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# Synthetic, electrochemical and structural aspects of a series of ferrocene-containing dicarbonyl $\beta$ -diketonato rhodium(I) complexes

Jeanet Conradie <sup>a</sup>, T. Stanley Cameron <sup>b</sup>, Manuel A. S. Aquino <sup>c</sup>, Gert J. Lamprecht <sup>a</sup>, Jannie C. Swarts <sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, University of the Free State, P.O. Box 339, Nelson Mandela Drive, Bloemfontein 9300, South Africa <sup>b</sup> Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3 <sup>c</sup> St. Francis Xavier University, P.O. Box 5000, Antigonish, Nova Scotia, Canada B2G 2W5

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## Abstract

Treatment of  $[Rh(\beta-diketonato)(cod)]$  with CO resulted in better yields of  $[Rh(FcCOCHCOR)(CO)_2]$  than by treating  $[Rh(Cl)(CO)_2]_2$  with FcCOCH<sub>2</sub>COR, R = CF<sub>3</sub> (Hfctfa), CH<sub>3</sub> (Hfca), Ph (Hbfcm, Ph = phenyl) and Fc (Hdfcm, Fc = ferrocenyl). The single crystal structure of the fctfa rhodium(I) complex  $[C_{16}H_{10}F_3FeO_4Rh]$ , monoclinic, C 2/c(15), a = 13.266(3) Å, b = 19.553(3) Å, c = 13.278(3) Å,  $\beta = 100.92(2)^\circ$ , Z = 8 showed both rotational and translational displacement disorders for the CF<sub>3</sub> group. An electrochemical study revealed that the formal reduction potential,  $E^{0'}$ , for the electrochemically reversible one electron oxidation of the ferrocenyl group varied between 0.304 (for the fctfa complex) and 0.172 V (for the dfcm complex) versus Fc/Fc<sup>+</sup> in a manner that could be directly traced to the group electronegativities,  $\chi_R$ , of the R groups on the  $\beta$ -diketonato ligands, as well as to the  $pK'_a$  values of the free  $\beta$ -diketones. Anodic peak potentials,  $E_{pa,Rh}$ , for the dominant cyclic voltammetry peak associated with rhodium(I) oxidation were between 0.718 (bfcm complex) and 1.022 V (dfcm complex) versus Fc/Fc<sup>+</sup>. Coulometric experiments implicated a second, much less pronounced anodic wave for the apparent two-electron Rh<sup>I</sup> oxidation that overlaps with the ferrocenyl anodic wave and that the redox processes associated with these two Rh<sup>I</sup> oxidation waves are in slow equilibrium with each other.

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## 1. Introduction

Rhodium(I) dicarbonyl complexes were made famous by the use of  $[Rh(CO)_2(I)_2]^-$  as catalyst in the Monsanto process of converting methanol to acetic acid [1]. Much less is known about  $\beta$ -diketonato-dicarbonyl complexes although the kinetics of oxidative addition and  $\beta$ -diketonato substitution in complexes of the type  $[Rh(\beta$ -diketonato)(CO)(PPh<sub>3</sub>)] have been thoroughly studied [2,3]. In contrast, studies on complexes of the type  $[Rh(\beta\text{-diketonato})(CO)_2]$  are rare. No electrochemical properties relating to metal-containing  $\beta$ -diketonato-dicarbonyl rhodium complexes have to our knowledge been published. Only one kinetic study in which cyclooctadiene (cod) was used to substitute the two carbonyl ligands [4] of  $[Rh(\beta\text{-diketo$  $nato})(CO)_2]$  complexes, has been documented. Hickey and Maitlis [5] reported on the kinetics of oxidative addition of methyl iodide to the related dicarbonyl  $[Rh(CO)_2(I)_2]^-$  complex and Borrini and Ingrosso [6] reported on the reaction between allene and  $[Rh(\beta\text{-diketonato})(CO)_2]$  complexes.

<sup>&</sup>lt;sup>\*</sup> Corresponding author. Tel.: +2751 4012781; fax: +2751 4307805. *E-mail address:* swartsjc.sci@mail.uovs.ac.za (J.C. Swarts).





Scheme 1. The synthesis of the  $[Rh(\beta-diketonato)(CO)_2]$  complexes 9– 12 were achieved in higher yields by cyclooctadiene displacement from 5–8 with CO than by direct treatment of the dimer  $[Rh(Cl)(CO)_2]_2$  with  $\beta$ -diketones 1–4. Fc = ferrocenyl, Ph = phenyl.

The development of new materials [7] possessing multiple metal centres are lately receiving an increasing amount of attention in applications such as molecular wires [8], catalysis [9] and luminescence-based sensors [10]. In many of these cases, the iron-containing ferrocenyl fragment is employed as an electron reservoir [7]. We recently reported [11] the synthesis of a series of new ferrocene-containing  $\beta$ -diketones including 1–4 (Scheme 1) and their rhodium-cod complexes 5-8, as well as the kinetics [12] of  $\beta$ -diketonato substitution of 5–8 with 1,10-phenathroline. We now describe a further portion of our ongoing investigation into the chemistry of rhodium-ferrocene complexes that specifically focuses on the structural and electrochemical properties of the ferrocene-containing β-diketonato dicarbonyl rhodium complexes 9–12 (Scheme 1).

## 2. Results and discussion

#### 2.1. Cyclic voltammetry

Red [Rh( $\beta$ -diketonato)(CO)<sub>2</sub>] complexes with  $\beta$ -diketonato = fctfa (9), fca (10), bfcm (11) and dfcm (12) were obtained by two different pathways (Scheme 1) in yields up to 80% following the general guidelines of published procedures [13]. The complexes 9–12 have two redox centres, the iron centre of the sandwich ferrocenyl group and the square planar rhodium(I) centre.

The ferrocenyl (Fc) group is seemingly oxidised to the ferrocenium species at less positive potentials than the rhodium centre (but see later). CV experiments in a potential range where rhodium(I) did not exhibit any obvious redox activity indicated reversible electrochemical behaviour for the ferrocenyl group in compounds 9-11 with  $\Delta E_{\rm p} = E_{\rm pa} - E_{\rm pc} \leq 90 \text{ mV}$  at scan rates up to 250 mV s<sup>-1</sup> in acetonitrile (Table 1, Fig. 1). In comparison, we found that for ferrocene itself  $\Delta E_p = 74 \text{ mV}$ ,  $i_{pc}/i_{pa} = 0.98$ ,  $E^{0\prime} = 0.087 \text{ V}$  versus Ag/Ag<sup>+</sup> (as 0.01 mol dm<sup>-3</sup> AgNO<sub>3</sub> in CH<sub>3</sub>CN). Determinable peak cathodic/peak anodic current ratios for 9-12 were in the range  $0.83 < i_{\rm pc}/i_{\rm pa} < 1$  and the formal reduction potentials,  $E^{0_{\prime}} = 1/2(E_{pa} + E_{pc})$ , were scan rate independent between 50 and 250 mV s<sup>-1</sup>. Complex **12**, having two ferrocenyl groups in its structure, exhibited two poorly resolved ferrocene-based waves (Fig. 1). Although the free ligand Hdfcm has two spectroscopically equivalent ferrocenyl groups (as indicated by the <sup>1</sup>H NMR spectrum), they are not oxidised simultaneously during cyclic voltammetry [14].  $E^{0}$  values for Hdfcm were reported as 0.178 and 0.287 V versus Fc/ Fc<sup>+</sup> (after correcting for the reference electrode Ag/  $Ag^+$  by subtracting 0.087 V). For complex 12, the two ferrocenyl-based  $E^{0'}$  values are estimated to be 0.172 and 0.277 V versus Fc/Fc<sup>+</sup>, respectively. The smaller formal reduction potential of these two is also the least po-

Table 1

Cyclic voltammetry and coulometry data of the ferrocenyl (Fc) moiety for 1 mmol dm<sup>-3</sup> solutions of [Rh(FcCOCHCOR)(CO)<sub>2</sub>] in acetonitrile containing 0.1 mol dm<sup>-3</sup> ( $^{n}$ Bu)<sub>4</sub>NPF<sub>6</sub> at 25 °C and a scan rate of 50 mV s<sup>-1</sup>

Complex (R)	$\chi_{R}^{a}$	$pK'_a{}^b$	$E_{\rm pa,  Fc}  ({\rm V})^{\rm c}$	i <sub>pa,Fc</sub> (μA)	$\Delta E_{\rm p,Fc} ({\rm mV})$	$\frac{i_{pc,Fc}}{i_{pa,Fc}}$	$E^{0\prime}$ (V) <sup>c</sup>	$E_{\rm coul} ({\rm V})^{\rm cd}$	n <sup>e</sup>
9 (CF <sub>3</sub> )	3.01	5.65	$0.345, (0.457)^{\rm f}$	21.68, (–) <sup>f</sup>	82, (±74) <sup>f</sup>	-, (-) <sup>f</sup>	$0.304, (\pm 0.421)^{\rm f}$	0.713	3
10 (CH <sub>3</sub> )	2.34	10.01	0.224	18.82	68	0.85	0.190	0.563	3
11 $(C_6H_5)$	2.21	10.41	0.235	20.31	72	0.86	0.199	0.513	3
12 (Fc)	1.87, (2.82) <sup>g</sup>	13.1, (6.80) <sup>h</sup>	0.207, (0.312) <sup>i</sup>	18.2, (18.6) <sup>i</sup>	69, (70) <sup>i</sup>	$1.00, (0.83)^{i}$	0.172, (0.277) <sup>i</sup>	0.513	4

<sup>a</sup> Group electronegativities of the indicated R-groups [14].

<sup>b</sup> For the free  $\beta$ -diketone, FcCOCH<sub>2</sub>COR [12,14]. A pK'<sub>a</sub> of 6.53 is also reported [14] for the CF<sub>3</sub>  $\beta$ -diketone.

<sup>c</sup> All potentials are vs. the Fc/Fc<sup>+</sup> couple.

<sup>d</sup> Coulometry experiments were performed at  $E_{pa,Fc}$ , as well as at  $E_{coul}$ .

<sup>e</sup> Total amount of electrons per molecule that were counted during the oxidation of 9–12 at  $E_{\text{pa,Fc}}$  as well as at  $E_{\text{coul}}$ .

<sup>f</sup> The second data set is associated with the ferrocenyl peak in  $[Rh^{\text{oxidised}}(FcCOCHCOCF_3)(CO)_2(\text{solvent})_x]$  and manifests as a shoulder to the main ferrocenyl wave. Poor resolution of these two peaks prevented accurate determination of data other than  $E_{pa}$ .

<sup>g</sup> The value in brackets is the group electronegativity of the oxidised ferrocenium species,  $Fc^+$ .

<sup>h</sup>  $pK'_a$  of Fc<sup>+</sup>COCH<sub>2</sub>COFc.

<sup>i</sup> The first data entry is associated with electron transfer of the first ferrocenyl group, the second with that of the second ferrocenyl group.



Fig. 1. Cyclic voltammetry of 1 mmol dm<sup>-3</sup> solutions of complexes in acetonitrile at 25 °C utilising a glassy carbon working electrode. Scan rate = 100 mV s<sup>-1</sup>, supporting electrolyte = 0.1 mol dm<sup>-3</sup> ("Bu)<sub>4</sub>NPF<sub>6</sub>. *Inset bottom right*. Osteryoung square wave voltammetry (scan rate = 15 mV s<sup>-1</sup>) clearly indicates two inequivalent electron transfer processes for the two ferrocenyl groups of [Rh(dfcm)(CO)<sub>2</sub>].

sitive formal reduction potential observed in the compound series 9–12. Osteryoung square wave voltammemore clearly demonstrated try (OSWV) the electrochemical inequivalence of the two ferrocenyl groups of 12 with peak maxima at 157 and 259 mV, respectively (inset bottom right, Fig. 1). To understand the electrochemical inequivalence of the two ferrocenyl groups of [Rh(FcCOCHCOFc)(CO)<sub>2</sub>], one should recognise that the first oxidised intermediate species is the mixed-valent species [Rh(Fc<sup>+</sup>COCHCOFc)(CO)<sub>2</sub>] similarly to what was found for the free  $\beta$ -diketone [14]. The inequivalence of the ferrocenyl and ferrocenium groups of this intermediate is highlighted in terms of their group electronegativities [11,14]:  $\chi_{Fc} = 1.87$ ,  $\chi_{\rm Fc^+} = 2.82$ . The electron withdrawing power of the ferrocenium group is almost as high as that of the CF<sub>3</sub> group ( $\chi_{CF_3} = 3.01$ ). As there is good communication (via conjugation) between the Fc and Fc<sup>+</sup>  $\beta$ -diketonato pendent side groups on the pseudo-aromatic core of the intermediate [Rh(Fc<sup>+</sup>COCHCOFc)(CO)<sub>2</sub>], oxidation of the second Fc group to yield the final oxidised species  $[Rh(Fc^{+}COCHCOFc^{+})(CO)_{2}]$  takes place at a more positive potential than observed for the oxidation of the first Fc group. Different formal reduction potentials for side groups on symmetrical complexes in which mixed-valent intermediates are generated are well known in systems that allow electron delocalisation, either through bridge mediated paths or from a direct metal-metal interaction [14-18]. The spread in formal reduction potentials of the Fc groups in 9-12 is 132 mV, which is in the same order than that observed for the free  $\beta$ -diketones (129 mV) [14].

The cyclic voltammogram of the ferrocenyl group of 9, [Rh(FcCOCHCOCF<sub>3</sub>)(CO)<sub>2</sub>], introduced a phenomenon that probably also exists for complexes 10-12, but was not measurable under our experimental conditions. Just one peak was expected for the ferrocenyl-based electron transfer process but two poorly resolved peaks were clearly detected in the potential range 0.0 < E < 0.7 V, Fig. 2. OSWV also shows these two peaks at 0.289 and 0.419 V versus Fc/Fc<sup>+</sup>. To explain this dual peak observation, comparison of the <sup>1</sup>H NMR spectrum of this compound in CDCl<sub>3</sub> and CD<sub>3</sub>CN, Fig. 2, is instructive. The elemental analysis [13] of compounds 9–12 showed them to be pure. The <sup>1</sup>H NMR spectrum obtained from poorly co-ordinating  $CDCl_3$  solutions is, therefore, that of pure 9 and the crystal structure determination of 9 is discussed at the end of this publication. However, with deuterated acetonitrile as solvent, the existence of a second species alongside the main species is clearly observed. At 10 mmol  $dm^{-3}$ , the minor species is thought to be an acetonitrile adduct of 9, viz. [Rh(FcCOCHCOCF<sub>3</sub>)(CO)<sub>2</sub>(CD<sub>3</sub>CN)] while the main component in solution is considered as "free" 9. Rhodium(I) complexes do favour a four coordinate 16 electron square-planar co-ordination sphere [19], but 18-electron five co-ordinated trigonal bipyrimidal complexes have been isolated [20,21]. The possibility also exists that the additional set of peaks observed in the CD<sub>3</sub>CN spectrum of 9 is that of a second rhodium species in the sample and that the use of CD<sub>3</sub>CN rather than CDCl<sub>3</sub> simply provided sufficient additional shift dispersion to permit the minor species to be observed. To eliminate this possibility in favour of the equilibrium

$$[\operatorname{Rh}(\operatorname{FcCOCHCOCF}_3)(\operatorname{CO})_2] + \operatorname{CD}_3\operatorname{CN} \\ \stackrel{K'_c}{\rightleftharpoons} [\operatorname{Rh}(\operatorname{FcCOCHCOCF}_3)(\operatorname{CO})_2(\operatorname{CD}_3\operatorname{CN})]$$
(1)

one should recognise that all equilibria are temperature dependent according to the equation  $\ln K'_{c2} = \ln K'_{c1} - (\Delta H/R)(T'_2 - T'_1)$  with  $K'_{c1}$  and  $K'_{c2}$  the observed equilibrium constants at temperatures  $T_2$  and  $T_1$ ,  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $\Delta H$  the reaction enthalpy [22]. Temperature dependent <sup>1</sup>H NMR of a sample of **9** in acetonitrile showed that  $K'_c$  applied to the above equilibrium changed from  $K'_c[CD_3CN] = [Rh(FcCOCHCOCF_3)-(CO)_2(CD_3CN)]/[Rh(FcCOCHCOCF_3)(CO)_2] = (inte$ gral of the 2H peak at 4.80 ppm)/(integral of the 2Hpeak at 4.75 ppm) varies from 0.11 at 35 °C to 0.082 at60 °C. One can also expect that the position of the above $equilibrium should be [Rh(FcCOCHCOCF_3)(CO)_2] con$  $centration dependent. At 20 °C, the value of <math>K'_c[CD_3CN]$ changed as follows (values in brackets are the initially weighed concentration [Rh(FcCOCHCOCF\_3)(CO)\_2] in



Fig. 2. *Left*. CVs of solutions of **9** at scan rates of 50, 100, 150 and 200 mV s<sup>-1</sup>, with conditions as per Fig. 1, show two ferrocenyl waves. Peak 1 represents the ferrocenyl-based redox process associated with of  $[Rh(FcCOCHCOCF_3)(CO)_2(CH_3CN)]$  (**9b**) while peak 2 is associated with the ferrocenyl group of  $[Rh^{\text{oxidised}}(FcCOCHCOCF_3)(CO)_2(\text{solvent})_x]$ . *Inset*. OSWV analysis confirmed the presence of peaks 1 and 2 at 0.289 and 0.419 V, respectively. Scan rate = 4 mV s<sup>-1</sup>. *Right*. The <sup>1</sup>H NMR spectrum in the region 4–6.5 ppm of **9** in CD<sub>3</sub>CN (bottom) clearly shows the existence of the adduct  $[Rh(FcCOCHCOCF_3)(CO)_2(CD_3CN)]$  (**9b**) alongside that of the parent compound **9**. In weakly co-ordinating CDCl<sub>3</sub> (top), only one species, free **9**, is observable. Assignments (CD<sub>3</sub>CN): <sup>1</sup>H NMR: 4.25 (s, C<sub>5</sub>H<sub>5</sub> of **9**, 5H), 4.30 (s, C<sub>5</sub>H<sub>5</sub> of **9b**, 5H), 4.76 (t, C<sub>5</sub>H<sub>4</sub> of **9b**, 2H), explanation (CD<sub>3</sub>CN) (condition) with C<sub>5</sub>H<sub>4</sub> of **9**, 2H), 6.350 (s, COCHCO of **9b**, 1H), 6.364 (s, COCHCO of **9**, 1H).

mmol dm<sup>-3</sup>): 0.14 (15.2); 0.18 (9.35); 0.28 (5.79); 0.55 (2.34); 5.4 (0.93). The observed trend is in agreement with the expectation that equilibrium 1 should be driven more quantitatively to the right when the relative amount of CH<sub>3</sub>CN in a sample is increased over that of [Rh(FcC- $OCHCOCF_3)(CO)_2$ ]. It is also instructive to realise that observation of the acetonitrile adducts, such as [Rh(FcC-OCHCOCF<sub>3</sub>-  $(CO)_2(CD_3CN)$ ], is not a unique occurrence in transition metal chemistry, although it is scarce. CH<sub>3</sub>CN adducts were also observed [23], for example, in copper/phenanthroline complexes of the type [Cu(ophen)<sub>2</sub>(CH<sub>3</sub>CN)](BF<sub>4</sub>)<sub>2</sub> with o-phen various substituted 1,10-phenanthroline derivatives. We conclude that the reason why the above equilibrium is not forced completely to the right under the conditions of our cyclic voltammetry experiments is a consequence of the smallness of the  $K'_{c}$  value in the product  $K'_{c}$  [CD<sub>3</sub>CN]. However, it is not so small that the equilibrium condition can be treated independent of the solvent because  $K'_{c}$  is [Rh(FcC- $OCHCOCF_3)(CO)_2$  concentration dependent. Hence we prefer to present the apparent equilibrium constant as obtained from <sup>1</sup>H NMR data not as  $K'_c$ , but rather as the product  $K'_{c}$  [CD<sub>3</sub>CN]. It should be stressed that the above sited values for  $K'_{c}[CD_{3}CN]$  does not represent a true thermodynamic equilibrium constant which amongst others also implies compound activity coefficient = 1, but merely represents the observed equilibrium constant under the physical conditions of each experiment.

From the equilibrium constants sited above, it follows that in CD<sub>3</sub>CN, at 0.93 mmol dm<sup>-3</sup>, approximately 84% of the total rhodium species in solution has to be

[Rh(FcCOCHCOCF<sub>3</sub>)(CO)<sub>2</sub>(CD<sub>3</sub>CN)]. the adduct, Since our electrochemistry was performed in CH<sub>3</sub>CN containing 1 mmol dm<sup>-3</sup> total rhodium, peak 1 in the of the solution containing [Rh(FcCOCH-CV  $COCF_3)(CO)_2$  (Fig. 2) is assigned to the ferrocenyl group of the [Rh(FcCOCHCOCF<sub>3</sub>)(CO)<sub>2</sub>(CH<sub>3</sub>CN)] adduct. Peak 2 is thought to be associated with the ferrocenyl wave of either solvent-free [Rh(FcCOCH- $COCF_3$ -(CO)<sub>2</sub>] or, more consistent with our bulk electrolyses results which are discussed below, with the ferrocenyl wave of the rhodium-oxidised species [Rh<sup>oxi-</sup>  $^{\text{dised}}(\text{FcCOCHCOCF}_3)(\text{CO})_2(\text{solvent})_x], \text{Rh}^{\text{oxidised}}$  is either Rh<sup>II</sup> or Rh<sup>III</sup>. In principle, peak 2 could also represent minute traces of rhodium(I) oxidation, but rhodium oxidation is not electrochemically or chemically reversible. A clear reduction wave for peak 2 is, however, apparent in the cathodic sweep (Fig. 2) at  $E_{pa}$ approximately 383 mV. At a scan rate of 50 mV  $s^{-1}$  it follows that  $\Delta E_p = E_{pa} - E_{pc} \approx 74 \text{ mV}$  for peak 2. This value is in good agreement with the theoretical value of 59 mV for one electron transfer electrochemical reversible processes, and with the  $\Delta E_{\rm p}$  value which we obtained under our experimental conditions for free ferrocene itself. An obvious feature of peak 2 is that it becomes less prominant than peak 1 at faster scan rates. This observation will be explained after the oxidation of rhodium(I) has been discussed.

Having determined that peak 1 in the CV of 9 (Figs. 1 and 2) actually corresponds to the species [Rh(FcC-OCHCOCF<sub>3</sub>)(CO)<sub>2</sub>(CH<sub>3</sub>CN)], the question now arises as to whether the single ferrocenyl peak in the CV of



Fig. 3. *Bottom.* A linear relationship between group electronegativities,  $\chi_R$ , of each R group and  $E^{0'}$  (ferrocenyl group) of [Rh(FcC-OCHCOR)(CO)<sub>2</sub>(CH<sub>3</sub>CN)] demonstrates good communication between the ferrocenyl group and each of the R-groups CF<sub>3</sub>, Fc<sup>+</sup>, Ph, CH<sub>3</sub> and Fc on the β-diketonato ligand. The  $pK'_a$  of 6.53 (marked with  $\bullet$ , see ref. [14]) was ignored as it does not find the trend line. *Top*. The formal reduction potential,  $E^{0'}$ , of the ferrocenyl group of [Rh(FcCOCHCOR)(CO)<sub>2</sub>(CH<sub>3</sub>CN)] is inversely proportional to  $pK'_a$ of the free β-diketone FcCOCH<sub>2</sub>COR which also confirms good communication via the pseudo-aromatic β-diketonato core between the ferrocenyl group and R-groups pendent to the β-diketonato ligand.

**10–12** are those of the "free" complex or of the acetonitrile adduct. To decide which one, the linear relationship between group electronegativity,  $\chi_{\rm R}$ , of each R-group of **9–12** (Table 1) and  $E_{\rm Fc}^{0\prime}$  (Fig. 3) is instructive. This linear relationship clearly demonstrates that very good communication between the ferrocenyl group and each of the R-groups on [Rh(FcCOCHCOR)(CO)<sub>2</sub>] via the pseudo-aromatic core of these complexes exists. Furthermore, this linear relationship would be very fortuitous indeed if **10–12** were entirely in the free form while **9** is in the adduct form. The linearity of the  $\chi_R/E_{Fc}^{\circ\prime}$  relationship is regarded as consistent with the view that **10–12**, under the conditions of this electrochemical study, are also in the adduct form: [Rh(FcCOCHCOR)(CO)<sub>2</sub>(CH<sub>3</sub>CN)].

In contrast to the ferrocenyl group, the rhodium core of complexes 9-12 does not exhibit reversible behaviour at all. Anodic (oxidation) peak potentials of these complexes varied between 0.718 V, for the bfcm complex 11, and 1.022 V for the dfcm complex 12, Table 2 and Fig. 4. In all the complexes 9–12, when the rhodium(I) nucleus was oxidised at these potentials, the ferrocenyl fragments of the molecule were already in the ferrocenium oxidation state. The spread in peak rhodium anodic potentials is 304 mV, more than double that observed for the ferrocenyl fragment (132 mV). This increase is partly attributable to the large amount of electrochemical work that has to be performed in going from a tetra co-ordinated square planar dicarbonyl rhodium(I) reactant complex, either to an oxidised Rh<sup>III</sup> complex, which normally has octahedral co-ordination geometry [24], or to a Rh<sup>II</sup> species. If Rh<sup>II</sup> is formed, a co-ordination sphere change also has to take place. In contrast, the co-ordination sphere of the ferrocenvl fragment does not change during oxidation or reduction. The nature of the additional new ligands of the electrochemically generated oxidised rhodium complexes during the course of the cyclic voltammetry studies is not known, but probably are solvent molecules, here acetonitrile (donor number = 14.1, see ref. [25,26]).

For the reduction of the newly generated oxidised rhodium species, two separate cathodic waves were observed in the potential range  $-1.2 < E_{pc,Rh} < -0.7 V$ versus Fc/Fc<sup>+</sup> (Table 2, Fig. 5). That these small cathodic waves (for example, for the fca complex, **10**,  $i_{pc}/i_{pa} \sim 0.16$  at a scan rate of 50 mV s<sup>-1</sup>, becoming slightly

Table 2

Cyclic voltammetry and coulometry data relating to the Rh<sup>I</sup> nucleus in [Rh(FcCOCHCOR)(CO)<sub>2</sub>] complexes in acetonitrile containing 0.1 mol dm<sup>-3</sup> ("Bu)<sub>4</sub>NPF<sub>6</sub> at 25 °C and a scan rate of 100 mV s<sup>-1</sup>

Complex (R)	$E_{\rm pa,Rh}^{a}$	$i_{\rm pa,Rh}$	$E_{\rm pc,Rh}^{\rm ab}$	$i_{\rm pc,Rh}$	$N  (\mathrm{mol})^{\mathrm{c}}$	Q/C	Q/NF	$N^{\mathbf{d}}$
9 (CF <sub>3</sub> )	0.901	6.5	$-0.687, (-1.091)^{e}$	12.7, (3.5) <sup>g</sup>	$5.2 \times 10^{-6}$	1.46	2.91	3
10 (CH <sub>3</sub> )	0.844	18.2	$-0.920, (-1.187)^{e}$	$4.1, (2.5)^{g}$	$6.3 \times 10^{-6}$	1.78	2.93	3
11 $(C_6H_5)$	0.718	16.3	$-0.831, (-1.113)^{e}$	$4.9, (3.7)^{g}$	$6.8 \times 10^{-6}$	1.99	3.03	3
12 (Fc)	1.022	13.5	$-0.82^{\rm f}, (-0.99)^{\rm f}$	$6.9^{\rm f}, (-)^{\rm f}$	$4.0 \times 10^{-6}$	1.53	3.96	4

<sup>1</sup> All potentials are vs. Fc/Fc<sup>+</sup>.

<sup>b</sup> Within the potential window possible for acetonitrile, two Rh<sup>III</sup> reduction peaks are observed for 9–12.

<sup>c</sup> Amount of moles of [Rh(FcCOCHCOR)(CO)<sub>2</sub>] used during coulometric experiments.

<sup>d</sup> Total amount of electrons per [Rh(FcCOCHCOR)(CO)<sub>2</sub>] molecule that were counted during oxidation of 9–12 at an applied coulometric potential of  $E_{pa,Rh}$ , as well as 1113 mV.

<sup>e</sup> Value in brackets are the more negative of two peak cathodic potentials associated with Rh<sup>III</sup> reduction in 9–12.

<sup>f</sup> Poor resolution between cathodic peaks for this compound made meaningful measurements impossible. The indicated values are only estimates. <sup>g</sup> Current in brackets are associated with the more negative of the two  $E_{pc,Rh}$  waves.



Fig. 4. CVs of [Rh(FcCOCHCOCF<sub>3</sub>)(CO)<sub>2</sub>] solutions, conditions are as per Fig. 1. Rh<sup>I</sup> oxidation is at  $E_{\rm pa,Rh} > 0.700$  V, reversible ferrocenyl-based redox processes are at 0.172 V  $< E^{0'} < 0.421$  V while Rh<sup>III</sup> reduction was observed as two weak cathodic waves at  $E_{\rm pc,Rh} < -0.7$  V. The insets are enlargements of the ferrocenyl wave of [Rh(dfcm)(CO)<sub>2</sub>] (**12**).

larger at faster scan rates:  $i_{pc}/i_{pa} \sim 0.28$  at 250 mV s<sup>-1</sup>) correspond to rhodium reduction were confirmed in two ways. Firstly, in experiments where scans were initiated at -0.287 V in a negative direction, the cathodic peaks were absent. Fig. 5 demonstrates this for **10**. It follows that the peaks at -1.2 to -0.7 V are not artefacts of the experimental set-up (e.g., impurities in the solvent). Rather, they must be an integral part of the CVs of **9–12**. In the second approach, a switching potential of 0.413 V versus Fc/Fc<sup>+</sup> for scans in the positive direction was imposed on the system. This meant that the cathodic sweep was initiated *before* the oxidised rho-

dium species could electrochemically be generated at potentials  $E_{\text{pa,Rh}} > 0.7 \text{ V}$ . The ferrocenyl group was, however, oxidised. As demonstrated for complex 10 in Fig. 5, these experiments clearly showed the ferrocenyl reduction at 0.156 V and one weak cathodic peak at -1.187 V. The peak at -0.920 V (complex 10) is, however absent. It follows that the peak at -0.920 V must be associated with reduction of the rhodium species that forms during the oxidation wave at 0.844 V. The source of the reducing wave at -1.187 V is assigned to reduction of an oxidised rhodium species that was generated in small quantities at a potential overlapping with the peak associated with ferrocenyl oxidation (peak 1) in the anodic sweep. Compelling proof that small quantities of Rh<sup>1</sup>are oxidised when the ferrocenyl group is oxidised will be presented when coulometric experiments are discussed. The described experiments clearly indicate that the reduction peaks between -1.2 and -0.7 V are associated with the rhodium centre of 9–12.

To get an indication of whether rhodium(I) is oxidised to a rhodium(II) or a rhodium(III) species, a coulometric study was performed. In these experiments, electron counting was performed to see how many electrons were transferred per molecule for each anodic wave observed in the CV of each compound. When bulk electrolyses was performed at potentials 200-300 mV less positive than  $E_{pa,Fc}$ , (Table 1), no electrons were counted. When the potential of electrolyses were set to be just at the onset of the ferrocenyl anodic wave, electron counts were so small (<0.4 after 6 h of electrolyses) that they were not regarded as meaningful due to a lack of electrochemical driving force. A surprising result was, however, obtained during bulk electrolyses when a potential equal to  $E_{pa,Fc}$  was applied to solutions containing 9–12. This potential is sufficiently positive to oxidise the ferrocenyl substituent but is significantly negative of



Fig. 5. Left. CVs of solutions of  $[Rh(fca)(CO)_2]$  (10) at a scan rate of 100 mV s<sup>-1</sup>, with conditions as per Fig. 1. (a) When scanning commenced at -287 mV in the negative direction (---) no cathodic reducing waves corresponding to Rh<sup>III</sup> reduction were observed. (b) When scanning was initiated in a positive direction and a switching potential of 0.413 V imposed on the system (...), Rh<sup>III</sup> reduction at -1.187 V was observed. (c) When positive initiated scans are subjected to a switching potential of 1.113 V, (--), two Rh<sup>III</sup> reductions (at -0.920 and -1.187 V) are observed. Right. CV of solutions of  $[Rh(fca)(CO)_2]$  (10) at scan rates of 50, 100, 150, 200 and 250 mV<sup>-1</sup>. The ratio  $i_{pa,Rh}/i_{pa,Fc}$  becomes smaller with slower scan rates indicating Rh<sup>I</sup> oxidation at 0.844 V becomes less prominent while Rh<sup>I</sup> oxidation occurring at ca. 0.2 V increases in intensity.

the peak anodic potential of the rhodium centre (Table 2). It was expected to count one electron for the ferrocenvl nucleus of 9–11 and two electrons for 12. In practice. three electrons were counted for 9-11 and four for 12. This result is consistent with the simultaneous formation of rhodium(III) on bulk electrolyses time scales. Three (or four in the case of 12) electrons were also counted when the applied potentials for couloumetric analysis were at the deepest point of the trough between the two anodic waves shown in Fig. 4 (values for these potentials are indicated as  $E_{\text{coul}}$  in Table 1). In separate experiments, when the applied potential was  $E_{pa,Rh}$  of the rhodium-based anodic wave (Table 2), or 1113 mV (i.e., about 200 mV larger than  $E_{pa,Rh}$ ), three and four electrons were counted each time for 9-11 and 12, respectively. Fig. 6 (left) shows the net amount of electrons transferred per molecule of indicated complex, n = Q/NF, that was obtained during these bulk electrolyses experiments.

This unexpected result led to two conclusions. For the first, from the reversible nature of the ferrocenyl couple, it is clear that each ferrocenyl moiety is involved in a reversible one-electron transfer process, while the rhodium nucleus most probably is involved in an irreversible two electron transfer process to possibly generate rhodium(III) during oxidation on the bulk electrolyses time scale. For the second, to explain why rhodium(III) apparently can be generated quantitatively by electrolyses at potentials substantially less than  $E_{pa,Rh}$ , i.e., at  $E_{pa,Fc}$ , one explanation would involve the chemically irreversible nature of the rhodium oxidation wave. The Nernst equation has a log term in it and, no matter what the value of the electrode potential, there should always be at least a small amount of each

half of the rhodium redox couple present in solution. The peak anodic potential where rhodium(I) is oxidised is where the redox reaction occurs at the highest rate. Given the chemically irreversible nature of the rhodium oxidation wave, it is possible that oxidation of the rhodium centre occurs at potentials significantly more negative than the peak potential. However,  $E_{pa,Fc}$  is so much smaller than  $E_{pa,Rh}$  (from 0.483 V for 11 till 0.814 V for 12), it is difficult to explain the high rate of rhodium electrolyses from this argument. We conclude that, apart from  $E_{pa,Rh} > 0.7 V$ , there must exist a second means of generating rhodium(III) at potentials overlapping with the ferrocenvl anodic wave. Whatever the means are by which the two electron transfer process to possibly generate rhodium(III) at potentials overlapping closely with  $E^{\circ'}$  of the ferrocenyl group, this redox process can only occur to the extent that it draws small currents because  $i_{pc}/i_{pa}$  ratios for the ferrocenyl wave does not deviate substantially from one (Table 1). This low-potential process must, however, be in slow equilibrium with the process observed at  $E_{pa,Rh}$  (Table 2) to explain why a full electron count of three electrons transferred per molecule of 9-11 or four electrons transferred for 12 during coulometric experiments is observed at potentials substantially less positive than  $E_{pa,Rh}$ . Further proof for this slow equilibrium was found in  $i_{pa,Rh}$ /  $i_{pa,Fc}$  ratios. We were able to demonstrate that  $i_{pa,Rh}$  decreased faster than  $i_{pa,Fc}$  when scan rates were systematically made slower. For example, for 10,  $i_{\text{pa,Rh}}/i_{\text{pa,Fc}}$ ratios (scan rates in mV  $s^{-1}$  are given in brackets) were found to be 0.77 (250), 0.75(200), 0.70(150), 0.63(100) and 0.54(50), respectively (Fig. 5). This is a consequence of more and more of an oxidised rhodium species being generated by the equilibrium process, as scan rates



Fig. 6. Left. Coulometry experiments on [Rh( $\beta$ -diketonato)(CO)<sub>2</sub>] solutions indicate that the overall amount of electrons that flows during oxidation of 9 ( $\bullet$ ), 10 ( $\bullet$ ) and 12 ( $\blacktriangle$ ) is n = Q/NF = 3, 3 and 4, respectively. Inset. The definite biphasic current flow for the dfcm complex, 12, is consistent with two separate electron transfer processes taking place. The first is associated with the ferrocenyl groups, the second with Rh<sup>1</sup> oxidation. Right. CVs of samples taken from a solution of [Rh(FcCOCHCOCH<sub>3</sub>)(CO)<sub>2</sub>] on which bulk electrolysis was performed. Curve 1 (---) was obtained before electrolyses commenced, i.e., at t = 0. Curve 2 (—) was obtained at t = 10 min, curve 3 (—) at t = 23 min after ca. 2 electrons per molecule has flown and curve 4 (…) at t = 90 min after 3 electrons has flown.

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decrease, at potentials close to  $E_{pa,Fc}$  The result is depletion of the remaining Rh<sup>I</sup> species concentration and hence the main electrochemical Rh<sup>I</sup> oxidation wave which is represented by the second anodic peak in the CVs of **9–12** becomes relatively smaller. This observation must invariably point to the fact that  $i_{pc}/i_{pa}$  ratios for the reversible ferrocenyl wave must come closer to one at faster scan rates. This was indeed observed. Using complex **10** again as an example, the  $i_{pc}/i_{pa}$  ratio, indicated in brackets next to a specific scan rate (mV s<sup>-1</sup>), were as follows: 50 (0.83), 100 (0.85), 150 (0.88), 200 (0.90) and 250 (0.92).

To remove doubt that the ferrocene waves of 9–12 is masking or hiding a small rhodium(I) oxidation wave which overlaps with it, the CV of the ferrocene-free  $\beta$ diketonato complex [Rh(PhCOCHCOCF<sub>3</sub>)(CO)<sub>2</sub>] was also recorded in acetonitrile (CVs not shown). Two irreversible Rh<sup>I</sup> oxidation peaks were clearly observed: the first at 0.727 and the second at 1.373 V versus Fc/Fc<sup>+</sup>. When the CV of  $[Rh(PhCOCHCOCF_3)(CO)_2]$  was recorded in CH<sub>2</sub>Cl<sub>2</sub>, the two irreversible oxidation waves collapsed into one broad peak at 1.191 V versus Fc/  $Fc^+$ . Complex 9, [Rh(FcCOCHCOCF<sub>3</sub>)(CO)<sub>2</sub>], only showed rhodium(I) oxidation in dichloromethane at 1.195 V versus Fc/Fc<sup>+</sup>. These observations are consistent with our findings in the cyclic voltammetry of the present ferrocene-containing β-diketonato complexes that the two rhodium oxidation processes are in equilibrium with each other in acetonitrile medium. A full electrochemical study of ferrocene-free β-diketonato dicarbonyl rhodium(I) complexes in coordinating and non-coordinating solvents is at present underway. Further proof that there is a second rhodium oxidation wave overlapping with the ferrocenyl anodic wave will be presented when CVs of the bulk electrolyses solution at different time intervals during the course of the electrolyses are discussed.

Having confirmed the slow dynamic equilibrium 1, and the fact that their actually are two oxidation waves for the Rh<sup>I</sup> centre, one at potentials  $E_{pa,Rh} > 0.7$  V and the other at potentials overlapping with the ferrocenylbased electrochemical waves, the observation that peak 2 becomes relatively stronger in relation to peak 1 (Fig. 2) at slower scan rates can now be explained. It was already established that peak 1 is associated with the redox activity of the ferrocenyl group of [Rh(FcC- $OCHCOCF_3)(CO)_2(CH_3CN)]$ . The described electrochemical results is now consistent with the view that the rhodium(I) core in the solvent-free species, [Rh(FcC- $OCHCOCF_3)(CO)_2$ , probably is oxidised at potentials very close to that associated with peak 1, but before peak 2 is invoked. This causes depletion of the equilibrium concentration of [Rh(FcCOCHCOCF<sub>3</sub>)(CO)<sub>2</sub>]. At fast scan rates, the equilibrium 1 is too slow to be maintained and the observed intensity ratio for peaks 1 and 2 in Fig. 2 are indicative of the equilibrium

concentrations of [Rh(FcCOCHCOCF<sub>3</sub>)(CO)<sub>2</sub>] and [Rh(FcCOCHCOCF<sub>3</sub>)(CO)<sub>2</sub>(CH<sub>3</sub>CN)]. However, at slower scan rates, [Rh(FcCOCHCOCF<sub>3</sub>)(CO)<sub>2</sub>-(CH<sub>3</sub>CN)] is noticeably dissociating to try and regenerate [Rh(FcC- $OCHCOCF_3)(CO)_2$  according to equilibrium 1 as the Rh centre of the solvent-free compound is electrochemically oxidised. As additional [Rh(FcCOCHCOCF<sub>3</sub>)-(CO)<sub>2</sub>] is formed from the dissociation process, its Rh centre is continuously oxidised which leads to a buildup of the rhodium-oxidised product, [Rhoxidised(FcC- $OCHCOCF_3)(CO)_2(solvent)_x]$ , before the potential is reached to invoke formation of peak 2. Hence, when the potential is reached to induce the oxidation of the ferrocenyl group that is associated with [Rhoxidised(FcC- $OCHCOCF_3)(CO)_2$  (solvent)<sub>x</sub>] at peak 2, a build-up of the intermediate product [Rh<sup>oxidised</sup>(FcCOCHCOCF<sub>3</sub>)- $(CO)_2$  (solvent)<sub>x</sub>] has already taken place at slow scan rates. This would explain why peak 2 draws relatively more current under slow-scanning experimental conditions. Arguments that the rhodium(I) core in [Rh(FcC-OCHCOCF<sub>3</sub>)(CO)<sub>2</sub>(CH<sub>3</sub>CN)] is oxidised first, rather than [Rh(FcCOCHCOCF<sub>3</sub>)(CO)<sub>2</sub>], would only be feasible if peak 1 is assigned to ferrocenyl oxidation of  $[Rh(FcCOCHCO-CF_3)(CO)_2]$ , but this would be in violation of the <sup>1</sup>H NMR equilibrium study that was performed.

The above described electrochemical results is consistent with the following general electrochemical scheme in the solvent acetonitrile:

 $\begin{array}{c} CH_3CN + [Rh^1(FeCOCHCOR)(CO)_2] & \longrightarrow [Rh^1(FeCOCHCOR)(CO)_2(CH_3CN)] \\ & & & \downarrow \\ [Rh^{ox}(FeCOCHCOR)(CO)_2(CH_3CN)_x] & [Rh^{1}(Fe^+COCHCOR)(CO)_2(CH_3CN)] \\ & & & & & & \\ & & & & & \\ [Rh^{ox}(Fe^+COCHCOR)(CO)_2(CH_3CN)_x] \end{array}$ 

To try and characterise the fully oxidised product in the above scheme, samples was taken during different time intervals of the bulk electrolyses experiments. CVs and IR spectra were recorded of it, to try and establish what the properties of the proposed final oxidised product  $[Rh^{\text{oxidised}}(Fc^{+}COCHCOR)(CO)_{2} \text{ (solvent)}_{x}]$  are. Fig. 6 (right) show these CVs for 10 at times t = 0, 10, 10, 1023 and 90 min of electrolyses. At 24 min 2 electrons were counted, at 74 min and longer 3. Between 23 and 90 min the bulk electrolyses solution changed colour via orangebrown to brown black. It turns out that the electrochemical generated product is unstable. It is clear that the reduction peaks at  $E_{\rm pc,Rh} \leqslant -0.7 \ {\rm V}$  becomes larger and that the Rh<sup>1</sup> oxidation waves at  $E_{pa,Rh} \ge 0.7$  V becomes smaller during the initial stages of the electrolyses. After 23 min, the wave associated with  $E_{pa,Rh}$  was for all practical purposes gone. The Rh<sup>I</sup> oxidation peak that overlapped with the ferrocenyl peak was also disappearing because  $i_{pa,Fc}$  became smaller while  $i_{pc,Fc}$  remained almost constant during the first 10-min period. Between t = 10 and  $t = 23 \min i_{pc,Fc}$  did become slightly smaller, but this is interpreted as evidence that the sample begins

to disintegrate. After 90 min of bulk electrolyses, the ferrocenyl wave has also disappeared, indicating that the entire molecule has fallen apart.

To determine whether the final rhodium oxidised species still had carbonyl ligands bound to it, the IR study of the bulk electrolyses solution was instructive. The IR spectrum of bulk electrolyses solutions of 10 in acetonitrile in the presence of supporting electrolyte, but before bulk electrolyses was initiated, showed two sharp CO peaks at 2009 and 2083  $\text{cm}^{-1}$ . In chloroform, in the absence of supporting electrolyte, these peaks are at 2014 and 2068, respectively. As bulk electrolyses continued, under air free conditions and when one electron was counted, weak peak pairs at 2015 and 1994 as well as at 2087 and 2064  $\text{cm}^{-1}$  could be observed. When two electrons was counted, the first-mentioned peak pair was gone while the latter peak was low in intensity. When three electrons were counted, no trace of any carbonyl peak was left on the IR. This indicates, as did the CV, that the entire molecule has disintegrated, probably to a Rh<sup>III</sup> species without any CO bound to it. The carbonyl IR peaks observed after electrolyses led to the transfer of two electrons are not really in a position where one would expect Rh<sup>III</sup> carbonyl peaks to be. It has been observed before that CO stretching frequencies shift about 76 cm<sup>-1</sup> to longer wave numbers upon moving from a Rh<sup>I</sup> to a Rh<sup>III</sup> species [13]. This has been the case in moving from [Rh<sup>I</sup>(FcCOCHCOCH<sub>3</sub>)(CO)-(PPh<sub>3</sub>)] with v(CO) = 1980 to [Rh<sup>1</sup>(FcCOCHCOCH<sub>3</sub>)- $(CO)(PPh_3)(CH_3)(I)$ ] with  $v(CO) = 2056 \text{ cm}^{-1}$ . When bulk electrolyses were performed but air (i.e., oxygen) was allowed to enter the system, an IR set of peaks with maxima at 2106 and 2137 were observed for a short time during bulk electrolyses. However, they also disappeared completely by the time 3 electrons were counted during electrolyses. A sample of the bulk electrolyses solution after 2 electrons has flown was also taken and tested for stability by IR monitoring. The complex(es) in solution decomposed completely with no trace of any CO peaks within 10 min.

The above described IR study is consistent with a Rh<sup>II</sup> carbonyl species being formed initially before product decomposition sets in to liberate a Rh<sup>III</sup> species without any CO or ferrocene-containing ligands bound to it. Rhodium(III) may be obtained directly in a two-electron transfer process or it may be obtained after in situ generated rhodium(II) decomposes either in a disproportionation process, viz

 $\begin{aligned} FcRh^{I} &\rightleftharpoons Fc^{+}Rh^{I} \rightleftharpoons Fc^{+}Rh^{II}; \quad \text{then} \\ 2Fc^{+}Rh^{II} &\rightleftharpoons Fc^{+}Rh^{I} + Fc^{+}Rh^{III} \to Rh^{III} \end{aligned}$ 

or via intramolecular electron transfer from the in situ electrochemically generated rhodium(II) to the ferrocenium moiety

$$\begin{aligned} & FcRh^{I} \rightleftharpoons Fc^{+}Rh^{I} \rightleftharpoons Fc^{+}Rh^{II}; \quad then \\ & Fc^{+}Rh^{II} \rightleftharpoons FcRh^{III} \to \to \to Rh^{III} \end{aligned}$$

Rhodium(II), a paramagnetic  $d^7$  species [24], can exist as a monomer, or as a dimer involving a Rh–Rh bond. Neither IR nor anyone of the three electrochemical techniques utilised in this study clearly demonstrated the existence of a rhodium(II) intermediate. Further studies are required to determine the co-ordination sphere and structure of the initially oxidised species before molecular disintegration takes place.

Finally, an attempt was made to correlate the observed  $pK'_{\alpha}$  (Table 1) of the free  $\beta$ -diketones with the formal reduction potentials of the ferrocenyl group of complexes 9-12. As can be seen in Fig. 3, the formal reduction potential of the ferrocenyl fragment is nearlinear and inversely proportional to  $pK'_a$  of the free  $\beta$ diketones. This result implies that the group electronegativity of the R-groups,  $\chi_R$ , and observed  $pK'_a$  values of  $\beta$ -diketones 1–4 are, as was found before [14], inversely proportional to each other, and that this property is largely transferred to complexes of the type [Rh(FcCOCH-COR)(CO)<sub>2</sub>]. However, the  $pK'_a$ - and  $\chi_R$ -potential relationship breaks down when compared with the peak anodic potentials of the Rh nucleus of these complexes because of the irreversibility of the rhodium couples. Since the sited rhodium anodic peak potentials does not represent a true thermodynamic potential, little is made of the observation that the anodic peak potential of the rhodium centre does not correlate well with group electronegativity or  $pK_a$  values.

# 2.2. Crystal structure

To further the characterisation of complexes 9–12, we present here the results of a single crystal structure determination for 9. A perspective view showing atom labelling of [Rh(FcCOCHCOCF<sub>3</sub>)(CO)<sub>2</sub>] is shown in Fig. 7, crystal data, and selected bond lengths and angles may be found in Tables 3 and 4, respectively. The structure showed a rotational as well as a translational displacement disorder for the CF<sub>3</sub> group. The rhodium atom has a square planar co-ordination sphere. The Rh(1)-O(3) bond is 0.033 Å longer than the Rh-O(4)bond, because of the stronger electron donating properties of the ferrocenyl group ( $\chi_{Fc} = 1.87$ ) compared to that of the CF<sub>3</sub> group ( $\chi_{CF_3} = 3.01$ ) on the  $\beta$ -diketonato ligand fctfa. One would also expect this electronic trans influence of the ferrocenyl group to manifest in a shorter Rh-C(12) bond, that is the bond *trans* to Rh-O(3) bond. However, the poor accuracy of the bonds Rh-C(11) = 1.83(2) and Rh-C(12) = 1.84(1) A prevented clear identification of this effect. An obvious feature of the [Rh(FcCOCHCOCF<sub>3</sub>)(CO)<sub>2</sub>] complex was the inaccuracy of many of the bond lengths. Bond lengths in



Fig. 7. A perspective view of [Rh(fctfa)(CO)<sub>2</sub>] showing atom labelling. The view at right highlights the disordered trifluoromethyl group, the square planar geometry around the Rh nucleus and the eclipsed conformation of the cyclopentadienyl groups.

Table 3	
Crystal data for complex 9	
Empirical formula	C16H10F3FeO4Rh
Formula weight	482.00
Crystal size (mm <sup>3</sup> )	0.06×0.15×0.23
Crystal system	monoclinic
Space group	<i>C</i> 2/ <i>c</i> (15)
Unit cell dimensions	
a (Å)	13.266(3)
b (Å)	19.553(3)
<i>c</i> (Å)	13.278(3)
β (°)	100.92(2)
$V(\text{\AA}^3)$	3382(1)
Density (calculated) (g/cm <sup>3</sup> )	1.893
Ζ	8
Temperature (K)	296(1)
Mo K $\alpha$ wavelength (Å); $\mu$ (cm <sup>-1</sup> )	0.71069; 18.79
Final <i>R</i> indices $[I > 3\sigma(I)]^{a}$	R = 0.057, Rw = 0.065
$a P = \sum   F   =  F   / \sum  F   = 0.0540$	and

 $R = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}| = 0.0549$  and  $Rw = [\sum w(|F_{o}| - |F_{c}|)^{2} / \sum wF_{o}^{2}]^{0.5} = 0.0622.$ 

complexes of the type [Rh(FcCOCHCOCF<sub>3</sub>)(PPh<sub>3</sub>)-(CO)] [27], [Rh(FcCOCHCOCF<sub>3</sub>)(PPh<sub>3</sub>)(CO)(CH<sub>3</sub>)(I)] [28], or [Rh(FcCOCHCOCF<sub>3</sub>)(cod)] [29], have been determined more accurately. To our knowledge, the only two other crystallographically characterised complexes of the type [Rh( $\beta$ -diketonato)(CO)<sub>2</sub>] are [Rh(acetylacetonato)(CO)<sub>2</sub>] [30,31] and [Rh(benzoyltrifluoroacetonato)(CO)<sub>2</sub>] [32]. They showed similar large errors as the complex in the present study in their bond lengths and angles, see Table 5. The conclusion drawn is that these large errors probably are due to an inherent property of the sighted [Rh( $\beta$ -diketonato)(CO)<sub>2</sub>] complexes to form poor quality or weak crystals (we observed significant crystal decay during data collection for crystals) and probably explains why [Rh( $\beta$ -diketo-

Table 4			
Selected bond length	s (Å) and ang	gles (°) for complex 9	
Bond lengths			
Rh(1)–O(3)	2.049(8)	Rh(1)–O(4)	2.016(9)
Rh(1)–C(11)	1.83(2)	Rh(1)–C(12)	1.84(1)
O(1)–C(11)	1.14(1)	O(2)–C(12)	1.12(2)
O(3)–C(13)	1.26(1)	O(4)–C(15)	1.29(1)
C(6)-C(13)	1.46(2)	C(13)–C(14)	1.42(2)
C(14)–C(15)	1.36(2)		
Bond angles			
O(3)-Rh(1)-O(4)	90.1(4)	O(3)-Rh(1)-C(11)	91.0(5)
O(3)-Rh(1)-C(12)	177.9(5)	O(4)-Rh(1)-C(11)	178.2(5)
O(4)-Rh(1)-C(12)	89.9(5)	C(11)-Rh(1)-C(12)	89.0(6)
Rh(1)–O(3)–C(13)	128.1(9)	Rh(1)-O(4)-C(15)	122.8(8)
Rh(1)–C(11)–O(1)	179(1)	Rh(1)-C(12)-O(2)	179(1)
C(1)-C(2)-C(3)	107(2)	C(7)-C(6)-C(10)	107(1)
C(6)-C(13)-C(14)	120(1)	O(4)-C(15)-C(14)	131(1)
C(7)–C(6)–C(13)	127(1)	C(10)-C(6)-C(13)	125(1)
O(3)-C(13)-C(14)	124(1)	C(13)-C(14)-C(15)	125(1)

nato)(CO)<sub>2</sub>] crystal structures are virtually unavailable. The complexity of the disorder found in this particular structure must also contribute to bond length and bond angle inaccuracies. This inherent inaccurate Rh–C bond lengths makes it impossible to forecast which carbonyl group will be replaced by PPh<sub>3</sub> in the substitution reaction

$$[Rh(\beta-diketonato)(CO)_2] + PPh_3$$

 $\rightarrow$  [Rh( $\beta$ -diketonato)(PPh<sub>3</sub>)(CO)] + CO

as a definite longer (i.e., weaker) Rh–C bond to the carbonyl group cannot be identified with certainty from crystallographic data. Although the bond angles in the rhodium polyhedron are within experimental error of the expected ideal for  $dsp^2$  hybridisation (90°), devia-

Table 5 Selected crystallographic data for [Rh(β-diketonato)(CO)<sub>2</sub>] complexes

Complex	Angle (C-Rh-C') (°)	Rh–O distance (Å)	Rh-O' distance (Å)	Rh-C distance (Å)	Rh-C' distance (Å)	Space group
[Rh(acac)(CO) <sub>2</sub> ] [30]	85	2.06	2.05	1.75	1.76	$P\bar{1}$
[Rh(acac)(CO) <sub>2</sub> ] [31]	88.9(3)	2.044(4)	2.040(4)	1.831(7)	1.831(7)	$P\overline{1}$
[Rh(tfba)(CO) <sub>2</sub> ] [32]	87(1)	2.02(2)	2.02(2)	1.79(3)	1.82(3)	Pbac
[Rh(fctfa)(CO) <sub>2</sub> ] <sup>a</sup>	89.0(6)	2.049(8)	2.016(9)	1.84(1)	1.83(2)	C2/c

O' is the  $\beta$ -diketonato oxygen atom nearest to the most electronegative group on the  $\beta$ -diketonato ligand. C' is the carbon atom of the carbonyl group *trans* to O'.

<sup>a</sup> This study.

tions of up to 11° were found in the sp<sup>2</sup> hybridised C atoms of the  $\beta$ -diketonato skeleton. The largest of these is  $O(4)-C(15)-C(14) = 131(1)^{\circ}$ . Although the free  $\beta$ diketonato ligand Hfctfa, 1 [14], and the cyclooctadiene complex [Rh(FcCOCHCOCH<sub>3</sub>)(cod)], [29], were clearly asymmetrically enolised or asymmetrically co-ordinated, no asymmetric co-ordination pattern could clearly be identified for the present complex, 9. The Rh...Rh distance is 3.346(2) Å, which is incompatible with metal-metal bonding. The C-C bond lengths of the cyclopentadienyl rings (mean 1.41(3) with the longest and shortest bond lengths being 1.43(3) and 1.39(3) Å, respectively) are similar to the length of an aromatic C-C bond, 1.395(3) Å [33]. The cyclopentadienyl rings are almost planar with a dihedral angle of 2.34° and for all practical purposes are in the eclipsed ( $D_{5h}$  symmetry) arrangement. The dihedral angle between the pseudo-aromatic system forming a plane defined by the atoms C(13), C(14) and C(15), and the planar cyclopentadienyl ring of the aromatic ferrocenyl moiety bound to it, is 7.18°.

In conclusion, it was demonstrated that ferrocenylcontaining complexes of the type [Rh(FcCOCH- $COR)(CO)_2$  with  $R = CF_3$ ,  $CH_3$ , Ph and Fc are oxidised reversibly at less positive potentials than the rhodium nucleus while a slow equilibrium process allows rhodium(I) oxidation at potentials associated with those of ferrocene oxidation as well as at substantially more positive potentials. Coulometric results in acetonitrile were consistent with the oxidation of the rhodium(I) centre to ultimately give a decomposed Rh<sup>III</sup> species without any carbonyl or ferecene-containing ligand bound to it. In acetonitrile solutions, complexes of the type [Rh(FcCOCHCOR)(CO)<sub>2</sub>] are in slow equilibrium with the adduct [Rh(FcCOCHCOR)(CO)<sub>2</sub>(CH<sub>3</sub>CN)]. The latter is the dominant species at lower concentrations. Electronic communication between the Fc fragment and the R-groups via the pseudo-aromatic  $\beta$ diketonato core of the complexes were efficient enough to allow a linear relationship between group electronegativity,  $\chi_{\rm R}$ , and  $E^{0\prime}$  of the ferrocenyl group and an almost linear relationship between free  $\beta$ -diketone pK<sub>a</sub> and  $E^{0'}$  of the ferrocenyl group. The relationship between anodic potential potentials of the Rh nuclei and  $\chi_{\mathbf{R}}$  as well as  $\beta$ -diketone p $K_{\mathbf{a}}$  are non-specific.

#### **3.** Experimental section

#### 3.1. Reagents

Literature methods were used to prepare 1-8 [11] and 9-12 [13]. Dry acetonitrile (Aldrich) was obtained by refluxing under nitrogen over calcium hydride, distilled onto alumina for storage, and redistilled just prior to use.

## 3.2. Electrochemistry

Cyclic voltammetry measurements on ca. 1 mmol  $dm^{-3}$  of solutions of 9–12 in dry acetonitrile containing  $0.100 \text{ mol dm}^{-3}$  tetra-*n*-butylammonium hexafluorophosphate ( $({}^{n}Bu)_{4}NPF_{6}$ , Fluka, electrochemical grade) as supporting electrolyte were conducted under a blanket of purified argon at 25.0 °C utilizing a BAS model CV-27 voltammograph interfaced with a personal computer. A three-electrode cell, which utilised a Pt auxiliary electrode, a glassy carbon working electrode, and a Ag/Ag<sup>+</sup> (0.0100 mol dm<sup>-3</sup> AgNO<sub>3</sub>) reference electrode mounted on a Luggin capillary was used [14,34]. Data, uncorrected for junction potentials, were collected with an Adalab-PC<sup>™</sup> and Adapt<sup>™</sup> data acquisition kit (Interactive Microwave, Inc.) with locally developed software, and analysed with Hyperplot (JHM International, Inc.). All cited potentials were referenced against the Fc/Fc<sup>+</sup> couple, which exhibited  $E^{0'} = 0.087 \text{ V}$  versus Ag/Ag<sup>+</sup>,  $i_{\rm pc}/i_{\rm pa} = 0.98$ ,  $\Delta E_{\rm p} = 74$  mV under our experimental conditions. OSWV measurements were perform under the same conditions as described for CV measurements utilising a BAS 100B/W electrochemical workstation interfaced with a personal computer.

Bulk electrolyses were carried out utilising a BAS CV-27 voltammograph at 25.0(1) °C in acetonitrile. A three-electrode cell equipped with a Pt wire auxiliary electrode (isolated from the sample by means of a 0.1 mol dm<sup>-3</sup> ("Bu)<sub>4</sub>NPF<sub>6</sub>/CH<sub>3</sub>C N salt bridge), a glassy carbon working electrode (electro-active area  $\pm 3$  cm<sup>2</sup>) and a Ag/Ag<sup>+</sup> (0.010 mol dm<sup>-3</sup> AgNO<sub>3</sub> in 0.1 mol dm<sup>-3</sup> ("Bu)<sub>4</sub>NPF<sub>6</sub>/CH<sub>3</sub>CN) reference electrode mounted on a Luggin capillary were employed. Current readings and the integrated current (coulombs) were recorded manually at different times, t, during the course of the experiments.

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#### 3.3. X-ray structure determination

Crystals of 9 were obtained from hot hexane by slowly cooling the reaction mixture. A dark red block crystal was mounted on a glass fiber rod and intensity data were collected on a Rigaku AFC5R diffractometer using graphite monochromated Mo Ka radiation and a rotating anode generator. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centred reflections in the range  $28.44^{\circ} < 2\theta < 36.52^{\circ}$ , corresponded to a Ccentred monoclinic cell. Of the 5291 reflections which were collected, 5091 were unique ( $R_{int} = 0.040$ ). The linear absorption coefficient,  $\mu$ , for Mo K $\alpha$  radiation was 18.79 cm<sup>-1</sup>. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.69 to 1.00. The data were corrected for Lorentz and polarisation effects.

The structure was solved by direct methods (SHELXS-86) [35] and expanded using Fourier techniques (DIRDIF-94) [36]. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were included but not refined. The CF<sub>3</sub> group is disordered with both rotational disorder and with the carbon atom in slightly different positions. The groups were refined as two rigid groups with isotropic thermal parameters and with the C–F distances defined as 1.31 Å. The final cycle of full-matrix least-squares refinement on F was based on 1418 observed reflections ( $I > 3.00\sigma(I)$ ) and 194 variable parameters. All calculations were performed using the teXsan [37] crystallographic software package of the Molecular Structure Corporation. Relevant crystal data are given in Table 3.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.ica.2005.02.010.

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