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Introduction

Monsanto initiated development of its rhodium- and iodidecatalysed process for the carbonylation of methanol to acetic acid in 1966.¹ To date the Monsanto $[Rh(CO)_2(I)_2]^-$ complex is one of the best known rhodium(1) catalysts.²⁻⁴ The methyl iodide oxidative addition reaction that forms the rhodium(III) alkyl reaction intermediate $[Rh(CO)_2(I)_3(CH_3)]^-$ is the ratedetermining step of the catalytic cycle.⁵ Square planar rhodium(I) complexes containing a β -diketonato ligand have been extensively studied as precursors and model compounds in catalysis.⁶ Another important class of catalysts is based on rhodium(1) complexes containing more electron-donating ligands (than CO or I in the Monsanto complex), such as phosphine,⁷ biphosphine ligands^{2,8} or phosphite ligands.⁹ A previous kinetic study of the rhodium(ι)–β-diketonato–phosphite complex $[Rh(CH_3COCHCOCH_3)(CO)(P(OCH_2)_3CCH_3)]^{10}$ showed that the oxidative addition reaction of CH₃I to this complex is first order in both the Rh(1) complex and CH₃I. It further showed that, compared to the oxidative addition of methyl iodide to the Monsanto catalyst [Rh(CO)₂I₂]⁻, this complex accelerates the oxidative addition step by ca. 400 times (at 35°), but inhibits the CO insertion step. It has also been shown that while inclusion of the electron withdrawing CF_3 group on the β -diketonato backbone in

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Chemical and electrochemical oxidation of [Rh(β-diketonato)(CO)(P(OCH₂)₃CCH₃)]: an experimental and DFT study

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An experimental and computational chemistry study of the reactivity of [Rh(β -diketonato)(CO)-(P(OCH₂)₃CCH₃)] complexes towards chemical and electrochemical oxidation shows that more electron withdrawing groups on the β -diketonato ligand reduce electron density on the rhodium atom to a larger extent than electron donating groups. This leads to a slower second-order oxidative addition rate, k_1 , and a higher electrochemical oxidation potential, E_{pa} (Rh), linearly related by ln $k_1 = -11(1) E_{pa}$ (Rh) – 2.3(5). The reactivity of these complexes can be predicted by their DFT calculated HOMO energies: $E_{HOMO} = -0.34(8)E_{pa}$ (Rh) – 5.04(4) = 0.032(5) ln $k_1 - 4.96(4)$. k_1 of [Rh(β -diketonato)(CO)(P(OCH₂)₃CCH₃)] complexes is slower than that of related [Rh(β -diketonato)(CO)(PPh₃)] and [Rh(β -diketonato)(P(OPh)₃)₂] complexes due to the better π -acceptor ability of the CO–phosphite–rhodium combination than that of CO–PPh₃–rhodium or di-phosphite–rhodium.

[Rh(CH₃COCHCOCF₃)(CO)(P(OCH₂)₃CCH₃)] leads to a slower oxidative addition step, the strong electron donation of P(OCH₂)₃CCH₃ over CO still accelerates the oxidative addition step by ca. 20 times (at 35°), compared to that of the Monsanto catalyst.¹¹ For this purpose we report with this communication the synthesis, characterization and oxidative addition kinetics of three new $[Rh(\beta-diketonato)(CO)(P(OCH_2)_3CCH_3)]$ complexes in order to extend the series of [Rh(β-diketonato)(CO)-(P(OCH₂)₃CCH₃)] complexes ranging from complexes containing electron donating groups (CH₃), to complexes containing electron withdrawing groups (CF_3) on the β -diketonato ligand. For the first time, results are presented here on the electrochemical oxidation of Rh^I to Rh^{III} for this series of complexes. In addition, relationships are established between experimental values (kinetic rate constants and oxidation potential, as measured by cyclic voltammetry), electronic parameters of the β -diketonato ligand (electronegativity of the groups,¹² the Hammett *meta* substituent σ constants,^{13–15} the Lever ligand parameters¹⁶ and the pK_a of the free β -diketone (R'COCH₂COR)) and density functional theory (DFT) calculated energies. Establishing relationships that can predict the reactivity of oxidative addition, for a series of complexes, is of great importance in the design of new catalysts with a specific reactivity.

Results and discussion

Synthesis and identification of complexes

The new $[Rh(R'COCHCOR)(CO)(P(OCH_2)_3CCH_3)]$ complexes with substituents R and R' = CH₃, Ph (3), Ph, CF₃ (5) and CF₃,

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 CF_3 (6) of this study are synthesized as described previously for complexes CH₃, CH₃ (1),¹⁰ Ph, Ph (2)¹⁷ and CH₃, CF₃ (4).¹¹ (See Scheme 1 for complex numbering.) Heating a DMF solution of $RhCl_3 \cdot xH_2O$ leads to the formation of the salt $[NH_2(CH_3)_2]^+[Rh (CO)_2Cl_2$ ^{-.18} Addition of the appropriate β -diketone to the reaction mixture results in the precipitation of [Rh(β-diketonato)(CO)₂]. Adding a slight excess of the phosphite 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane to an ethanolacetone solution of $[Rh(\beta-diketonato)(CO)_2]$ leads to the formation of the $[Rh(\beta-diketonato)(CO)(P(OCH_2)_3CCH_3)]$ product (see Scheme 1). For [Rh(β-diketonato)(CO)(P(OCH₂)₃CCH₃)] complexes (3), (4) and (5), containing an unsymmetrical β -diketonato ligand RCOCHCOR', with $R \neq R'$, two isomers of $[Rh(\beta-diketonato)(CO)(P(OCH_2)_3CCH_3)]$ are possible: one with the (P(OCH_2)_3CCH_3) group trans to the $O_{\beta\text{-diketonato}}$ nearest to the R' group (isomer A) and the other with the $(P(OCH_2)_3CCH_3)$ group *cis* to the O_{β -diketonato nearest to the R' group (isomer B) (see Scheme 1). The presence of both isomers for complexes (3), (4) and (5) was observed by NMR at a ratio of isomer A: isomer B (%) = 37:63 for (3), 47:53 for (4) and 46:54 for (5). Two isomers for the related $[Rh(\beta-diketonato)(CO)(PPh_3)]$ complexes containing an unsymmetrical β-diketonato ligand were also observed by NMR¹⁹ and in some cases isolated in the solid state and characterized by means of solid state X-ray crystallography.20-23

two steps that can be expressed as follows:

$$Rh^{I} + CH_{3}I \xrightarrow{k_{1}} Rh^{III}$$
-alkyl $\xrightarrow{k_{2}} Rh^{III}$ -acyl
First step Second step

The first reaction step involves the oxidative addition step of CH₃I to the rhodium complex, which is [CH₃I] dependent, *i.e.* k_1 is a second order rate constant obtained from the observed rate constant $k_{obs1} = k_1$ [CH₃I]. The second reaction step involves the migratory insertion of the methyl group of the Rh^{III}-alkyl into the carbonyl group, which is [CH₃I] independent, *i.e.* $k_{obs2} = k_2$ is a first order rate constant. It was found that $k_{-1} \approx 0 \approx k_{-2}$.

Infrared study

IR spectroscopy is ideal to identify the reactants and products of rhodium complexes containing CO groups, since CO bonds in Rh^I-monocarbonyl complexes resonate at ~1980–2050 cm⁻¹ and at ~2050–2150 cm⁻¹ for Rh^{III}-alkyl complexes. CO bonds in Rh^{III}-acyl complexes resonate at ~1700–1750 cm⁻¹.^{24,25}

A representative series of the spectra obtained by IR when following the two reaction steps of the reaction between CH₃I and [Rh(β-diketonato)(CO)(P(OCH₂)₃CCH₃)] are shown in Fig. 1 (a) for complex (3). For complex (3) the first, relatively fast reaction step $(t_{1/2} \approx 370 \text{ s})$ shows that the rate of disappearance of the Rh^I complex (disappearance of the Rh^I–CO signal at 2018 cm⁻¹, $k_{obs1} = 1.87(7) \times 10^{-3} \text{ s}^{-1}$ basically corresponds to the rate of formation of the Rh^{III}-alkyl complex (formation of the Rh^{III}-CO signal at 2110 cm⁻¹, $k_{obs1} = 2.00(6) \times 10^{-3} \text{ s}^{-1}$). The second much slower reaction step ($t_{1/2} \approx 15$ hours), as observed by the IR spectra, is illustrated in Fig. 1(b). The formation of the Rh^{III}-acyl species (formation of the Rh^{III}–COCH₃ signal at 1714 cm⁻¹, k_{obs2} = $13.3(3) \times 10^{-6} \text{ s}^{-1}$) corresponds to the depletion of the Rh^{III}alkyl (disappearance of the Rh^{III}–CO signal at 2110 cm⁻¹, k_{obs2} = $12.7(2) \times 10^{-6} \text{ s}^{-1}$). It was not possible to distinguish between the two isomers of complexes (3), (4) and (5) by IR.

UV/vis study

The kinetic data obtained for the reaction between CH_3I and complexes (1)-(6) showed that the reaction proceeds through

UV/vis time scans of the first reaction step exhibit a single isosbestic point, indicating the formation of a single product on



Fig. 1 Illustration of the oxidative addition reaction between CH_3I and $[Rh(PhCOCHCOCH_3)(CO)(P(OCH_2)_3CCH_3)]]$, (**3**), as monitored on the IR spectrophotometer between 1650–2200 cm⁻¹ in chloroform at 25 °C. (a) The first reaction step (left, measured at 90 s intervals for the first 15 scans) is indicated by the disappearance of Rh^{II} (peak at 2018 cm⁻¹) and the simultaneous appearance of Rh^{III} -alkyl (peak at 2110 cm⁻¹) at the same rate. (b) The second reaction step (only the final scan is shown) is indicated by the simultaneous disappearance of Rh^{III} -alkyl (peak at 2110 cm⁻¹) and the formation of an Rh^{III} -acyl (peak at 1714 cm⁻¹) species. The insets give the absorbance vs. time data of the indicated species. Initial concentrations are: $[CH_3I] = 0.1234$ mol dm⁻³, and $[Rh] = 2.7 \times 10^{-3}$ mol dm⁻³.

Kinetics

Paper



Fig. 2 Left: selected repetitive UV/vis scans (at 25 minute intervals) for the first reaction step of the oxidative addition of CH₃I to [Rh(PhCOCHCOCF₃)(CO)-(P(OCH₂)₃CCH₃)], **(5**), measured in acetone at 25.0(1) °C. Inset: absorbance–time data collected at 397 nm. Initial concentrations are: [CH₃I] = 0.3519 mol dm⁻³ and [Rh] = 2.5×10^{-4} mol dm⁻³, and k_{obs1} = 0.000141(3) s⁻¹. Right: temperature and methyl iodide concentration dependence for observed pseudo-first-order rate constants k_{obs1} for the oxidative addition of methyl iodide to [Rh(PhCOCHCOCF₃)(CO)(P(OCH₂)₃CCH₃)], **(5**), in acetone at 397 nm; [Rh] = 2.5×10^{-4} mol dm⁻³. Inset: Eyring plot according to eqn (2).



Fig. 3 Temperature and methyl iodide concentration dependence for the observed pseudo-first-order rate constants k_{obs1} for the oxidative addition of methyl iodide to [Rh(PhCOCHCOCF₃)(CO)(P(OCH₂)₃CCH₃)], **(5**), in chloroform at 392 nm; [Rh] = 2.6×10^{-4} mol dm⁻³. Inset and right: the determination of the activation parameters ($\Delta H^{\#}, \Delta S^{\#}$) is illustrated by the different Eyring plots according to eqn (2)–(4) respectively (see calculations in the experimental details section).

this timescale: see Fig. 2 for selected UV/vis scans for the first reaction step of the oxidative addition of CH₃I to [Rh(PhCOCH-COCF₃)(CO)(P(OCH₂)₃CCH₃)], complex (5), in acetone at 25.0(1) °C. The inset in Fig. 2 shows the change in absorbance at 397 nm for this reaction. Fig. 2 (right) and Fig. 3 (left) show the plots obtained by measuring k_{obs1} for a different initial [CH₃I] and at different temperatures, for the first reaction step of the oxidative addition reaction in acetone and chloroform as solvents respectively. Values for k_1 , obtained from the slopes of the plots of the k_{obs1} vs. [CH₃I], for complexes (1)–(6) are summarized in Table 1. The second reaction step for the CO insertion (with rate $k_{obs2} = k_2$) was not followed on UV/vis due to the long half-life of this reaction step, namely $t_{1/2} > 11$ hours.

The determination of the activation parameters $(\Delta H^{\#}, \Delta S^{\#})$ of the [Rh(PhCOCHCOCF₃)(CO)(P(OCH₂)₃CCH₃)] + CH₃I oxidative addition reaction, in acetone and chloroform as solvent, is illustrated by the different Eyring plots in Fig. 2 and 3 respectively. The experimentally determined activation parameters of complexes (1)-(6) are given in Table 1. The relatively small $\Delta H^{\#}$ values, accompanied by large negative $\Delta S^{\#}$ values, indicate an associative mechanism including bond formation and/or partial charge creation (electrostriction) during the formation of the transition state. A high pressure kinetic study of the oxidative addition of CH₃I to [Rh(CH₃COCHCOCH₃)(CO)-(P(OCH₂)₃CCH₃)] (1) yields an experimental volume of activation, $\Delta V^{\#}$ of -28(1) cm³ mol⁻¹ in the relatively polar solvent acetone.¹⁰ This result might allow for a charge creation in the transition state, favouring the formation of an ion-pair intermediate, which would suggest that the oxidative addition of methyl iodide to [Rh(CH₃COCHCOCH₃)(CO)(P(OCH₂)₃CCH₃)], (1), most probably proceeds *via* a linear transition state. An intimate two-step S_N2 mechanism, similar to that presented by Swaddle and co-workers,²⁶ for the oxidative addition of methyl iodide to β-diketonatobis(triphenylphosphite) complexes of rhodium(1), is therefore proposed for the oxidative addition step (first reaction step) of methyl iodide to all [Rh(β-diketonato)(CO)(P(OCH₂)₃CCH₃)] complexes (1)-(6):



			Oxidative	e addition rea	ction							
			$10^3 k_1$ (d	$m^3 mol^{-1} s^{-1}$)	•#	• o#	• ~#	# . 3	_		
Method	Solvent	TS/ε	15 °C	25 °C	35 °C	$\Delta H''$ (kJ mol ⁻¹)	$\Delta S'''$ (J K ⁻¹ mol ⁻¹)	$\Delta G''$ (kJ mol ⁻¹)	$\Delta V''/cm^3$ mol ⁻¹	E_{a} (kJ mol ⁻¹)	k_2 (s ⁻¹)	Ref.
[Rh(CH ₃ COCHCOCH ₃)(CO)- (P(OCH ₂) ₃ CCH ₃)] (1)												10
IR UV/vis	Chloroform Benzene Chloroform Acetone	4.8 2.3 4.8 20.7		$17.5(3) \\ 0.45(2) \\ 17.34(4) \\ 5.54(7) \\ 26.0(5) $			- -168(15) -143(3) -145(9) 56(11)	92 83 86	 -28(1)		0.0000127(8) 0.0000119(1) 	
DFT	Methanol	32.6 Linear Bent	17.9(3)	36.0(5)	—	64(3) 26 139	-56(11) -160 -177	81 73 192		25	_	
[Rh(PhCOCHCOPh)(CO)- (P(OCH ₂) ₃ CCH ₃)] (2)												17
IR UV/vis	Chloroform Chloroform Acetone	4.8 4.8 20.7	5.85(5)	10.12(2) 10.57(9) 4.81(9)	- 18.07(10) 10.00(9)	- 39.0(1.5) 44.8(5.3)	-152.0(4.9) -138(12)			—	0.0000152(8)	
DFT	Acetone Chloroform Methanol	20.7 20.7 4.8 Linear Bent	2.70(7)	4.01(9)	10.00(3)	24 29 24 139	-192 -170 -194 -192	82 80 82 196	 	26 29 26 146		
[Rh(CH ₃ COCHCOPh)(CO)- (P(OCH ₂) ₃ CCH ₃]] (3)												This study
IR UV/vis	Chloroform Chloroform Acetone		— 6.98(8) 3.08(6)	15.4(5) 13.4(2) 5.63(6)	 23.53(8) 10.26(6)	-42.4(1) 41.9(8)	-158(4) -147(3)	 90 86			0.0000133(2)	
DFT	Methanol					31 29	-167 -196	81 88	_	31 31		
$ \begin{array}{l} [Rh(CH_{3}COCHCOCF_{3})(CO)-\\ (P(OCH_{2})_{3}CCH_{3})] (4) \end{array} $												11
IR UV/vis	Chloroform Chloroform Acetone		 	0.87(3) 0.78(1) 0.48(1)	 			91			0.00004(1) 	
DFT	Methanol	Linear B Linear A Front				27 28 105	-192 -195 -170	84 82 156		29 30 111	 	
	Chloroform	Bent Linear B Linear A		_		140 30 32	-188 -196 -195	196 89 90	_	147 32 34		
	Acetone	Linear B Linear A	_	_	_	24 27	-189 -165	80 76	_	26 27	_	

Table 1 Kinetic rate constants and activation parameters for the oxidative addition of methyl iodide to the indicated $[Rh((\beta-diketonato)(CO)(P(OCH_2)_3CCH_3)]$ complexes **(1)–(6)**, in various solvents, as monitored by IR and UV/vis spectrophotometry at the indicated temperatures. k_1 (second order) and k_2 (first order) are the rate constants associated with the first and second stages of the reaction between CH₃I and $[Rh(\beta-diketonato)(CO)(P(OCH_2)_3CCH_3)]$. The DFT calculated activation parameters are also given in selected solvents

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			Oxidative &	addition react	ion							
			$10^3 k_1 ({\rm dm}$	$^{3} \text{ mol}^{-1} \text{ s}^{-1}$		#1 V	^{#0} A	# <u></u>	A 1#1,0003	1		
Method	Solvent	TS/ε	15 °C	25 °C	35 °C	$\frac{\Delta n}{(k m o l^{-1})}$	$(J K^{-1} mol^{-1})$	ΔG (kJ mol ⁻¹)	mol ⁻¹	$(kJ mol^{-1})$	$k_2 (s^{-1})$	Ref.
[Rh(CF ₃ COCHCOPh)(CO)- (plocu) CCU)1(5)												This study
(r (~~12)3~~113)] (J) IR	Chloroform			0.642(9)							0.0000172(8)	
UV/vis	Chloroform		0.433(1)	0.73(6)	1.21(2)	35.5(2)	-185.8(7)	91				
	Acetone		0.236(5)	0.409(7)	0.823(6)	43.7(4)	-163(14)	92				
DFT	Methanol	Linear B	;	;		36	-169	87		36		
		Linear A				35	-169	85		34		
[Rh(CF ₃ COCHCOCF ₃)(CO)- [P[OCH ₂) ₃ CCH ₃]] (6) [R DFT	Chloroform Methanol	Linear		0.0029(9) 		42	 -139			40	1.1	This study

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Density functional theory results previously obtained for complexes (1), (2) and (4), as well as results obtained by calculation for complexes (3), (5) and (6) of this study, show *trans* addition of methyl iodide to $[Rh(\beta-diketonato)(CO)-(P(OCH_2)_3CCH_3)]$ *via* a linear transition state (see following section). The resulting *trans*-Rh^{III}-alkyl reaction product of the first reaction step, can easily undergo an acyl formation reaction (since CH₃ and CO are located *cis* to each other). The second reaction step is therefore:



CV study

The cyclic voltammograms of complexes (1)-(6) all exhibited one irreversible oxidation peak on the forward scan and one small reduction peak separated more than 700 mV from the oxidation peak on the backward scan. Fig. 4 shows the cyclic voltammogram of [Rh(PhCOCHCOPh)(CO)(P(OCH₂)₃CCH₃)] complex (2), as a representative example, and the data are tabulated in Table 2. The oxidation peak is assigned to the oxidation of Rh(1) to Rh(111). The irreversible two electron electrochemical oxidation of rhodium(1) in the $[Rh(\beta-diketonato)(CO) (P(OCH_2)_3CCH_3)$ complexes of this study is followed by a fast chemical reaction which is proposed to be the coordination of two solvent molecules (see Scheme 2) similar to that which was found for a series of $[Rh(\beta-diketonato)(CO)(PPh_3)]$,^{27,28} $[Rh(\beta-diketonato)(CO)_2]$,²⁹ $[Rh(\beta-diketonato)(cod)]$ (cod = 1,5cyclooctadiene)³⁰ and $[Rh(\beta-diketonato)(P(OPh)_3)_2]$ complexes.³¹ It was not possible to distinguish between the oxidation potential of the two isomers of complexes (3), (4) and (5) with CV.

Inclusion of the strong electron withdrawing CF₃ group (group electronegativity on the Gordy scale $\chi_{CH_3} = 2.34$ and $\chi_{CF_3} = 3.01^{32}$) on the β -diketonato ligand in [Rh(β -diketonato)(CO)-(P(OCH₂)₃CCH₃)] in moving from [Rh(CH₃COCHCOCH₃)-(CO)(P(OCH₂)₃CCH₃)] (**1**, $E_{pa} = 317$ mV vs. Fc/Fc⁺) to [Rh-



Fig. 4 Cyclic voltammetric response of [Rh(PhCOCHCOPh)(CO)(P(OCH₂)₃CCH₃)] in 0.1 mol dm⁻³ TBAPF₆/CH₃CN on a glassy carbon working electrode at ν = 100 mV s⁻¹, *T* = 25.0(1) °C. Scan initiated in the positive direction as shown by the arrow.

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Table 2 Electrochemical and chemical oxidative addition kinetic data, electronic and calculated parameters of complexes (1)–(6). Oxidation and reduction peak potentials were measured in 0.1 mol dm⁻³ [N⁽ⁿBu₄)] [PF₆]/CH₃CN on a glassy carbon electrode at 25.0(1) °C. All potentials were measured at a constant sweep rate of 0.100 V s⁻¹ and are reported vs. Fc/Fc⁺. Complex numbering is according to Scheme

			Experimental				Electro	nic parameters			Calculated		17 (2A)		т /1-1 1-1
No	R	R'	Isomer distribution/%	$\frac{k_1/\mathrm{dm}^3}{\mathrm{mol}^{-1}}\mathrm{s}^{-1a}$	$E_{ m pa}({ m Rh})/{ m V}$ vs. Fc/Fc $^{+b}$	$E_{ m pc}({ m Rh})/{ m V}$ $ u s. { m Fc/Fc}^{+c}$	pK_{a}^{d}	$(\chi_{\mathrm{R}} + \chi_{\mathrm{R}'})/$ (Gordy scale) ^e	$\Sigma E_{\rm L}^{f} \nu s.$ SHE/V	$\left(\sigma_{\mathrm{R}}+\sigma_{\mathrm{R}'} ight)^{\!\!\!\mathcal{G}}$	Population	E _{HOMO} /eV	^L _{HOMO} /eV according to population	$E_{\rm a}/{\rm kJ}$ mol ⁻¹	E _a /KJ mot according to population
1	CH_3	CH_3	100	0.00554	0.317	I	8.95	4.68	-0.080	-0.14	100.0	-5.080	-5.080	25	25
2	C_6H_5	C_6H_5	100	0.00481	0.242	-0.480	9.35	4.42	-0.040	0.12	100.0	-5.148	-5.148	26	26
3A	CH_3	C_6H_5	37	0.00563	0.295	-0.560	8.7	4.55	-0.060	-0.01	33.4	-5.119	-5.120	31	31
3B	C_6H_5	CH_3	63								66.6	-5.121		31	
4B	CF_3	CH_3	53	0.000480	0.482	-0.630	6.3	5.35	0.030	0.36	53.9	-5.202	-5.202	29	29
4A	CH_3	CF_3	47								46.1	-5.201		30	
5B	CF_3	C_6H_5	54	0.000409	0.417	-0.610	6.3	5.22	0.050	0.49	53.3	-5.242	-5.242	36	35
5A	C_6H_5	CF_3	46								46.7	-5.243		34	
9	CF_3	CF_3	100	0.0000029	0.938	-0.380	4.71	6.02	0.170	0.86	100.0	-5.352	-5.352	40	40
^a In calcı	acetone ılated o	$E^{b}E_{pa}(R)$	th) accurate withi ordy scale with $\chi_{\rm C}$	n 0.006 V. $^{c}E_{\rm F3} = 3.01, \chi_{\rm CH}$	pc(Rh) accura = 2.34, $\chi_{\rm Ph}$ =	te within 0.0 = 2.21 from n	10 V. ^d ef. 32. ^f	Acid dissociatio Lever electroche	n constant mical ligan	$pK_{\rm a}$ at 21° d paramete	from ref. 39 r $E_{\rm L}$ of β -diket	and 40. ^{<i>e</i>} Th onato, from 1	e group electro ef. 16. ^g The H	onegativit ammett	y $(\chi_{\rm R} + \chi_{\rm R'})$ is values $\sigma_{\rm R} + \sigma_{\rm R'}$

R, IS. from ref. 13–15 with $\sigma_{\text{CF3}} = 0.43$, $\sigma_{\text{CH3}} = -0.069$, $\sigma_{\text{Ph}} = 0.06$ and $\sigma_{\text{Fe}} = -0.15$.



Scheme 2 The proposed mechanism for the electrochemical oxidation of [Rh- $(\beta$ -diketonato)(CO)(P(OCH₂)₃CCH₃)] complexes. S = solvent molecule = CH₃CN.

 $(CF_3COCHCOCH_3)(CO)(P(OCH_2)_3CCH_3)]$ (4, $E_{pa} = 482$ mV vs. Fc/Fc^+) and to $[Rh(CF_3COCHCOCF_3)(CO)(P(OCH_2)_3CCH_3)]$ (6, $E_{\rm pa}$ = 938 mV vs. Fc/Fc⁺) results in a progressively more positive peak anodic potential, $E_{pa}(Rh)$. With a strong electron withdrawing CF_3 side group on the β -diketonato ligand, the $[Rh(\beta-diketonato)(CO)(P(OCH_2)_3CCH_3)]$ Rh(I) centre in becomes more positive and it accordingly becomes more difficult to be oxidized. The relationship between the electrochemical oxidation E_{pa} and the experimental chemical oxidation of Rh^I to Rh^{III} as measured by k_1 is linear:

ln
$$k_1 = -11(1) E_{pa}(Rh) - 2.3(5) (R^2 = 0.97)$$

Computational study

Density functional theory (DFT) calculations have been performed to gain more insight into the geometry, transition state and products of the [Rh(β-diketonato)(CO)(P(OCH₂)₃CCH₃)] + CH_3I reaction for complexes (1)-(6). Two rhodium(1) isomers are possible for complexes (3), (4) and (5); see Scheme 1. Experimentally it was only possible to distinguish between the isomers on NMR. Using computational chemistry, however, it is possible to determine the geometry of each rhodium(1) isomer, as well as the different transition states of CH₃I oxidative addition to each isomer and the different rhodium(III) reaction products. In Tables 1 and 2 the DFT results of both isomers of complexes (3), (4) and (5) are given with the isomer and complex numbering according to Scheme 1. The calculated population of complexes (3), (4) and (5) is also given. There is good agreement between the experimental isomer distribution of complexes (3), (4) and (5) as measured in chloroform on ¹H NMR and the calculated isomer distribution. When comparing experimental and calculated data of complexes (3), (4) and (5), an effective calculated energy was determined by using the ratio of the relative population of the two isomers as determined by the Boltzmann equation.

DFT calculations on complexes (1)-(6) indicated that the oxidative addition reaction between [Rh(β-diketonato)(CO)-(P(OCH₂)₃CCH₃)] and CH₃I involves a two-step S_N2 mechanism with (i) the nucleophilic attack of the metal on the methyl carbon to displace iodide to form a metal-carbon bond and (ii) coordination of iodide to the five-coordinated intermediate to give a six-coordinated trans alkyl complex; see Fig. 5 for complex (6) as an example. During the nucleophilic attack of the metal on the methyl carbon, electron density is donated from the HOMO of $[Rh(\beta-diketonato)(CO)(P(OCH_2)_3CCH_3)]$ (mainly d_{z2} character) to the empty p_z orbital on C_{CH_2-I} to be oxidized to Rh(m). Calculated activation parameters for the oxidative addition step are summarized in Table 1 together with



Fig. 5 The DFT calculated optimized structure of (a) reactants, (b) linear transition state (c) intermediate and (d) product of the $[Rh(CF_3COCHCOCF_3)(CO)(P-(OCH_2)_3CCH_3)] + CH_3I$ reaction. In (b) the displacement vector (blue arrow) indicates the movement of the CH_3^+ group at the imaginary frequency (-230.3 cm⁻¹ with a calculated intensity of -399.5). Distances (Å, black), angles (°) and colour code (online version) of the atoms are as indicated.

the experimentally measured values. The agreement between experiment and theory for the individual components $\Delta H^{\#}$ and $\Delta S^{\#}$ to $\Delta G^{\#} = H^{\#} - T\Delta S^{\#}$ is not as good as for $\Delta G^{\#}$ itself. Large compensating variations $\Delta H^{\#}$ and $\Delta S^{\#}$ with a modest change in $\Delta G^{\#}$ were also found by Ziegler.⁵ Fig. 6(a) displays the relative energy of the linear transition state and the most stable alkyl reaction product of complexes (1)–(6).

The experimentally measured second order rate constant k_1 of the oxidative addition of methyl iodide to [Rh(β -diketonato)-(CO)(P(OCH₂)₃CCH₃)] is related to the activation energy E_{act} by the Arrhenius equation:

$$\ln k_1 = -\frac{E_a}{RT} + \ln A$$

where R = gas constant, T = temperature and A = pre-exponential factor. Fig. 6(b) shows the relationships between the DFT calculated quantity E_{act} and the experimentally measured



Fig. 7 Visualization of (a) the LUMO (lowest unoccupied molecular orbital) of CH₃I, (b) the HOMO (highest occupied molecular orbital) of [Rh(PhCOCHCOPh)-(CO)(P(OCH₂)₃CCH₃)] and (c) the HOMO of the linear transition state of [Rh-(PhCOCHCOPh)(CO)(P(OCH₂)₃CCH₃)] + CH₃I. Note the d_{z²}-orbital at the rhodium centre of the HOMO diagrams and the p_z-orbital at the methyl group of the LUMO diagram. The colour code (online version) of the atoms is as indicated in Fig. 5.

kinetic parameter $\ln k_1$:

$$E_{\text{act}}$$
 (eV) = -0.018(5) ln k_1 + 0.19(4)

To understand the role of the HOMO (highest occupied molecular orbital) in the TS, the HOMO of [Rh(PhCOCHCOPh)-(CO)(P(OCH₂)₃CCH₃)] (2) and the HOMO of the linear TS of the [Rh(PhCOCHCOPh)(CO)(P(OCH₂)₃CCH₃)] + CH₃I reaction are presented in Fig. 7 together with the LUMO of CH₃I. Rh(1) is a $d_{x2}^2 d_{y2}^2 d_{x2}^2 d_{x2-y2}^0$ complex of which the HOMO exhibits mainly a d_{z2} character (Fig. 7(b)). In the TS the bond between Rh and C_{CH₃} forms as the bond between C_{CH₃} and I breaks to form the filed d_{z2} HOMO of the rhodium atom with the empty p_z LUMO (lowest unoccupied molecular orbital) of the methyl carbon of CH₃I. Table 2 gives the calculated HOMO (E_{HOMO}) energies of the [Rh(PhCOCHCOPh)(CO)-(P(OCH₂)₃CCH₃)] complexes.

The kinetic characteristics of the $[Rh(\beta-diketonato)(CO)-(P(OCH_2)_3CCH_3)] + CH_3I$ reaction can therefore be assessed by considering frontier molecular orbital (FMO) interactions, since these are likely to be the major initial interactions as reactants approach each other. The FMO theory simplifies reactivity to interactions between the HOMO of one species



Fig. 6 (a) The DFT calculated energies of $[Rh(\beta-diketonato)(CO)(P(OCH_2)_3CCH_3)] + CH_3I$ (left), the activation energy of the linear transition state and the energy of the *trans* $[Rh(\beta-diketonato)(CO)(P(OCH_2)_3CCH_3)]$ -alkyl reaction product for complexes **(1)–(6)**, indicated by coloured bars. The energy of the reactants is taken as zero. (b) Linear relationship between $In k_1$, the second-order rate constant for the oxidative addition of CH_3I to $[Rh(\beta-diketonato)(CO)(P(OCH_2)_3CCH_3)]$ and the calculated activation energy of the $[Rh(\beta-diketonato)(CO)(P(OCH_2)_3CCH_3)] + CH_3I$ reaction. Data are shown in Table 2. Complex and isomer numbering is according to Scheme 1.



Fig. 8 (a) Linear relationship between ln k_1 , the second-order rate constant for the oxidative addition of CH₃I to [Rh(β -diketonato)(CO)(P(OCH₂)₃CCH₃)] and the calculated HOMO energy of [Rh(β -diketonato)(CO)(P(OCH₂)₃CCH₃)]. (b) Linear dependence of the experimental quantity E_{pa} (Rh) on the calculated HOMO energy of [Rh(β -diketonato)(CO)(P(OCH₂)₃CCH₃)]. (b) Linear dependence of the experimental quantity E_{pa} (Rh) on the calculated HOMO energy of [Rh(β -diketonato)(CO)(P(OCH₂)₃CCH₃)]. (b) Linear dependence of the experimental quantity E_{pa} (Rh) on the calculated HOMO energy of [Rh(β -diketonato)(CO)(P(OCH₂)₃CCH₃)]. (b) Linear dependence of the experimental quantity E_{pa} (Rh) on the calculated HOMO energy of [Rh(β -diketonato)(CO)(P(OCH₂)₃CCH₃)]. (b) Linear dependence of the experimental quantity E_{pa} (Rh) on the calculated HOMO energy of [Rh(β -diketonato)(CO)(P(OCH₂)₃CCH₃)]. (b) Linear dependence of the experimental quantity E_{pa} (Rh) on the calculated HOMO energy of [Rh(β -diketonato)(CO)(P(OCH₂)₃CCH₃)]. (b) Linear dependence of the experimental quantity E_{pa} (Rh) on the calculated HOMO energy of [Rh(β -diketonato)(CO)(P(OCH₂)₃CCH₃)]. (b) Linear dependence of the experimental quantity E_{pa} (Rh) on the calculated HOMO energy of [Rh(β -diketonato)(CO)(P(OCH₂)₃CCH₃)]. (b) Linear dependence of the experimental quantity E_{pa} (Rh) on the calculated HOMO energy of [Rh(β -diketonato)(CO)(P(OCH₂)₃CCH₃)]. (b) Linear dependence of the experimental quantity E_{pa} (Rh) on the calculated HOMO energy of [Rh(β -diketonato)(CO)(P(OCH₂)₃CCH₃)]. (b) Linear dependence of the experimental quantity E_{pa} (Rh) on the calculated HOMO energy of [Rh(β -diketonato)(CO)(P(OCH₂)₃CCH₃)]. (b) Linear dependence of the experimental quantity E_{pa} (Rh) on the calculated HOMO energy of [Rh(β -diketonato)(CO)(P(OCH₂)₃CCH₃)]. (c) Linear dependence of the experimental quantity E_{pa} (Rh) on the calculated

and the LUMO of the other.³³ The reactivity of an [Rh(β -diketonato)(CO)(P(OCH₂)₃CCH₃)] complex is therefore related to the energy of its HOMO. An excellent relationship between the energy of the HOMO, E_{HOMO} (in eV) of [Rh(β -diketonato)(CO)-(P(OCH₂)₃CCH₃)] and the rate constant k_1 (in dm³ mol⁻¹ s⁻¹) is obtained, see Fig. 8(a), data are shown in Table 2.

$$E_{\text{HOMO}} = 0.032(5) \ln k_1 - 4.96(4) \ (R^2 = 0.92)$$

Electro-oxidation of a complex corresponds to the removal of electrons from the highest occupied molecular orbital, *i.e.* the HOMO of the complex. A relationship between the HOMO energy E_{HOMO} of [Rh(β -diketonato)(CO)(P(OCH₂)₃CCH₃)] and the anodic peak potential E_{pa} (Rh) of the electrochemical oxidation of the Rh(i) nucleus is therefore expected,³⁴ see Fig. 8(b), data are shown in Table 2.

$$E_{\text{HOMO}} = -0.34(8) E_{\text{pa}}(\text{Rh}) - 5.04(4) (R^2 = 0.80)$$

The relationship obtained between E_{HOMO} and $E_{\text{pa}}(\text{Rh})$ of [Rh-(β -diketonato)(CO)(P(OCH₂)₃CCH₃)] is in agreement with the DFT-Koopmans's theorem stating that the first (vertical) ionization energy of a system is related to the negative of the corresponding Kohn–Sham HOMO energy.^{34–36}

Reactivity correlations

j

Effect of the β-diketonato ligand. Parameters that are related to the electronic effect of the R and R' groups (of the β-diketonato ligand) on rhodium in $[Rh(β-diketonato)(CO)-(P(OCH_2)_3CCH_3)]$ are group electronegativities ($\chi_R + \chi_{R'}$), Hammett *meta* substituent constants ($\sigma_R + \sigma_{R'}$), Lever electronic parameters ΣE_L and the pK_a of the free β-diketone. These parameters are tabulated in Table 2. The relationships between these electronic parameters and the electrochemical oxidation potential $E_{pa}(Rh)$ (in eV), the chemical oxidation potential ln k_1 (k_1 in dm³ mol⁻¹ s⁻¹), and the HOMO energy E_{HOMO} (in V)

are determined as below:

$$\begin{split} E_{\rm pa}({\rm Rh}) &= 0.40(7) \; (\chi_{\rm R} + \chi_{\rm R'}) - 1.6(3) \; (R^2 = 0.90) \\ E_{\rm pa}({\rm Rh}) &= 0.6(2) \; (\sigma_{\rm R} + \sigma_{\rm R'}) + 0.28(7) \; (R^2 = 0.78) \\ E_{\rm pa}({\rm Rh}) &= 2.6(5) \; \Sigma E_{\rm L} + 0.42(4) \; (R^2 = 0.87) \\ E_{\rm pa}({\rm Rh}) &= -0.12(3) \; {\rm pK_a} + 1.3(2) \; (R^2 = 0.79) \\ \ln \; k_1 &= -4.6(6) \; (\chi_{\rm R} + \chi_{\rm R'}) + 16(3) \; (R^2 = 0.93) \\ \ln \; k_1 &= -8(1) \; (\sigma_{\rm R} + \sigma_{\rm R'}) - 5.2(5) \; (R^2 = 0.91) \\ \ln \; k_1 &= -31(3) \; \Sigma E_{\rm L} - 7.0(3) \\ \ln \; k_1 &= 1.4(3) \; {\rm pK_a} - 18 \; (2) \; (R^2 = 0.86) \\ E_{\rm HOMO} &= -0.15(3) \; (\chi_{\rm R} + \chi_{\rm R'}) - 4.4(2) \; (R^2 = 0.83) \\ E_{\rm HOMO} &= -0.266(9) \; (\sigma_{\rm R} + \sigma_{\rm R'}) - 5.116(4) \; (R^2 = 1.00) \\ E_{\rm HOMO} &= -1.05(6) \; \Sigma E_{\rm L} - 5.178(5) \; (R^2 = 0.99) \\ E_{\rm HOMO} &= 0.05(1) \; {\rm pK_a} - 5.55(7) \; (R^2 = 0.86) \end{split}$$

On evaluating the relationships between the calculated energy ($E_{\rm HOMO}$), electronic parameters of the β -diketonato ligand (R'COCHCOR)⁻ (($\chi_{\rm R} + \chi_{\rm R'}$), p $K_{\rm a}$, ($\sigma_{\rm R} + \sigma_{\rm R'}$) and $\Sigma E_{\rm L}$) and experimental data ($E_{\rm pa}({\rm Rh})$ and ln k_1), we observe that the linear correlations with the p $K_{\rm a}$ and the Gordy scale group electronegativities are generally less accurate. Regarding relationships between experimental data and calculated parameters, relationships involving ln k_1 are 3% to 13% more accurate than relationships with $E_{\rm pa}({\rm Rh})$.

Effect of the phosphite group. On comparing the second order oxidative addition rate constant k_1 of the oxidative

Table 3 Second order kinetic rate constants, k_1 in dm³ mol⁻¹ s⁻¹, for the oxidative addition step of CH₃I to the indicated rhodium– β -diketonato complexes (1)–(6), in acetone as a solvent, where β -diketonato = (R'COCHCOR)⁻

	R	R'	[Rh(β-diketonato)(CO)- (P(OCH ₂) ₃ CCH ₃)]	Reference	[Rh(β-diketonato)- (CO)(PPh ₃)]	Reference	[Rh(β-diketonato)- (P(OPh) ₃) ₂]	Reference
1	CH_3	CH_3	0.00554(7)	10	$0.024(3)^{a}$	41	0.096(2)	26
2	C_6H_5	C_6H_5	0.00481(9)	17	0.00961	42	0.0149(3)	26
3	C_6H_5	CH ₃	0.00563(6)	This study	0.00930	42	0.0342(5)	26
4	CF_3	CH_3	0.00048(1)	11	0.00146	42	0.0056(1)	26
5	C_6H_5	CF ₃	0.00041(2)	This study	0.00112	42	0.00263(5)	26
6	CF_3	CF_3	0.0000029(9)	This study	$0.00013(1)^b$	43	0.00024(3)	26
^a Val	lue in 1,2-c	lichloroeth	ane. ^{<i>b</i>} Value in chloroform.					

addition step of the complexes (1)–(6) of the current study with the k_1 of related rhodium- β -diketonato complexes (Table 3), we observe that k_1 of [Rh(β -diketonato)(CO)(P(OCH₂)₃CCH₃)] < k_1 of [Rh(β -diketonato)(CO)(PPh₃)] < k_1 of [Rh(β -diketonato)-(P(OPh)₃)₂] by a factor 3 and 10 respectively. This result is in agreement with the π -acceptor ability order, as will be discussed below:

 $\begin{array}{ll} (\text{best π-donating}) \ PPh_3 < P(OPh)_3 \approx P(OCH_2)_3 CCH_3 \\ < CO \ (\text{best π-acceptor}). \end{array}$

The Tolman's electronic parameter³⁷ is often used to rank phosphine and phosphite π donor abilities. The higher the Tolman's electronic parameter, the lesser the π -donating (best π -acceptor) ability of the phosphine/phosphite. Accordingly, the P(OCH₂)₃CCH₃ ligand of this study with a Tolman's electronic parameter of ν (CO) = 2087.3 cm⁻¹ is less π -donating (better π -acceptor) than PPh₃ with ν (CO) = 2068.9.³⁸ Consequently in a metal-phosphine complex, the better π -back donation to the phosphite ligand P(OCH₂)₃CCH₃ tends to reduce electron density on the central metal atom to a larger extent than with ligand PPh₃. The strong delocalization of electron density away from the metal center in the phosphite complex is expected to have a marked influence on the reactivity of the (rhodium) metal towards, for example, oxidative addition, where the metal acts as a Lewis base. A progressively slower oxidative addition rate (k_1) is therefore expected when moving from $[Rh(\beta-diketonato)(CO)(PPh_3)]$ to $[Rh(\beta-diketonato)-$ (CO)(P(OCH₂)₃CCH₃)]. Experimentally, the oxidative addition rate of [Rh(β-diketonato)(CO)(P(OCH₂)₃CCH₃)] is found to be 2 to 4 times slower than that of $[Rh(\beta-diketonato)(CO)(PPh_3)]$, in agreement with the larger Tolman's electronic parameter of $P(OCH_2)_3CCH_3$.

CO is a better π -acceptor than all phosphines and phosphites, therefore a metal–CO–phosphite complex (better π -acceptor) will reduce electron density on the central metal atom more than a metal–di-phosphite complex (for the same phosphite group). This predicts a slower oxidative addition rate to the metal–CO–phosphite than to the metal–di-phosphite complex. Since the Tolman electronic parameter of P(OCH₂)₃CCH₃ (2087.3 cm⁻¹) is similar to that of P(OPh)₃ (2085.3 cm⁻¹), it can be predicted that a metal–CO–P (OCH₂)₃CCH₃ complex will have a slower oxidative addition rate than metal–di-P(OPh)₃. The experimentally 3 to 18 times

slower oxidative addition found for the $[Rh(\beta-diketonato)(CO)-(P(OCH_2)_3CCH_3)]$ complexes relative to the $[Rh(\beta-diketonato)-(P(OPh)_3)_2]$ complexes is in agreement with this.

Conclusion

The rates of oxidative addition of CH_3I to $[Rh(\beta-diketonato)(X)-$ (Y)] complexes (X and Y = CO, PPh₃, P(OPh)₃ or P(OCH₂)₃- CCH_3) are determined by the electronic properties of the β-diketonato ligand, as well as groups X and Y. More electron withdrawing groups on the β -diketonato ligand coordinated to $[Rh(\beta-diketonato)(CO)(P(OCH_2)_3CCH_3)]$ reduce electron density on the central metal atom to a larger extent compared to electron donating groups, thus leading to a slower oxidative addition rate. The second-order oxidative addition rate (k_1) of $[Rh(\beta-diketonato)(CO)(P(OCH_2)_3CCH_3)]$ complexes is slower than that of related [Rh(β-diketonato)(CO)(PPh₃)] and [Rh- $(\beta$ -diketonato)(P(OPh)₃)₂] complexes, due to the better π -acceptor ability of the CO-phosphite-rhodium combination than that of the CO-PPh3-rhodium or di-phosphite-rhodium combinations. The reactivity of the $[Rh(\beta-diketonato)(CO)-$ (P(OCH₂)₃CCH₃)] complexes towards CH₃I oxidative addition or electrochemical oxidation can be predicted by the DFT calculated HOMO energy of the [Rh(β-diketonato)(CO)- $(P(OCH_2)_3CCH_3)$] complex: $E_{HOMO} = -0.34(8) E_{pa}(Rh) - 5.04(4)$ $= 0.032(5) \ln k_1 - 4.96(4).$

Experimental

Materials and apparatus

Solid reagents used in preparations (Merck, Aldrich and Fluka) were used without further purification. Liquid reactants and solvents were distilled prior to use; water was doubly distilled. Organic solvents were dried according to published methods.⁴⁴

Synthesis

The general procedure to synthesize the $[Rh(\beta-diketonato)-(CO)_2)]$ and $[Rh(\beta-diketonato)(CO)(P(OCH_2)_3CCH_3)]$ complexes is as described previously.^{10,11,17} $[Rh(CO)_2Cl_2]^{-45}$ was prepared *in situ* by refluxing RhCl₃·3H₂O (0.2 g, 0.76 mmol) in DMF (3 ml) until the colour changed from red to yellow

(ca. 30 minutes).⁴⁶ The solution was allowed to cool on ice and an equivalent amount of solid β -diketone (0.76 mmol) was slowly added while stirring. After 30 min of stirring at room temperature, the crude $[Rh(\beta-diketonato)(CO)_2]$, complex was precipitated with an excess of water and filtered, dried in air and recrystallised from hexane. The $[Rh(\beta-diketonato)(CO)_2)]$ complex (0.200 mmol) was redissolved in 5 ml of an 8:2 (v/v) mixture of ethanol and acetone and a slight excess of solid resublimed 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane⁴⁷ (0.242 mmol) was added. The bright vellow precipitate, which separated after a few minutes, was redissolved by heating the stirred solution to ca 50 °C. Hot filtration through a short Celite column yielded a dark-yellow concentrated solution. Brightly yellow prismatic crystals separated upon cooling down the concentrated solution in a covered container. Characterization data are as given below.

[Rh(CH₃COCHCOCH₃)(CO)(P(OCH₂)₃CCH₃)] **1** IR (KBr): ν /cm⁻¹: 1998 (C=O). ¹H NMR (δ /ppm, CDCl₃): 0.78 (s, 3H, phosphite-CH₃); 1.95 (s, 3H, chelate ring-CH₃); 2.01 (s, 3H, chelate ring-CH₃); 4.23 (d, 6H, 3× OCH₂); 5.45 (s, 1H, CH). ³¹P NMR ((δ /ppm, CDCl₃): 113.282 (d, 1P, phosphite-P, ¹*J*_{Rh-P} = 285.04 Hz).

[Rh(PhCOCHCOPh)(CO)(P(OCH₂)₃CCH₃)] **2** IR (KBr): ν /cm⁻¹: 1992 (C=O). ¹H NMR (δ /ppm, acetone-d): 0.935 (s, 3H, phosphite-CH₃); 4.47 (d, 6H, 3× OCH₂); 7.105 (s, 1H, CH), 7.43–7.57 and 8.07–8.14 (2× m, 10 H, phenyl). ³¹P NMR ((δ /ppm, acetone-d): 114.513 (d, 1P, phosphite-P, ¹J_{Rh-P} = 282.029 Hz).

[Rh(CH₃COCHCOPh)(CO)(P(OCH₂)₃CCH₃)] **3** IR (KBr): ν/cm^{-1} : 1998 (C=O). ¹H NMR (δ/ppm, acetone-d₆): 0.90/0.915 (s, 3H, phosphite-CH₃), 2.08/2.18 (s, 3H, chelate ring-CH₃), 4.40/4.435 (d, 6H, 3× OCH₂), 6.355/6.39 (s, 1H, CH), 7.37–7.53 and 7.93–7.98 (2× m, 2× 3H/2× 2H, aromatic protons of both isomers undistinguishable). ³¹P NMR ((δ/ppm, acetone-d₆): 114.704/114.297 (d, 1P, phosphite-P, ¹J_{Rh-P} = 280.765/283.642 Hz).

[Rh(PhCOCHCOCF₃)(CO)(P(OCH₂)₃CCH₃)] **5** IR (KBr): ν /cm⁻¹: 2000 (C=O). ¹H NMR (δ /ppm, acetone-d₆): δ 0.935 (broad s, 2× 3H, 2× phosphite-CH₃), 4.42–4.53 (broad d, 2× 6H, 2× (3× OCH₂)), 6.77–6.80 (broad s, 2× 1H, 2× CH), 7.48–7.68 and 8.07–8.12 (2× m, 2× 3H/2× 2H, aromatic protons of both isomers undistinguishable). ³¹P NMR (acetone): δ 113.507 (d, 2× 1P, 2× phosphite-P, ¹*J*_{Rh-P} = 283.158 Hz). Isomers not distinguishable on ³¹P NMR.

[Rh(CF₃COCHCOCF₃)(CO)(P(OCH₂)₃CCH₃)] **6** IR (KBr): ν/cm^{-1} : 2008 (C=O). ¹H NMR (δ /ppm, acetone-d₆): δ 0.93 (s, 3H, phosphite-CH₃), 4.49 (d, 6H, 3× OCH₂), 6.44 (s, 1H, CH).

Spectroscopy and spectrophotometry

NMR measurements at 298 K were recorded on a Bruker Avance DPX 300 NMR spectrometer (1 H 300.130 MHz). The

chemical shifts were reported relative to SiMe₄ (0.00 ppm). Positive values indicate a downfield shift. 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 spectrophotometer equipped with a multi-cell thermostated cell holder (± 0.1 °C).

Kinetic measurements

Oxidative addition reactions were monitored on the IR (by monitoring the formation and disappearance of the carbonyl peaks in chloroform) and on the UV/vis (by monitoring the change in absorbance at the indicated wavelength and solvent) spectrophotometers. All kinetic measurements were monitored under pseudo-first-order conditions with [CH₃I] in a 50 to 2000 times access over the concentration of the $[Rh(\beta-diketo$ nato)(CO)(P(OCH₂)₃CCH₃)] complex. The concentration of [Rh- $(\beta$ -diketonato)(CO)(P(OCH₂)₃CCH₃)] \cong 0.0002 mol dm⁻³ for UV/vis measurements and $\cong 0.003$ mol dm⁻³ for IR measurements. Kinetic measurements, under pseudo-first-order conditions for different concentrations of [Rh(β-diketonato)(CO)(P(OCH₂)₃CCH₃)] at a constant [CH₃I], confirmed that the concentration of [Rh- $(\beta$ -diketonato)(CO)(P(OCH₂)₃CCH₃)] did not influence the observed kinetic rate constant. The observed first-order rate constants were obtained from least-squares fits of absorbance vs. time data.⁴⁸ The [Rh(β -diketonato)(CO)(P(OCH₂)₃CCH₃)] complexes were tested for stability in solution by means of an overlay of IR and UV/vis spectra for at least 24 hours.

Calculations

Pseudo-first-order rate constants, k_{obs} , were calculated by fitting⁴⁸ kinetic data to the first-order equation⁴⁹

$$A_t - A_\infty = (A_0 - A_\infty) \mathrm{e}^{(-k\mathrm{obs} \times t)}$$

with A_t , A_∞ and A_0 = the absorbance of the indicated species at time *t*, infinity and 0 respectively. 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 methyl iodide ligand. Non-zero intercepts implied that $k_{obs} = k_1[CH_3I] + k_{-1}$.

All kinetic and other mathematical fits were done utilizing the fitting program MINSQ.⁴⁸ The error of all the data is indicated according to crystallographic conventions, for example $k_{obs} = 0.0236(1) \text{ s}^{-1}$ implies $k_{obs} = (0.0236 \pm 0.0001) \text{ s}^{-1}$.

The activation parameters were determined by a least squares fit to the Eyring equation⁴⁹

$$k = \frac{Tk_{\rm B}}{h} \exp\left(-\frac{\Delta H^{\#}}{RT} + \frac{\Delta S^{\#}}{R}\right) \tag{2}$$

as well as from two linear forms of the equation⁵⁰

$$\ln\frac{k}{T} = -\frac{\Delta H^{\#}}{RT} + \frac{\Delta S^{\#}}{R} + \ln\frac{k_{\rm B}}{h} \tag{3}$$

and

$$T\ln\frac{k}{T} = T\left(\ln\frac{k_{\rm B}}{h} + \frac{\Delta S^{\#}}{R}\right) - \frac{\Delta H^{\#}}{R}$$
(4)

with $\Delta H^{\#}$ = activation enthalpy, $\Delta S^{\#}$ = activation entropy, k = second order rate constant, $k_{\rm B}$ = Boltzmann's constant, T = temperature, h = Planck's constant, R = universal gas constant. Values determined for $\Delta H^{\#}$ and $\Delta S^{\#}$ using eqn (2)–(4) were the same (see Fig. 3 for [Rh(PhCOCHCOCF₃)(CO)(P(OCH₂)₃CCH₃)]). The calculated standard errors obtained from $\Delta H^{\#}$ and $\Delta S^{\#}$ relate to the average experimental temperature⁵¹ within 8 K:

$$\frac{\sigma(\Delta H^{\#})}{\sigma(\Delta S^{\#})} = T_{\rm av} \tag{5}$$

The activation Gibbs energy was calculated from equation⁴⁹

$$\Delta G = \Delta H - T \Delta S \tag{6}$$

Computational chemistry

Density functional theory (DFT) calculations were carried out using the ADF (Amsterdam Density Functional) 2012 programme⁵²⁻⁵⁴ with the GGA (Generalized Gradient Approximation) functional PW91 (Perdew-Wang, 1991).55 The TZP (Triple ζ polarised) basis set with a fine mesh for numerical integration, a spin-restricted formalism and full geometry optimization with tight convergence criteria was used for minimum energy and transition state (TS) searches. Approximate structures of the TS have been determined with linear transit (LT) scans, with a constrained optimization along a chosen reaction coordinate, to sketch an approximate path over the TS between reactants and products. Numerical frequency analyses,56,57 where the frequencies are computed numerically by differentiation of energy gradients in slightly displaced geometries, have been performed to verify the TS geometries. Finally, the TS was allowed to relax after displacing the atoms according to the reaction coordinate as determined by the eigenvectors. This gave the reactants (relax from minimum stretch of frequency gave a rhodium(1) complex and CH₃I) and the products (relax from maximum stretch of frequency gave a cationic five coordinated complex and I-) respectively. Throughout, all calculations have been performed with no symmetry constraint (C_1) and all structures have been calculated as singlet states.

Zero point energy and thermal corrections (vibrational, rotational and translational) were made in the calculation of the thermodynamic parameters. The enthalpy (H) and Gibbs energy (G) were calculated from⁴⁹

$$U = E_{\text{TBE}} + E_{\text{ZPE}} + E_{\text{IE}}$$

$$H = U + RT$$
 (gas phase) or $H = U$ (solution)

$$G = H - TS$$

where *U* is the total energy, E_{TBE} is the total bonding energy, E_{ZPE} is the zero point energy, E_{IE} is the internal energy (sum of vibrational, rotational and translational energies), *R* is the gas

constant, T is the temperature and S is the entropy. The entropy (S) was calculated from the temperature dependent partition function in ADF at 298.15 K. The computed results assume an ideal gas.

Solvent effects were taken into account for all calculations reported here. The COSMO (Conductor like Screening Model) model of solvation^{58–60} was used as implemented⁶¹ in ADF. The COSMO model is a dielectric model in which the solute molecule is embedded in a molecule-shaped cavity surrounded by a dielectric medium with a given dielectric constant (ε_0). The type of cavity used is Esurf⁶² and the solvent used is methanol (ε_0 = 32.6). Selected activation parameters were also calculated in chloroform (ε_0 = 4.8) and acetone (ε_0 = 20.7) as solvents.

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