the large change in absorbance for the second reaction at this wavelength and the small change in absorbance for the third reaction and because the first step is more than 70 times slower than the rate of the second reaction steps. The first reaction step represents the oxidative addition process whereby the Rh<sup>I</sup> nucleus converts to the Rh<sup>III</sup>-alkyl1 reaction intermediate in equilibrium with the Rh<sup>III</sup>-acyl1 reaction intermediate. The second reaction step represents formation of the Rh<sup>III</sup>-alkyl2 reaction intermediate, and the third reaction step represents formation of the final Rh<sup>III</sup>acyl2 reaction product. Plots of  $k_{obs}$  for the first reaction of 1-4vs [CH<sub>3</sub>I] are linear (see, for example, Figure 5b for 4), indicating the reaction to be first order in CH<sub>3</sub>I and hence second order overall. The second and third reactions followed by UV/ vis spectrophotometer are independent of [CH<sub>3</sub>I]; see, for example, Figure 5c for the second reaction of 4. The obtained rate constants are listed in Table 2. The activation entropies (Table 2) for the first oxidative addition step were determined from a variable temperature (15-40 °C) study. They are all large and negative, as frequently found for oxidative addition of CH<sub>3</sub>I to square planar d<sup>8</sup> metal complexes,<sup>14</sup> which is generally thought to proceed via an S<sub>N</sub>2 mechanism.<sup>15</sup>

Taking into account that two main isomers exist for each reactant and reaction product, the complete reaction sequence for the oxidative addition of  $CH_3I$  to 1-4 can be presented by



**Figure 5.** (a) Absorbance vs time data for the UV monitoring of the reaction between 0.0004 mol dm<sup>-3</sup> [Rh(FcCOCH-COCH<sub>3</sub>)(CO)(PPh<sub>3</sub>)], **2**, and 0.0942 mol dm<sup>-3</sup> CH<sub>3</sub>I at 493 and 410 nm. (b) Temperature and CH<sub>3</sub>I concentration dependence of the oxidative addition reaction of CH<sub>3</sub>I to [Rh(FcCOCHCOFc)-(CO)(PPh<sub>3</sub>)], **4**, as monitored by UV/vis spectrometry in chloroform at 525 nm for the first reaction Rh<sup>I</sup> + CH<sub>3</sub>I  $\Rightarrow$  {Rh<sup>III</sup>-alkyl1  $\Rightarrow$ Rh<sup>III</sup>-acyl1} and (c) at 525 and 380 nm for the second reaction {Rh<sup>III</sup>-alkyl1  $\Rightarrow$  Rh<sup>III</sup>-acyl1}  $\Rightarrow$  Rh<sup>III</sup>-alkyl2.

Scheme 1. In Scheme 1, the proposed molecular geometries of the  $Rh^{III}$  products are based on single-crystal X-ray crystallographic, NMR, and DFT computational chemistry studies either on 1-4 themselves or on related complexes that react

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<sup>(15)</sup> Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; W.B. Saunders Company: Philadelphia, 1977; pp 938–948.

Scheme 1. Proposed Geometries in the Reaction Sequence<sup>*a*</sup>



# $R = CF_3$ , $CH_3$ , Ph or Fc

<sup>*a*</sup> The proposed geometries stem from the following information. Rh<sup>1</sup> isomers: The single-crystal X-ray structure of one of the isomers of **1** was solved and discussed in ref 8. Rh<sup>III</sup>-alkyl1 isomers: Geometry proposed in analogy to the geometries of [Rh(TfCOCHCOR)(CO)(PPh<sub>3</sub>)] with Tf = thionyl and R = Ph, CF<sub>3</sub>, or Tf that were obtained by solution NMR techniques and DFT calculations.<sup>9,10</sup> Rh<sup>III</sup>-acyl1 isomers: Only a possible geometry; no corresponding structure or geometry for any related  $\beta$ -diketonato complex has to date been determined by any technique. Rh<sup>III</sup>-alkyl2 isomers: One of the alkyl2 isomers of **1** was crystallographically characterized.<sup>6</sup> Rh<sup>III</sup>-acyl2 isomers: Proposed geometries are in analogy to the geometries of products of oxidative addition of CH<sub>3</sub>I to [Rh(ThCOCHCOR)(CO)(PPh<sub>3</sub>)] and [Rh(FcCOCHCOCF<sub>3</sub>)(CO)(PPh<sub>3</sub>)]; these were determined by DFT calculations.<sup>10,16</sup>



**Figure 6.** Some [Rh( $\beta$ -diketonato)(CO)(PPh<sub>3</sub>)] complexes with their CH<sub>3</sub>I oxidative addition rate constants (25 °C in CH<sub>3</sub>Cl except for **5–7** and **10**, which are measured in acetone). In **12** and **13**, R is either  $\beta$ -diketonato pendant substituent CH<sub>3</sub> or thionyl, C<sub>4</sub>H<sub>3</sub>S. Rate constants are from refs 6, 9, 13, and 17.

according to the same general reaction sequence as the ferrocenyl-containing rhodium complexes of this study.<sup>6,7,10,16</sup>

In an attempt to quantify the oxidative addition rate constants of a series of complexes [Rh(R<sup>1</sup>COCHCOR<sup>2</sup>)(CO)(PPh<sub>3</sub>)] in terms of group electronegativity,  $\chi_R$ , reaction rate constants of **1–4** were compared with those obtained for the related complexes<sup>6,9,13,17</sup> shown in Figure 6.

Because the Rh(I) nucleus acts as a nucleophile when it undergoes oxidative addition, it is to be expected that anything that affects the nucleophilicity (or electron-richness) of the central coordinating metal will influence the rate of oxidative addition reactions. Thus, any ligand bonded to the metal that will increase the electron density on the metal center will lead to an increased rate of oxidative addition, assuming all other influences, factors, and parameters remain constant. In the present series of  $\beta$ -diketonato ligands, the capability of the ligand to manipulate the electron density on the metal is considered a

function of group electronegativity,  $\chi_{\rm R}$ , of the  $\beta$ -diketonato R groups. Figure 7 illustrates that the sum of the group electronegativities of  $R^1$  and  $R^2$  of the  $\beta$ -diketonato ligand (R<sup>1</sup>COCHCOR<sup>2</sup>)<sup>-</sup> coordinated to [Rh(R<sup>1</sup>COCHCOR<sup>2</sup>)(CO)-(PPh<sub>3</sub>)] is linearly dependent on  $\ln k_1$ ,  $k_1$  being the second-order rate constant for the oxidative addition of CH<sub>3</sub>I to these rhodium complexes. The sum of the group electronegativities of R<sup>1</sup> and  $R^2$  of the  $\beta$ -diketonato ligand ( $R^1COCHCOR^2$ )<sup>-</sup> coordinated to complexes of the type [Rh(R<sup>1</sup>COCHCOR<sup>2</sup>)(CO)(PPh<sub>3</sub>)] therefore gives a good indication of the electron density (nucleophilicity) of rhodium in each complex. The effect of the  $pK_a$ value of the various  $\beta$ -diketones on the oxidative addition reaction rate is also shown in Figure 7. A lower  $pK_a$  value implies that the  $\beta$ -diketonato ligand will remove electron density from the Rh nucleus, making it a weaker nucleophile and thus less reactive toward oxidative addition. The relationship between  $pK_a$  and  $(\chi_{R1} + \chi_{R2})$  should thus also be linear, and this effect is demonstrated in Figure 7c.

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<sup>(17) (</sup>a) Basson, S. S.; Leipoldt, J. G.; Roodt, A.; Venter, J. A.; van der Walt, T. J. *Inorg. Chim. Acta* **1986**, *119*, 35. (b) Lamprecht, D. Electro-chemical, kinetic and molecular mechanic aspects of rhodium(I) and rhodium(III) complexes. Ph.D. Thesis, University of the Orange Free State R.S.A., 1998.

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<sup>(19)</sup> Ellinger, M.; Duschner, H.; Starke, K. J. Inorg. Nucl. Chem. 1978, 40, 1063.



**Figure 7.** (a) Linear relationship between ln  $k_1$ , the second-order rate constant for the first step of oxidative addition of CH<sub>3</sub>I to [Rh(R<sup>1</sup>COCHCOR<sup>2</sup>)(CO)(PPh<sub>3</sub>)], and the sum of the group electronegativities of R<sub>1</sub> and R<sup>2</sup>, ( $\chi_{R1} + \chi_{R2}$ ), of the  $\beta$ -diketonato ligand coordinated to rhodium complexes. Rate data for various complex are shown in Figure 6. (b) Relationship between ln  $k_1$  and the  $pK_a$  of the corresponding free  $\beta$ -diketone. (c) Relationship between  $\beta$ -diketone  $pK_a$  and ( $\chi_{R1} + \chi_{R2}$ ). Rate constants were obtained from refs 6, 9, 13, and 17. Individual group electronegativities were  $\chi_{CF3} = 3.01$ ,  $\chi_{CH_3} = 2.34$ ,  $\chi_{Ph} = 2.21$ ,  $\chi_{Th} = 2.10$ , and  $\chi_{Fc} = 1.87$  and were obtained from refs 3 and 18.  $pK_a$  values were from refs 3b, 5, and 18–20.

Figure 7 reveals that the ferrocene-containing complex **4** exhibits a remarkably high nucleophilicity. Indeed, **4** has the highest propensity toward oxidation addition of any known [Rh( $\beta$ -diketonato)(CO)(PPh<sub>3</sub>)] complex and has a higher reactivity than many Rh(I) carbonyl complexes. It is ca. 2000 times more reactive than the anionic Monsanto carbonylation catalyst, [Rh(CO)<sub>2</sub>I<sub>2</sub>]<sup>-1</sup>. Two of the few known Rh<sup>I</sup> complexes that undergo faster oxidative addition by CH<sub>3</sub>I than **4** include the [Rh<sup>IIII</sup>(*bis*-iminocarbazolido)(I)(CO)CH<sub>3</sub>] complex that reacts ca.  $5 \times 10^4$  times faster<sup>21</sup> and [Rh(methyl(2-methylamino-1-cyclopentene-1-dithiocarboxylato))(CO)(PPh<sub>3</sub>)] that reacts ca. two times faster than **4**.<sup>22</sup>

The data from Figure 7 can be fitted to eqs 5-7.

$$\ln k_1 = -3.14(\chi_{\rm R1} + \chi_{\rm R2}) + 10.0 \tag{5}$$

$$\ln k_1 = 0.83 \text{p}K_a - 11.6 \tag{6}$$

$$pK_a = -3.484(\chi_{R1} + \chi_{R2}) + 24.6 \tag{7}$$

and allows prediction of CH<sub>3</sub>I oxidative addition rate constants of simple [Rh( $\beta$ -diketonato)(CO)(PPh<sub>3</sub>)] complexes as well as  $pK_a$  values of free  $\beta$ -diketone ligands if the group electronegativities of the R<sup>1</sup> and R<sup>2</sup> side groups are known.

## Conclusion

Kinetic studies on a series of [Rh(FcCOCHCOR)(CO)(PPh<sub>3</sub>)] complexes show that the oxidative addition reactions are first order in both the Rh(I) complex and the CH<sub>3</sub>I, with second-order rate constants significantly larger than those reported for related [Rh(R<sup>1</sup>COCHCOR<sup>2</sup>)(CO)(PPh<sub>3</sub>)] complexes. The high nucleophilicity of complex **4** (R = Fc) caused it to undergo the fastest oxidative addition with CH<sub>3</sub>I ( $k_1 = 0.16 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) yet observed for any [Rh( $\beta$ -diketonato)(CO)(PPh<sub>3</sub>)] complex. This is 30 times faster than that of the poorer nucleophilic complex **1** having an electron-withdrawing substituent, CF<sub>3</sub>, on the  $\beta$ -diketonato ligand. The rate of oxidative addition of all

complexes was found to be a function of electron density of the Rh<sup>I</sup> center, and the latter may conveniently be expressed as a function of the sum of  $\beta$ -diketonato R substituent group electronegativities,  $\chi_{R1} + \chi_{R2}$ . Utilizing this principle, CH<sub>3</sub>I oxidative addition reaction rates to any complex of the type [Rh(R<sup>1</sup>COCHCOR<sup>2</sup>)(CO)(PPh<sub>3</sub>)] may be estimated by the equation ln  $k_1 = -3.14(\chi_{R1} + \chi_{R2}) + 10$ , while the acidity of the free  $\beta$ -diketone ligand may be estimated by the equation  $pK_a = -3.484(\chi_{R1} + \chi_{R2}) + 24.6$ .

# **Experimental Section**

**Materials and Apparatus.** Complexes 1–4 were synthesized as described earlier.<sup>7</sup> NMR measurements, at 298 K unless otherwise stated, were recorded on a Bruker Advance DPX 300 NMR spectrometer [<sup>1</sup>H (300.130 MHz) and <sup>31</sup>P (121.495 MHz)]. Chemical shifts are reported as  $\delta$  values relative to SiMe<sub>4</sub> at 0 ppm for the <sup>1</sup>H spectra or relative to 85% H<sub>3</sub>PO<sub>4</sub> at 0 ppm for the <sup>31</sup>P spectra. Infrared spectra were recorded on a Hitachi 270-50 infrared spectrometer either in a KBr matrix or in chloroform solutions. UV measurements were recorded on a GBC-916 UV/vis spectrometer. Liquid reactants and solvents were distilled prior to use, and water was double distilled.

Kinetic Measurements. The kinetic rate constants were determined utilizing UV/vis (by monitoring the change in absorbance), IR (by monitoring formation and disappearance of the carbonyl peaks), and <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy (by monitoring the change in integration units of the various signals with time). A linear relationship between UV absorbance, A, and concentration, *C*, confirmed the validity of the Beer–Lambert law ( $A = \varepsilon Cl$  with l = path length = 1 cm for the complexes 1-4 at experimental wavelengths mentioned in Figure 7 for **2** and **4**. For **1**,  $\lambda_{exp} = 375$ , 400, 530, and 580 nm, and for **3**,  $\lambda_{exp} = 380$  nm for all three reaction steps. For 1–4,  $\lambda_{max}$  (nm) values [ $\varepsilon$  (dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> are given in brackets)] in chloroform are as follows: 1, 498 [2060(10)]; 2, 493 [880(10)]; **3**, 500 [1520(10)]; and **4**, 379 [12500(200)] and 473 [3780(20)]. All kinetic measurements were monitored under pseudo first-order conditions with CH<sub>3</sub>I concentrations 7-10000 times the concentration of the [Rh(FcCOCHCOR)(CO)(PPh<sub>3</sub>)] (R = CH<sub>3</sub>, Ph, and Fc) complex. At least five different concentrations within this range were utilized. The concentration of [Rh(FcCOCHCOR)(CO)-(PPh<sub>3</sub>)] was  $\leq 0.0004$  mol dm<sup>-3</sup> for UV/vis measurements and  $\leq 0.01 \text{ mol } \text{dm}^{-3}$  for IR and NMR measurements. The activation parameters  $\Delta H^{\#}$  and  $\Delta S^{\#}$  for the reaction in chloroform were

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<sup>(22)</sup> Roodt, A.; Steyn, G. J. J. Recent Res. Dev. Inorg. Chem. 2000, 2, 1.

obtained from kinetic experiments performed at least at four temperatures between 15.0 and 35.0 °C. The [Rh<sup>I</sup>( $\beta$ -diketonato)(CO)-(PPh<sub>3</sub>)] complexes **1**–**4** were tested for stability in chloroform by means of overlay IR and UV/vis spectra for at least 24 h. A <sup>1</sup>H NMR spectrum of complexes **1**–**4** after 48 h in solution of CDCl<sub>3</sub> confirmed solution stability.

**Calculations.** Pseudo first-order rate constants,  $k_{obs}$ , were calculated by fitting<sup>23</sup> kinetic data to the first-order equation<sup>24</sup>  $[A]_t = [A]_0 e^{(-k_{obs}t)}$  with  $[A]_t$  and  $[A]_0$  the absorbance of the indicated species at time t and at t = 0 (UV/vis or IR experiments) or integral values for suitable peaks, see Figures 3 and 4, in <sup>1</sup>H and <sup>31</sup>P NMR spectra. The experimentally determined pseudo first-order rate constants were converted to second-order rate constants,  $k_1$ , by

determining the slope of the linear plots of  $k_{obs}$  against the concentration of the incoming CH<sub>3</sub>I ligand. Nonzero intercepts implied that  $k_{obs} = k_1$ [CH<sub>3</sub>I] +  $k_{-1}$  and that the  $k_{-1}$  step in the proposed reaction mechanism exists.<sup>24</sup> Zero intercepts indicated  $k_{-1} = 0$ . The activation parameters were determined from the Eyring relationship ln  $k/T = -\Delta H^{\#}/RT + \Delta S^{\#}/R + \ln k_{\rm B}/h$  with  $\Delta H^{\#} =$  activation enthalpy,  $\Delta S^{\#} =$  activation entropy, k = rate constant,  $k_{\rm B} =$  Boltzmann's constant, T = temperature, h = Planck's constant, and R = universal gas constant. The activation free energy may be calculated from  $\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}.^{24}$ 

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<sup>(24)</sup> Espenson, J. H. Chemical Kinetics and Reaction Mechanisms, 2nd ed.; McGraw-Hill: New York, 1995; pp 15, 49, 70-75, 156.