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# Synthesis and characterisation of ferrocene-containing β-diketonato complexes of rhodium(I) and rhodium(III)

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### Abstract

The synthesis of new  $\beta$ -diketonato rhodium(I) complexes of the type [Rh(FcCOCHCOR)(CO)<sub>2</sub>] and [Rh(FcCOCH-COR)(CO)(PPh<sub>3</sub>)] with Fc = ferrocenyl and R = Fc, C<sub>6</sub>H<sub>5</sub>, CH<sub>3</sub> and CF<sub>3</sub> are described. <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR data showed that for each of the non-symmetric  $\beta$ -diketonato mono-carbonyl rhodium(I) complexes, two isomers exist in solution. The equilibrium constant,  $K_c$ , which relates these two isomers in an equilibrium reaction, are concentration independent but temperature and solvent dependent.  $\Delta_r G$ ,  $\Delta_r H$  and  $\Delta_r S$  values for this equilibrium have been determined and a linear relationship between solvent polarity on the Dimroth scale and  $K_c$  exists. The relationship between Rh–P bond lengths, d(Rh–P), and <sup>31</sup>P NMR peak positions as well as coupling constants <sup>1</sup>J(<sup>31</sup>P-<sup>103</sup>Rh) has been quantified to allow calculation of approximate d(Rh–P) values. Variations in d(Rh–P) for [Rh(RCOCHCOR')(CO)(PPh<sub>3</sub>)] complexes have also been related to the group electronegativities (Gordy scale) of the terminal  $\beta$ -diketonato R groups *trans* to PPh<sub>3</sub>. A measure of the electron density on the rhodium centre of [Rh(RCOCH-COR')(CO)(PPh<sub>3</sub>)] may be expressed in terms of the IR carbonyl stretching wave number,  $\nu$ (CO), the sum of the group electronegativities of the R and R' groups, ( $\chi_R + \chi_R$ ), or the observed pK'<sub>a</sub> values of the free  $\beta$ -diketones RCOCH<sub>2</sub>COR'. An empirical relationship between  $\nu$ (CO) and either pK'<sub>a</sub> or ( $\chi_R + \chi_R$ ) has also been quantified. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Rhodium complexes; Ferrocene complexes; Diketonato complexes

# 1. Introduction

Platinum group transition metal complexes are well known for their medical applications [1] and are often employed as either homogeneous [2] or heterogeneous [3] catalysts in a variety of chemical reactions. Rhodium-based homogeneous catalysts in particular may be used inter alia in carbon-carbon bond formation [4], cyclopropanation [5], decarbonylation of aldehydes [6]. hydroboration of olefins [7]. hydroformylation of olefins [8], hydrogenation [9], hydrosilation [10] and carbon monoxide insertion reactions [11,12]. Hydroformylation and alcohol carbonylation are major industrial processes involving platinum group metal catalysts [13]. The rhodium and iodide-catalysed carbonylation of methanol to acetic acid is to date probably the most successful example of an industrial process homogeneously catalysed by a metal complex in solution [12]. Leipoldt [14] and Roodt [15] have previously shown that some  $\beta$ -diketonato complexes of rhodium(I) can facilitate the formation of acyl species during oxidative addition of methyl iodide to complexes of the type  $[Rh(\beta-diketonato)(CO)(PPh_3)]$ . We were interested to establish whether the ferrocenecontaining β-diketones, FcCOCH<sub>2</sub>COR [16], may enhance acyl formation in complexes of the type [Rh(FcCOCHCOR)(CO)(PPh<sub>3</sub>)]. Towards this end, we report with this communication the synthesis and characterisation of a variety of new ferrocene-containing complexes of the type [Rh(FcCOCHCOR)(CO)<sub>2</sub>] and [Rh(FcCOCHCOR)(CO)(PPh<sub>3</sub>)]. The physical implications of some of their properties are also quantified.

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### 2. Experimental

# 2.1. Materials and apparatus

Solid reagents used in preparations (Merck, Aldrich and Sigma) were used without further purification. Liquid reactants and solvents were distilled prior to use, water was double distilled. DMF was dried according to published methods [17]. Flash chromatography was performed on Kieselgel 60 (Merck, grain size 0.063-0.2 mm, eluent ether-hexane 2:3 by volume unless otherwise stated) utilising an overpressure that never exceeded 100 Torr (1 Torr = 1 mmHg = 133.32 Pa). Melting points (m.p.) were determined with a Reichert Thermopan microscope with a Koffler hot-stage and are uncorrected. NMR measurements, at 298 K unless otherwise stated, were recorded on a Bruker Advance DPX 300 NMR spectrometer [<sup>1</sup>H (300 MHz), <sup>13</sup>C (75.476 MHz) and <sup>31</sup>P (121.497 MHz)]. Chemical shifts are reported as  $\delta$  values relative to SiMe<sub>4</sub> (0 ppm) for the <sup>1</sup>H spectra, relative to 85% H<sub>3</sub>PO<sub>4</sub> at 0 ppm for the <sup>31</sup>P spectra and referenced to CDCl<sub>3</sub> (77.04 ppm) as internal marker for <sup>13</sup>C spectra. Infrared stretching frequencies were recorded on a Hitachi 270-50 infrared spectrometer either in a KBr matrix or in chloroform or acetone solutions. Line fittings were performed with the aid of the fitting program MINSQ [18].

# 2.2. Synthesis

The ferrocene-containing  $\beta$ -diketones Hfctfa, Hfca, Hbfcm and Hdfcm [16], the [Rh( $\beta$ -diketonato)(cod)] complexes [16], and di- $\mu$ -chloro-bis( $\eta^4$ -cycloocta-1,5-diene) dirhodium(I), [Rh<sub>2</sub>Cl<sub>2</sub>(cod)<sub>2</sub>] [19], were prepared according to published procedures.

# 2.2.1. $[Rh(\beta - diketonato)(CO)_2]$ complexes (2-5)

2.2.1.1. Route 1. The general procedure was as follows:  $[Rh_2Cl_2(CO)_4]$ , (1), was prepared in situ by refluxing  $RhCl_3 \cdot 3H_2O$  (0.2 g, 0.76 mmol) in DMF (3 ml) until the colour changed from red to yellow (ca. 30 min [20]). The dimer-containing solution was allowed to cool on ice and an equivalent amount of solid  $\beta$ -diketone (0.76 mmol) was slowly added while stirring. After 30 min of stirring at r.t., the crude  $[Rh(\beta\text{-diketonato})(CO)_2]$ , complexes 2–4, were precipitated with an excess of water and filtered, dried in air and recrystallised from hexane. Purification of the bfcm complex 4 required flash chromatography of the reaction residue ( $R_f = 0.70$ , sefadex, 4 hexane + 1 ethanol). Complex 5 can only be obtained in trace amounts utilising this route.

2.2.1.2. Route 2. The general procedure was as follows:  $[Rh(\beta-diketonato)(cod)]$  (7) (0.30 mmol) was dissolved in acetone (80 ml). CO gas was purged through the

solution through a sinter glass tube. The CO pressure in the reaction vessel was maintained at approximately 1 cm above atmospheric pressure for 20 min. [Rh( $\beta$ -diketonato)(CO)<sub>2</sub>] was precipitated with cold water (100 ml), stirred for 15 min and centrifuged. The precipitate was washed with water, filtrated and dried in a vacuum dessicator. Spectroscopically pure product [Rh( $\beta$ -diketonato)(CO)<sub>2</sub>] (2–5) was obtained in high (>75%) yield. Selected characterisation data of complexes 2–5 may be found in Tables 1 and 2, NMR data are as follows.

[*Rh*(*fctfa*)(*CO*)<sub>2</sub>] (2). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  4.21 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.64 (2H, t, C<sub>5</sub>H<sub>4</sub>), 4.86 (2H, t, C<sub>5</sub>H<sub>4</sub>) and 6.20 (1H, s, CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  192.67 (s, *C*-Fc), 165.82 (q, *C*-CF<sub>3</sub>, <sup>2</sup>*J*<sub>C-F</sub> = 32.6 Hz), 183.27 (d, Rh-*C*O,<sup>1</sup>*J*<sub>C-Rh</sub> = 73.8 Hz), 183.05 (d, Rh-*C*O,<sup>1</sup>*J*<sub>C-Rh</sub> = 74.6 Hz). The crystal structure of **2** is as per ref. [21].

[*Rh*(*fca*)(*CO*)<sub>2</sub>] (3). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.14 (3H, s, CH<sub>3</sub>), 4.17 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.46 (2H, t, C<sub>5</sub>H<sub>4</sub>), 4.77 (2H, t, C<sub>5</sub>H<sub>4</sub>) and 5.87 (1H, s, CH).

[*Rh*(*bfcm*)(*CO*)<sub>2</sub>] (4). The synthesis was performed under Ar and in dry, freshly distilled DMF over 2.5 h,  $R_{\rm f} = 0.70$  (sefadex, 4 hexane + 1 ethanol). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  4.15 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.49 (2H, t, C<sub>5</sub>H<sub>4</sub>), 4.85 (2H, t, C<sub>5</sub>H<sub>4</sub>), 6.50 (1H, s, CH), 7.4–7.5 (3H, m, C<sub>6</sub>H<sub>5</sub>) and 7.9 (2H, m, C<sub>6</sub>H<sub>5</sub>).

[*Rh*(*dfcm*)(*CO*)<sub>2</sub>] (5). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  4.18 (10H, s, C<sub>5</sub>H<sub>5</sub>), 4.47 (4H, t, C<sub>5</sub>H<sub>4</sub>), 4.83 (4H, t, C<sub>5</sub>H<sub>4</sub>) and 6.18 (1H, s, CH).

# 2.2.2. $[Rh(\beta - diketonato)(CO)(PPh_3)]$ complexes (8–11)

The general procedure was as follows: To a boiling solution of  $[Rh(\beta-diketonato)(CO)_2]$  (0.2 mmol) in *n*hexane (30 cm<sup>3</sup>) was added a solution of PPh<sub>3</sub> (0.2 mmol) in warm *n*-hexane (15 cm<sup>3</sup>). The resulting reaction mixture was stirred for 30 s in a boiling water bath until no more CO gas was released and filtered while still warm. Pure crystals of the desired complexes were obtained by slowly cooling the filtered reaction mixture. The characterisation data of complexes 8-11 are as per Tables 1 and 2, the crystal structure of 8 is as per ref. [22]. <sup>13</sup>C NMR (CDCl<sub>3</sub>) for 8: isomer 1,  $\delta$  191.72 (s, *C*-Fc), 167.43 (q, *C*-CF<sub>3</sub>,  ${}^{2}J_{C-F} = 31.8$  Hz), 189.00 (d.d., Rh–CO,  ${}^{1}J_{C-Rh} = 79.3$  Hz,  ${}^{2}J_{C-P} = 24.1$  Hz); isomer 2,  $\delta$  190.34 (s, *C*-Fc), 167.95 (q, *C*-CF<sub>3</sub>, <sup>2</sup>*J*<sub>C-F</sub> = 31.8 Hz), 189.07 (d.d., Rh–CO,  ${}^{1}J_{C-Rh} = 79.3$  Hz,  $^{2}J_{C-P} = 24.1$  Hz).

# 2.2.3. [*Rh*(β-diketonato)(*CO*)(*PPh*<sub>3</sub>)(*CH*<sub>3</sub>)(*I*)] complexes (**12**–**15**)

The syntheses of  $[Rh(FcCOCHCOR)(CO)(PPh_3)-(CH_3)(I)]$ , **12**, may serve as an example. Methyliodide (1.9 g, 13.4 mmol, a 130 fold excess) was added to  $[Rh(fctfa)(CO)(PPh_3)]$  (8) (75 mg, 0.1 mmol) dissolved in hexane (70 ml) at 30 °C. N<sub>2</sub> was purged through the reaction vessel before it was sealed and left at r.t. in the dark. After 5 days crystals suitable for X-ray structure

# Table 1

Compound numbers	β-Diketonato	Isomer numbers <sup>a</sup>	$\delta^{31}$ P (ppm)	<sup>1</sup> <i>J</i> (Hz) <sup>b</sup>	$\delta^{1}$ H (ppm)	I (%) °	K <sub>c</sub> <sup>a</sup>	$v(CO) (cm^{-1})$	$\chi_{\rm tot}$ <sup>d</sup>	Atom <i>trans</i> to PPh <sub>3</sub> <sup>e</sup>	d(Rh–P) (Å)	References <sup>f</sup>
8	fctfa	1	48.04	176.4	7.4–7.8, 6.08, 4.83, 4.47, 4.22	40	0.68	1986	4.88	0	2.232(1)	[22]
		2	48.04	176.4	7.4–7.8, 6.09, 4.25, 4.06, 3.98	60		1986		0		
9	fca	1	49.05	193.9	7.38–7.78, 5.73, 4.79, 4.37, 4.19, 1.71	19	0.23	1980	4.21	0		
		2	47.53	174.0	7.38–7.78, 5.78, 4.15, 4.08, 3.91, 2.19	83		1980		0		
10	bfcm	1	49.28	179.0	7–8, 6.46, 4.90, 4.43, 4.23	36	0.56	1977	4.08	0		
		2	47.43	176.7	7–8, 6.44, 4.21, 4.18, 3.95	64		1977		0		
11	dfcm		47.36	175.6	7.40–7.82, 6.11, 4.87, 4.41, 4.23, 4.18, 4.16, 3.94			1977	3.74	0		
12	fctfa Rh(III)–alkyl <sup>g</sup>	1	29.33	116.5	7.25–7.50, 5.31, 4.77, 4.48, 4.40, 4 30, 4 30, 1,78	82		2056			2.319(3)	[23]
		2	27.09	115.2.	7.25–7.50, 5.45, 4.80, 4.60, 4.38, 4.24, 4.24, 2.15	18		2056				
13	fca Rh(III)–alkyl <sup>g</sup>	1	30.10	124.5	7.30–8.20, 5.83, 4.53, 4.60, 4.27, 1.50	66		2077				
		2	33.31	120.1	7.30-8.20, 5.83, 4.40, 4.33, 1.42	34		2077				
14	bfcm Rh(III)–alkyl <sup>g</sup>	1			7.0–8.3, 6.55, 4.4–5.2, 4.30, 1.59	65		2078				
		2			7.0–8.3, 6.48, 4.4–5.2, 4.36, 1.50	35		2078				
15	dfem Rh(III)–alkyl <sup>g</sup>				7.35–8.20, 6.15, 4.92, 4.79, 4.68, 4.37, 4.41-4.45, 4.29, 1.50			2078				
16	tftma	1 2	47.85 47.85	172.9 172.9	7.3–8, 6.04, 0.70 7.3–8, 6.04, 1.26	42 58	0.72	1992 1992		0 0	2.238(3)	[35]
17	tfdma	1	47.75	178.0	7.3–8, 5.88, 2.30, 0.60	50	1.00	1984		0	2.239(2)	[36]

<sup>31</sup>P and <sup>1</sup>H NMR spectral parameters, IR carbonyl stretching wave numbers  $\nu$ (CO), Rh–P bond lengths d(Rh–P), equilibrium constants  $K_c$  and the percentage of the isomers (as illustrated in Scheme 2) in CDCl<sub>3</sub> at solutions at 298 K for selected [Rh(L,L'-BID)(CO)(PPh<sub>3</sub>)] and related rhodium(III) complexes

Table	1	(Continued)	

Compound numbers	β-Diketonato	Isomer numbers <sup>a</sup>	$\delta^{31}$ P (ppm)	<sup>1</sup> <i>J</i> (Hz) <sup>b</sup>	$\delta^{1}$ H (ppm)	I (%) °	K <sub>c</sub> <sup>a</sup>	$v(CO) (cm^{-1})$	$\chi_{tot}^{d}$	Atom <i>trans</i> to PPh <sub>3</sub> <sup>e</sup>	d(Rh–P) (Å)	References <sup>f</sup>
		2	48.72	175.7	7.3–8, 5.89, 2.71, 1.20	50		1984		0		
18	tta	1	47.78	176.7		47				0		[30]
		2	47.84	177.7		53				0	2.245(3)	
19a	ba	1	49.28	175.8	7-8, 6.08, 1.53	32	0.47	1980	4.55	0	2.248(3)	[37]
19b		2	49.37	174.8	7-8, 6.13, 2.23	68		1980		0	2.249(3)	
20	tfhd	1	49.14	177.2	7.3–8, 5.85, 2.05, 0.56	40	0.67	1986		0	2.252(3)	[38]
		2	47.86	174.8	7.3–8, 5.89, 2.50, 1.20	60		1986		0		
21	tfaa	1	49.57	177.7	7.3–7.8, 5.84, 1.75	35	0.54	1983	5.35	0		
		2	47.72	176.9	7.3–7.8, 5.88, 2.25	65		1983		0	2.231(3) <sup>h</sup>	[38]
22	tfba	1	49.94	175.8	7-8, 6.57	50	1.00	1983	5.22	0		
		2	48.06	177.0	7-8, 6.57	50		1983		0		
23	dbm		49.56	177.9	7.1-8.1, 6.85			1979	4.42	0	2.237(7)	[39]
24	acac		48.84	175.7	7.8–7.3, 5.45, 2.11, 1.62			1983	4.68	0	2.244(2)	[40]
25	bzaa		49.44	175.0						0	2.243(1)	[41]
26	sacac		35.36	144.5						S	2.300(2)	[42]
27	salnr									Ν	2.281(2)	[43]
28	dmavk	1	41.45	149.7						Ν	2.275(1)	[44]
		2	54.91	172.0						0		
29	dmavk (Rh(III)–acyl)		41.25	152.2							2.260(4)	[45]
30	dmavk (Rh(III)–alkvl)		21.35	107.1							2.356(3)	[32]
31 32	cacsm		45.2	144.6				1944 1956		N N	2.268(1) 2.269(1)	[32] [46]
33	hacsm	1	42.70	148.9				1965		S	2.283(1)	[32]

L,L'-BID, ligand containing co-ordinating donor atoms L and L' that forms a six-membered pseudoaromatic ring when co-ordinated to the Rh nucleus; tftma (1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedionato); tfdma (1,1,1-trifluoro-5-methyl-2,4-hexanedionato); tfhd (1,1,1-trifluoro-2,4-hexanedionato); tfba (1,1,1-trifluoro-4,4-hexanedionato); tfba (1,1,1-trifluoro-4,4-hexanedionato); tfba (1,1,1-trifluoro-4,4-hexanedionato); tfba (1,1,1-trifluoro-4,4-hexanedionato); tfba (1,1,1-trifluoro-4,4-hexanedionato); tfba (1,1,1-trifluoro-4,4-hexanedionato); dbm (1,3-diphenyl-1,3-propanedionato); acac (2,4-pentanedionato); tta (thenoyltrifluoroacetonato); and bzaa (3-benzyl-2,4-pentanedionato). Other abbreviations are defined in the abstract or Fig. 5.

<sup>a</sup> Only in compounds 8–10 do isomers 1 and 2 refer to Scheme 2. Compound 19 fits Scheme 2 when  $R = CH_3$  and the ferrocenyl group is replaced with a phenyl group, 16–18 and 20–22 fits Scheme 2 if  $R = CF_3$  and if the ferrocenyl group is replaced with the appropriate group for the specified  $\beta$ -diketonato ligand. In all cases, isomer 1 represents the expected isomer utilising electronic arguments as described in refs [22,30,31].

<sup>b</sup> For  ${}^{1}J({}^{31}P-{}^{103}Rh)$  couple.  ${}^{31}P$  NMR parameters for 18, 26, 28–31, and 33 are from Ref. [32].

<sup>c</sup> Percent I = % isomer at 298 K.

<sup>d</sup>  $\chi_{tot} = (\chi_R + \chi_{R'})$  on the Gordy scale,  $\chi_R$  and  $\chi_{R'}$  values are as per Refs [16,34].

<sup>e</sup> Donor atom of the co-ordinating ligand bound to the rhodium nucleus *trans* to PPh<sub>3</sub>.

<sup>f</sup> Refs for d(Rh–P).

<sup>g</sup> During oxidative addition of  $CH_3I$ , at least two alkyl and two acyl species were detected. From the kinetics study that we performed (results still to be published) the isolated products as well as the crystal structure of **12** and the cited NMR data corresponds to the dominant alkyl species that formed.

<sup>h</sup> d(Rh–P) for the P(p-C<sub>6</sub>H<sub>5</sub>Cl)<sub>3</sub> complex. A second molecule with d(Rh–P) = 2.231(2) Å was also observed.

 Table 2

 Characterisation data of ferrocene-containing mono- and dicarbonyl rhodium complexes

Complex	Yield a (%)	M.p. (°C)	Percent found (requires)		$v(CO) (cm^{-1})$	Complex <sup>b</sup>	Yield (%)	M.p. (°C)	Percent found (requires)	
			C	Н	-				C	Н
(2) $[Rh(fctfa)(CO)_2]^{\circ}$	66; 83	228	39.8(39.9)	2.1(2.1)	2008; 2074	(8) $[Rh(fctfa)(CO)(PPh_3)]^d$	90	256	55.2(55.3)	3.6(3.5)
(3) $[Rh(fca)(CO)_2]$	45; 79	164	44.8(44.9)	3.0(3.1)	2014; 2068	(9) $[Rh(fca)(CO)(PPh_3)]$	72	184	60.0(59.9)	4.4(4.3)
(4) $[Rh(bfcm)(CO)_2]$	38; 75	205	51.6(51.5)	3.1(3.1)	1998; 2074	(10) $[Rh(bfcm)(CO)(PPh_3)]$	93	165	62.8(63.0)	4.1(4.2)
(5) $[Rh(dfcm)(CO)_2]$	<5; 77	>255	50.1(50.2)	3.3(3.2)	2008; 2074	(11) $[Rh(dfcm)(CO)(PPh_3)]$	43	188	60.5(60.6)	4.2(4.1)

<sup>a</sup> The first percent is for route 1, the second for route 2.

<sup>b</sup> v(CO) values for 8–11 is in Table 1. For 12, [Rh(FcCOCHCOCF<sub>3</sub>)(CO)(PPh<sub>3</sub>)(CH<sub>3</sub>)(I)], d(Rh–C<sub>carbonyl</sub>) = 1.834(9) Å,  $v(CO) = 2056 \text{ cm}^{-1}$ .

<sup>c</sup> Rh-C bond lengths are 1.83(2) and 1.84(2) Å (ref. [21]).

<sup>d</sup> Rh-C bond length is 1.801(5) Å (ref. [22]).

determination [23] were obtained from the reaction mixture. Characterisation data of these complexes are as per Table 1.

# 3. Results and discussion

Two routes were utilised to obtain new dicarbonyl rhodium(I) complexes of general formula [Rh(Fc-COCHCOR)(CO)<sub>2</sub>]. The first consisted of the direct interaction between  $[Rh_2(Cl)_2(CO)_4]$  (1) and the  $\beta$ -diketones ferrocenoyltrifluoroacetone (Hfctfa), ferrocenoylacetone (Hfca), benzoylferrocenoylmethane (Hbfcm) or diferrocenoylmethane (Hdfcm) (route 1, Scheme 1) to give the red complexes  $[Rh(FcCOCHCOR)(CO)_2]$  (2)  $(R = CF_3, 66\% \text{ yield}), (3) (R = CH_3, 45\%), (4) (R =$  $C_6H_5$ , 38%) and (5) (R = Fc, impure trace amounts). To improve yields of 5, an alternative synthetic method involving the cyclooctadiene (cod) dimer of rhodium(I) was employed. In this alternative route,  $[Rh_2(Cl)_2(cod)_2]$ (6) was converted to [Rh(dfcm)(cod)] (7) which in an equilibrium process can undergo carbon monoxide exchange to liberate, in the presence of an excess CO, pure 5 in high (77%) yields (route 2, Scheme 1). To prevent 5 converting back to 7, it proved useful to precipitate it from the CO-saturated solvent, acetone, with water. This procedure results in liberated cod drifting as an oil on top of the aqueous phase while the desired Rh complex settles on the bottom and allows separation of 5 from the reaction mixture without regeneration of starting material, 7, in an equilibrium reaction during work up. Complexes 2-4 were also obtained efficiently (>75% yield) in this manner.

The new deep-red  $[Rh(\beta-diketonato)(CO)(PPh_3)]$ complexes 8–11 with  $\beta$ -diketonato = fctfa (8), fca (9), bfcm (10) and dfcm (11), respectively, were obtained by reacting an equivalent amount of PPh<sub>3</sub> with  $[Rh(\beta-dike$  $tonato)(CO)_2]$  in a *n*-hexane medium. This high-yield reaction (up to 92%) is immediate with precipitation of the product  $[Rh(\beta-diketonato)(CO)(PPh_3)]$ . The ferrocene-containing complexes 2–5 and 8–11 were all acid sensitive. They decomposed on silicagel and NMR studies had to be performed in CDCl<sub>3</sub> which were passed through basic alumina before use. The rhodium(I) complexes 8–11 all undergo oxidative addition with CH<sub>3</sub>I to give  $[Rh(\beta-diketonato)(CO)(CH_3)(I) (PPh_3)]$  (complexes 12–15) with  $\beta$ -diketonato previously defined. Complex 12 was isolated and stable in the solid state for months on end, but in solution IR spectroscopy indicated that CO insertion to an acyl species occurs at a slow rate.

<sup>1</sup>H NMR spectra showed that for each of the  $[Rh(\beta$ diketonato)(CO)(PPh<sub>3</sub>)] complexes 8-10 two isomers exist in solution (Fig. 1 and Scheme 2). Only 11, which has a symmetrical β-diketonato ligand co-ordinated to the rhodium(I) nucleus, exists as a single species in solution. Regarding the two possible isomers, we chose to label the isomer with CO trans to the oxygen atom nearest to the more electron-donating ferrocenyl group [16] of the  $\beta$ -diketonato chelate ring as isomer 1, while the other isomer is labelled isomer 2 (Scheme 2). Focussing on the positions of the signals of the <sup>1</sup>H NMR spectrum of [Rh(fca)(CO)(PPh<sub>3</sub>)] between 3.9 and 4.9 ppm (Fig. 1), the set of signals belonging to an isomer in the more downfield position is assigned to isomer 1. The other set of signals belongs to isomer 2. This assignment was done utilising the following arguments: It is known that electron-withdrawing substituents on ferrocene derivatives move the position of the proton signals of the substituted cyclopentadienyl ring downfield [24]. Acetylferrocene, by way of example, exhibits signals at 4.78 ppm (2H,  $C_5H_4$ ), 4.52 ppm (2H,  $C_5H_4$ ) and 4.21 ppm (5H,  $C_5H_5$ ), compared with the position of the singlet signal of ferrocene itself at 4.18 ppm. Conversely, any electron-donating substituents move the signal of the protons of both cyclopentadienyl rings to a more upfield position. For example, ethylferrocene exhibits signals at 4.01-4.05 ppm (4H, C<sub>5</sub>H<sub>4</sub>)



Scheme 1. Synthetic routes for the synthesis of the  $[Rh(\beta-diketonato)(CO)_2]$  complexes 2–5 and  $[Rh(\beta-diketonato)(CO)(PPh_3)]$  complexes 8–11 from  $RhCl_3 \cdot 3H_2O$ . Route 2 gave higher yields of 2–5. Oxidative addition of  $CH_3I$  to 8–11 to yield 12–15 was shown by <sup>1</sup>H NMR to be a slow equilibrium reaction. If 12–15 are not isolated in the solid state, carbonyl insertion to form an acyl species (not shown) takes place over several days. Fc, ferrocenyl,  $C_{10}H_9Fe$ .



Fig. 1. <sup>1</sup>H NMR (left, referenced to SiMe<sub>4</sub> at 0 ppm) and <sup>31</sup>P NMR spectra (right, referenced to 85% H<sub>3</sub>PO<sub>4</sub> at 0 ppm) of [Rh(fca)(CO)(PPh<sub>3</sub>)] (9) in CDCl<sub>3</sub> illustrate the existence of two isomers for this complex. Isomers 1 and 2 as well as  $K_c$  are defined in Scheme 2. <sup>1</sup>H NMR assignments: isomer 1:  $\delta$  1.71 (3H, s, CH<sub>3</sub>), 4.19 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.37 (2H, t, C<sub>5</sub>H<sub>4</sub>), 4.79 (2H, t, C<sub>5</sub>H<sub>4</sub>), 5.73 (1H, s, CH) and 7.38–7.78 (15H, m, 3 × C<sub>6</sub>H<sub>5</sub>); isomer 2:  $\delta$  2.19 (3H, s, CH<sub>3</sub>), 3.91 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.08 (2H, t, C<sub>5</sub>H<sub>4</sub>), 4.15 (2H, t, C<sub>5</sub>H<sub>4</sub>), 5.78 (1H, s, CH) and 7.38–7.78 (15H, m, 3 × C<sub>6</sub>H<sub>5</sub>). <sup>31</sup>P NMR assignments: isomer 1:  $\delta$  49.05 (d,  $J_{P-Rh} = 193.9$  Hz); isomer 2:  $\delta$  47.53 (d,  $J_{P-Rh} = 174.0$  Hz).

and 4.08 ppm (5H,  $C_5H_5$ ), respectively [24]. Utilising these observations, the influence of the electron-withdrawing CO and the electron-donating PPh<sub>3</sub> groups [25] (relative to each other) on the  $\beta$ -diketonato carbonyl group trans to the O-atom nearest to the ferrocenyl moiety in isomers 1 and 2 (Scheme 2) can be evaluated. In the case of isomer 2, the PPh<sub>3</sub> group donates electron density via a d-orbital  $\sigma$  bond to the rhodium nucleus and accordingly also to the oxygen trans to PPh<sub>3</sub> and nearest to the ferrocenyl group, while for isomer 1, the CO group withdraws electron density from the carbonyl group neighbouring the ferrocenyl moiety in the  $\beta$ -diketonato ligand. The net result of this electron withdrawing and electron donating action is a relatively higher electron density on the ferrocenyl group of isomer 2 than on the ferrocenyl group of isomer 1. Therefore, the higher electron density in the ferrocenyl group of isomer 2 manifest in <sup>1</sup>H NMR peak positions of its protons in a more upfield position compared with those of isomer 1. By applying the above concepts to each of the complexes 8-10, an equilibrium constant defined as  $K_c = [\text{isomer 1}]/[\text{isomer}]$ 2] and applicable to the equilibrium shown in Scheme 2, may be determined by calculating the ratio of peak integral values of non-overlapping corresponding signals of each isomer and averaging all answers. For  $[Rh(fca)(CO)(PPh_3)], K_c, may be calculated from the$ peak integrals of the methine proton of the β-diketonato ligand fca, giving  $K_c = 0.22/1.00 = 0.22$ . Other combinations of peak integration result in  $K_c = 0.46/$ 2.15 = 0.21 or 0.49/2.12 = 0.23 or 1.11/5.03 = 0.22 (integral values were taken from the NMR shown in Fig. 1). The average of these values is  $K_c = 0.22$ . The described <sup>1</sup>H NMR technique to determine  $K_c$  values was also a series of other [Rh(β-diketoapplied to

nato)(CO)(PPh<sub>3</sub>)] complexes 16–25, obtained  $K_c$  values are summarised in Table 1. It is notable that complexes 11 and 23–25, which have symmetrical  $\beta$ -diketonato ligands, have only one isomer in solution. <sup>31</sup>P NMR also differentiate between isomers 1 and 2 (Fig. 1 and Table 1). The time needed for each complex to reach the solution equilibrium position according to Scheme 2 varied. For both the new complexes [Rh(fctfa)(CO)-(PPh<sub>3</sub>)] (8) and [Rh(bfcm)(CO)(PPh<sub>3</sub>)] (10) the equilibrium set in quickly (less than 115 s, the time required to dissolve the complex and to record data for a <sup>1</sup>H NMR spectrum), but [Rh(fca)(CO)(PPh<sub>3</sub>)] (9) needed 10 min for the equilibrium to set in.

The ratio of isomers, i.e.  $K_c$ , is independent of concentration in the concentration range 0.0028-0.0200 mol dm<sup>-3</sup>, but temperature and solvent dependent. The variation of the  $K_c$  with temperature for the equilibrium shown in Scheme 2 may be mathematically quantified by

$$\ln K_{c2} = \ln K_{c1} - \frac{\Delta_r H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

with  $K_{c2}$  and  $K_{c1}$  the equilibrium constants at temperatures  $T_2$  and  $T_1$ , R = 8.314 J K<sup>-1</sup> mol<sup>-1</sup> and  $\Delta_r H$  the



Scheme 2. Equilibrium between the two isomers of unsymmetrical complexes of the type [Rh(FcCOCHCOR)(CO)(PPh<sub>3</sub>)] with  $R = CF_3$ , CH<sub>3</sub> and C<sub>6</sub>H<sub>5</sub>.  $K_c =$  [isomer 1]/[isomer 2].



Fig. 2. Temperature dependence of  $K_c$  for the equilibrium (Scheme 2) between the two isomers of  $[Rh(fctfa)(CO)(PPh_3)]$  (8)  $\blacktriangle$ ,  $[Rh(fca)(CO)(PPh_3)]$  (9)  $\bullet$ , and  $[Rh(bfcm)(CO)(PPh_3)]$  (10)  $\blacklozenge$ .

reaction enthalpy as defined elsewhere [26,27]. The above equation also implies that a graph of  $\ln K_c$  versus 1/T should be linear [27], with slope  $-\Delta_r H/R$ . Fig. 2 illustrates this linearity in CDCl<sub>3</sub> for [Rh(fctfa)-(CO)(PPh<sub>3</sub>)], [Rh(fca)(CO)(PPh<sub>3</sub>)] and [Rh(bfcm)(CO)-(PPh<sub>3</sub>)].  $\Delta_r H$  values at 298 K in CDCl<sub>3</sub> for the [Rh( $\beta$ diketonato)(CO)(PPh<sub>3</sub>)] complexes 8-10 are summarised in Table 3. The thermodynamic quantities Gibbs free energy,  $\Delta_r G$ , and reaction entropy,  $\Delta_r S$ , calculated [27] from the equations  $\Delta_r G = -RT \ln K_c$ and  $\Delta_{\rm r}G = \Delta_{\rm r}H - T\Delta_{\rm r}S$  at 298 K are also presented. It is instructive to note that the large temperature dependence of  $K_{\rm c}$  found in this study appears to be a direct consequence of the presence of the ferrocenyl group in our ligands. In contrast to what we found for our ferrocene-containing complexes, temperature studies by Trzeciak [28] and others on non-ferrocene-containing  $\beta$ -diketonato complexes noted that temperature does not influence the position of the equilibrium between different isomers of this type of complexes much. A <sup>1</sup>H NMR study of the equilibrium position between the two isomers of [Rh(fctfa)(CO)(PPh<sub>3</sub>)] in different solvents revealed that  $K_c$  is dependent on the polarity of the solvent,  $E_{\rm T}(30)$ , as measured on the Dimroth [29] scale. The observed relationship between  $E_{\rm T}(30)$  and  $K_{\rm c}$ (Fig. 3) is empirical and must at least in part reflect improved solvation of [Rh(fctfa)(CO)(PPh<sub>3</sub>)] by solvent molecules of higher solvent polarity.



Fig. 3. Linear dependence of the equilibrium constant  $K_c$  at 298 K for the equilibrium between the isomers of the [Rh(fctfa)(CO)(PPh<sub>3</sub>)] complex in different solvents as a function of solvent polarity,  $E_T(30)$ . Polarity data (on the Dimroth scale) are from ref. [29].

<sup>1</sup>H NMR spectra also distinguish between at least two main isomers, see Table 1, for the  $[Rh(\beta-diketo$ nato)(CO)(CH<sub>3</sub>)(I)(PPh<sub>3</sub>)] complexes 12–15. However, a thermodynamic study to determine thermodynamic data for the rhodium(III) isomers was not undertaken as these solutions were not stable. After 24 h, the existence of a slow equilibrium between the alkyl rhodium(III) complexes 12-15, acyl rhodium(III) complexes of the type the  $[Rh(\beta-diketonato)(COCH_3)(I)(PPh_3)]$ (not shown in Scheme 1) and the initial reactant rhodium(I) complexes 8-11 became apparent. Effects of temperature variations on the value of  $K_c$  between different isomers of complexes 12–15 will therefore not be uniquely attributable to only one equilibrium step, but will be a composite of effects due to the multiple equilibria observed for these solutions.

It is noteworthy that the equilibrium constants,  $K_c$  in CDCl<sub>3</sub>, summarised in Table 1, favour isomer 2 in Scheme 2, yet the crystal structure of [Rh(fctfa)(CO)-(PPh<sub>3</sub>)] that was previously reported [22] was that of isomer 1. In our previous communication [22] we argued that isomer 2 should be the dominant isomer based on electronic considerations [30] (*trans* influence) according to the polarisation theory put forward by Grinberg [31]. When we found in the structure determination that isomer 1 was isolated, we attributed the unexpected result to steric implications of the transition state during substitution of the carbonyl group in **2** with PPh<sub>3</sub>. This study, however, reveals that there is a

Table 3

Equilibrium constants  $K_c$  at 298 K and in CDCl<sub>3</sub> for the equilibrium shown in Scheme 2 as well as the thermodynamic data, also at 298 K, relevant to this equilibrium for [Rh( $\beta$ -diketonato)(CO)(PPh<sub>3</sub>)] complexes

Complex	K <sub>c</sub>	$\Delta_{\rm r} H ~({\rm kJ}~{\rm mol}^{-1})$	$\Delta_{\rm r} G \; ({\rm kJ} \; {\rm mol}^{-1})$	$\Delta_r S (J \text{ mol}^{-1} \text{ K}^{-1})$
[Rh(fctfa)(CO)(PPh <sub>3</sub> )]	0.68(2) <sup>a</sup>	6.2(3)	0.97(4)	17.6(6)
[Rh(fca)(CO)(PPh <sub>3</sub> )]	0.23(3)	7.6(3)	3.0(1)	15(1)
[Rh(bfcm)(CO)(PPh <sub>3</sub> )]	0.56(3)	8.6(3)	1.4(3)	24(2)

<sup>a</sup>  $K_c$  for the fctfa complex varied as follows in the deuterated solvents (solvent polarity [29] are given in brackets): cyclohexane, 1.03 (30.9); benzene, 0.86 (34.3); acetone, 0.33 (42.2); DMSO, 0.20 (45.1) and acetonitrile, 0.16 (54.6).

fast equilibrium between isomers 1 and 2, which largely invalidates our previous explanation. Previously, we have not given consideration to the possibility that the observed isomer simply crystallised because it had a more favourable crystallisation energy. The isomer that dominates in solution will definitely be the one that is thermodynamically more stable in solution. It is, however, also true that the isomer that dominates in solution will not necessarily be the one that possesses the most favourable crystallisation energy. The solvent dominant isomer will therefore not necessarily be the isomer that crystallises first from solution. Factors that may influence crystallisation energy include solvent temperature and solvent polarity. It will also be affected by crystal packing in the solid state that will be dependent on the relative orientations of the PPh<sub>3</sub> and ferrocenyl groups. Our previous explanation for the observed structure would only be correct if the obtained isomer also possesses the lowest energy of crystallisation in the particular solvent (hexane) employed and at the experimental temperature at which the crystal was grown. It is, however, interesting to note that the polarities [29] of hexane, 31.0, and cyclohexane, 30.9, are virtually identical, and that isomer 1 actually is present in slight excess in cyclohexane solutions  $(K_{c,cyclohexane} = 1.03)$ . This implies that, for the fctfa complex, the isomer which is thermodynamically favoured in solution may also be favoured in the solid state, and it would explain why we isolated isomer 1 of **8** from hexane for our structure determination and not isomer 2. In principle, this begs the question if isomer 2 may be obtained in crystalline form from more polar



Fig. 4. The linear relationship between the coupling constants,  ${}^{1}J({}^{31}P{}^{-103}Rh)$ , or the position of the phosphorous signal,  $\delta^{31}P$ , and the Rh–P bond distance, d(Rh–P) of the indicated rhodium phosphine complexes. Data and complex numbers are as per Table 1.

solvents such as acetone or acetonitrile (Fig. 3). Unfortunately, to date, we were not successful in isolating crystals suitable for crystallography from more polar media.

In previous communications [32], Roodt et al. reported that there exists an approximately linear relationship between Rh-P bond distances, d(Rh-P), and (a) chemical shift positions,  $\delta^{31}$ P (ppm), as well as (b) coupling constants,  ${}^{1}J({}^{31}P{}^{-103}Rh)$ , in  ${}^{31}P$  NMR spectra of rhodium complexes of the type [Rh(L,L'-BID)(CO)(PPh<sub>3</sub>)] with L,L'-BID = a symmetric or asymmetric bidentate ligand, and L or L' the coordinating donor atoms O, S or N that co-ordinates to the rhodium nucleus. The complex [Rh(fctfa)(CO)(PPh<sub>3</sub>)] (8) prepared in this study belongs structurally to the series reviewed by Roodt [32] but represents the first example in which the co-ordinating ligand, fctfa, contains the organometallic ferrocenyl group. We have found that the <sup>31</sup>P NMR parameters of 8 also fall on the linear trend observed as shown in Fig. 4. Fig. 4 clearly illustrates that larger d(Rh-P) values are associated with smaller  ${}^{1}J({}^{31}P{}^{-103}Rh)$  coupling constants as well as smaller  $\delta^{31}$ P peak positions, in ppm. A fit on the data of Fig. 4 implies that approximate d(Rh-P) values for the class of compounds under discussion may be calculated utilising the equations

$$d(Rh-P) = -0.0014(1) \times {}^{1}J({}^{31}P-{}^{103}Rh) + 2.49(2)$$
$$= -0.0041(3) \times \delta {}^{31}P + 2.44(1)$$

These two equations are applicable for d(Rh–P) values between 2.23 and 2.36 Å. Utilising these equations, it follows from <sup>31</sup>P NMR data (Table 1) that the average Rh-P bond length for isomers 1 and 2 of the fca and bfcm complexes 9 and 10 should be in the order of 2.24 and 2.25 Å, respectively. The Rh-P distance of the dfcm complex, 11, is calculated to be approximately 2.25 Å. The errors on the derived equations prohibit meaningful more accurate bond lengths. The data in Table 1 indicate that coupling constants,  ${}^{1}J({}^{31}P{}^{-103}Rh)$ , in complexes with PPh<sub>3</sub> trans to a N or a S atom are approximately equal in size, but appreciably smaller than  ${}^{1}J({}^{31}P-{}^{103}Rh)$  values for complexes in which PPh<sub>3</sub> is trans to an O atom. Rh-C bonds distance in these square-planar complexes follow a similar trend as the Rh–P bonds when compared with  ${}^{1}J({}^{13}C-{}^{103}Rh)$  values, but is much less accurate for reasons adequately explained elsewhere [32].

The Rh–P bond distance in square-planar complexes of the type  $[Rh(L,L'-BID)(CO)(PPh_3)]$  is also a good indicator of the relative *trans* influence (a ground state thermodynamic phenomenon that is defined as the ability of a ligand to weaken the metal–ligand bond *trans* to it) of the donor atoms L and L' in the bidentate ligand (L,L'-BID) [32]. Atoms co-ordinated to the rhodium nucleus with a larger *trans* influence will



Fig. 5. Structures of two isomers of [Rh(ba)(CO)(PPh<sub>3</sub>)] (19a) and (19b); [Rh(sacac)(CO)(PPh<sub>3</sub>)] (26); [Rh(salnr)(CO)(PPh<sub>3</sub>)] (27); [Rh(d-mavk)(CO)(PPh<sub>3</sub>)] (28); [Rh(cacsm)(CO)(PPh<sub>3</sub>)] (31); [Rh(macsm)(CO)(PPh<sub>3</sub>)] (32) and [Rh(hacsm)(CO(PPh<sub>3</sub>)] (33). Ba, benzoylacetone; sacac, thioacetylacetonato; salnr, *N-o*-tolylsalicylaldiminato; dmavk, dimethylaminovinylketonato; cacsm, methyl(2-cyclohexylamino-1-cyclopentene-1-dithiocarboxylato); macsm, methyl(2-methyl-amino-1-cyclopentene-1-dithiocarboxylato); hacsm, methyl(2-amino-1-cyclopentene-1-dithiocarboxylato).

lengthen the bond, here the Rh–P bond, *trans* to it. For the cited complexes in Table 1 the Rh–P bond distances, d(Rh–P), vary in the order

d(Rh-P) trans to O atoms

< d(Rh-P) trans to N atoms

< d(Rh-P) trans to S atoms

which implies S has a larger *trans* influence than N, while O has a smaller *trans* influence than N. One way of quantifying this observed tendency is to establish a relationship between atomic electronegativities of O, N and S, utilising the Pauling scale, and the observed Rh-P bond lengths trans to these co-ordinating atoms. To establish this relationship, the compounds considered need to be structurally related to each other and d(Rh-P) should be as accurate as possible. To satisfy these criteria, we considered three classes of O,O ligands, two classes of N,O ligands and the only available example of an S,O class of ligands. For the O,O ligands, i.e. β-diketonates, the first subclass is represented by the complexes 8, 16 and 17 and contains the CF<sub>3</sub> group adjacent to the carbonyl group trans to PPh<sub>3</sub>. The second subclass has a CH<sub>3</sub> group in this position, compounds 19a, 21, 24 and 25 are representative of this type. The third subclass in the O,O class has a phenyl group in this position and compound 19b represents the only suitable example of this subclass. The two available examples of N<sub>0</sub> family of ligands are represented by the salnr and dmavk complexes 27 and 28, while the only suitable available example of the family of complexes having a S,O ligand is the sacac complex 26 (Fig. 5 and Table 1). The average d(Rh–P) of the specified CF<sub>3</sub> containing  $\beta$ -diketonates was 2.235 Å, for the CH<sub>3</sub>  $\beta$ -diketonates it is 2.245 Å and for the indicated phenyl-containing  $\beta$ -diketonate it is 2.248 A. Fig. 6, upper graph, demonstrates how d(Rh-P) varies with the Pauling atomic electronegativity of O (3.5), N (3.0) and S (2.5). It is evident that there is a direct relationship between d(Rh-P) and the co-ordinating atoms of a ligand *trans* to the PPh<sub>3</sub> group provided that the complexes are structurally related. This explains why d(Rh-P) for the hacsm complex **33**, an N,S co-or-



Fig. 6. Upper graph: Relationship between d(Rh-P) and the Pauling atomic electronegativity of co-ordinating atoms O, N and S trans to the PPh<sub>3</sub> group in complexes of the type [Rh(L,L'BID)(CO)(PPh<sub>3</sub>)]. L,L'-BID, bidentate ligands possessing Q,O or N,O or S,O co-ordinating donor atoms. The indicated R<sup>N</sup> groups in the NO and NS series represents the third substituent on N. The individual compounds used are 27 and 28 (N,O series) or 31 and 32 (N,S series), while the S,O entry is for the sacac complex 26. Ph, phenyl; Me, methyl; Ch, cyclohexyl. Bottom graph: Relationship between d(Rh-P) and group electronegativities of the R groups CF<sub>3</sub>, Me or Ph adjacent to the carbonyl group of the  $\beta$ -diketonato ligand *trans* to the PPh<sub>3</sub> group in complexes of the type [Rh(RCOCHCOR')(CO)(PPh<sub>3</sub>)]. The CF<sub>3</sub> point is from the average d(Rh-P) of complexes 8, 16 and 17, the Me point is from the average d(Rh-P) for complexes 19a, 12, 24 and 25, while the Ph point is from 19b. The same compound sets were also used in the upper graph of the Q,O series. R' does not influence the position of the points of either series.

dinated ligand with PPh<sub>3</sub> trans to S, deviates so substantially from that of the S,O complex 26. A further point of interest is observed in the N,S co-ordinated complexes 31 and 32 with PPh<sub>3</sub> trans to N. Although they do not belong to the N,O class of compounds with PPh<sub>3</sub> trans to N, they would fit into this latter series of compounds in terms of d(Rh-P). These observations seem to imply that, provided the atomic or group electronegativity of the atoms or groups *cis* to the Rh–P bond is not substantially larger than those of the atoms or groups trans to the Rh-P bond, the influence of the cis group or atom can be ignored. This is to be expected, because the shape of d orbitals allows for more effective trans influences than cis influences. It also correlates well with the fact that the trans effect (a kinetic phenomenon that is defined as the ability of a ligand to influence the rate of substitution of a ligand bound to a metal trans to it) dominates the cis effect substantially [33]. The observed good relationship between d(Rh-P) and the Pauling atomic electronegativities of O, N and S in the indicated main classes of complexes begs the question how variations within a particular main group, such as the CF<sub>3</sub>, CH<sub>3</sub> and Ph sub-members of the O,O family of β-diketonato complexes, may manifest itself. The bottom graph in Fig. 6 demonstrates the relationship between group electronegativities of the indicated groups adjacent to the carbonyl group of the  $\beta$ -diketonato ligand *trans* to the PPh<sub>3</sub> group and d(Rh-P). The smaller spread of d(Rh-P) values within this family of β-diketonato of complexes, 2.235-2.248 Å, as compared with the much larger spread over the three main groups of ligand, 2.235–2.300 Å, are readily understood upon recognising that the latter is the result of an electronic effect by an atom directly bonded to the rhodium nucleus (a first order effect), while the first is an electronic effect as a result of a group of atoms separated from the rhodium nucleus by two atoms, i.e. a third order effect. Were it not for the fact that the  $\beta$ -diketonato skeleton is pseudo-aromatic which allows electronic communication via conjugation, the latter effect would probably not have been noticeable at all.

The IR spectrum of the complexes [Rh(FcCOCH-COR)(CO)<sub>2</sub>] (2–5) has two distinctive separate peaks (Table 2) at higher wave numbers than the observed single IR carbonyl stretching frequency for the monocarbonyl-phosphine rhodium(I) complexes 8–11 (Table 1). The lower CO wave number,  $\nu$ (CO), for monocarbonyl-phosphine rhodium(I) compounds is a result of the higher electron density on the rhodium centre due to electron donation of PPh<sub>3</sub> through the d orbital  $\sigma$  bond that binds it to the rhodium(I) nucleus. Oxidative addition of methyl iodide to the monocarbonyl(phosphine)rhodium(I) complexes results inter alia in the rhodium(III) complexes 12–15. The rhodium(III) nucleus is more electron deficient than the rhodium(I) nucleus and this manifests in a single, larger v(CO)stretching wave number than that observed for the monocarbonyl(phosphine)rhodium(I) complexes. By noting that shorter wavelengths (i.e. longer wave numbers) represent stronger C-O bond energies in carbonyl groups, and therefore weaker Rh-C bonds in Rh-CO complexes, it follows that the Rh(III)–C bond in  $[Rh(\beta$ diketonato)(CO)(PPh<sub>3</sub>)(CH<sub>3</sub>)(I)] complexes should be weaker (i.e. longer) than Rh(I)-C bonds in [Rh(β-diketonato)(CO)(PPh<sub>3</sub>)] complexes. On the same basis, both of the Rh(I)–C bonds in [Rh( $\beta$ -diketonato)(CO)<sub>2</sub>)] complexes should be weaker than the Rh(I)-C bond in the corresponding  $[Rh(\beta-diketonato)(CO)(PPh_3)]$ complexes. The crystallographic determined bond lengths (Table 2) for [Rh(fctfa)(CO)<sub>2</sub>], [Rh(fctfa)(CO)(PPh<sub>3</sub>)] and [Rh(fctfa)(CO)(PPh<sub>3</sub>)(CH<sub>3</sub>)(I)] are in agreement with all the described predictions.

From the foregoing it follows that for all the complexes of the type [Rh(RCOCHCOR')(CO)(PPh<sub>3</sub>)], the group electronegativity of the terminal R and R' groups on the β-diketonato ligand directly influences the electron density on the rhodium metal centre. Since the change in electron density on the metal is also reflected in changes in carbonyl stretching frequencies (increased electron density on a metal centre results in lower CO infrared frequencies), a relationship between this parameter and group electronegativities of R and R' should exist. We have previously determined apparent group electronegativities,  $\chi_R$ , on the Gordy scale from the formal reduction potential  $E^{\circ\prime}$  of five ferrocene-containing  $\beta$ -diketones as well as the IR stretching frequencies of eight different methyl esters [16,34]. These  $\chi_{\rm R}$ values were used to determine the sum of the group electronegativities of R and R', that is  $\chi_{R} + \chi_{R'}$ , of the  $\beta$ -diketonato ligand (RCOCHCOR')<sup>-</sup> in Table 1. Fig. 7 illustrates, as was expected, that in complexes of the type [Rh(RCOCHCOR')(CO)(PPh<sub>3</sub>)] the infrared CO stretching frequency, v(CO), increases linearly as R and R' are replaced by more electron withdrawing groups, i.e. groups with a higher group electronegativity. It follows that a measure of the electron density on the rhodium nucleus of this class of compounds may be expressed in terms of the sum of the group electronegativities of R and R' of the  $\beta$ -diketonato ligand  $(RCOCHCOR')^{-}$  co-ordinated to the rhodium nucleus. The larger this quantity is, the less will the electron density on the rhodium core be. Finally, we have previously shown that there is a linear relationship between  $pK'_a$  of ferrocene-containing  $\beta$ -diketones and the group electronegativities of substituents on them [16,34]. One would therefore also expect a linear relationship between v(CO) of  $[Rh(\beta-diketonato)(CO)-$ (PPh<sub>3</sub>)] complexes and  $pK'_a$  of the free  $\beta$ -diketones. This was found to be the case as illustrated in the insert of Fig. 7. From Fig. 7, it follows that v(CO) of complexes of the type [Rh(β-diketonato)(CO)(PPh<sub>3</sub>)] may be calculated by the equations



Fig. 7. Relationship between the carbonyl stretching wave number,  $\nu$ (CO), and the sum of the group electronegativities of R and R' ( $\chi_{\rm R} + \chi_{\rm R'}$ ) of the  $\beta$ -diketonato ligand (RCOCHCOR')<sup>-</sup> co-ordinated to [Rh(RCOCHCOR')(CO)(PPh<sub>3</sub>)]. The  $\beta$ -diketonato ligands are as indicated. The insert shows how  $\nu$ (CO) varies with the apparent pK'<sub>a</sub> values of the free  $\beta$ -diketone ligands RCOCH<sub>2</sub>COR' of the same complexes. Values of individual group electronegativities,  $\chi_{\rm R}$  and  $\chi_{\rm R'}$ , are as per refs [16,34].

$$v(CO) = 5(1)(\chi_R + \chi_{R'}) + 1959(6)$$
  
= -1.3(3)pK'<sub>a</sub> + 1993(2)

#### 4. Conclusions

New rhodium complexes of the type [Rh(FcCOCH- $COR)(CO)_2],$ [Rh(FcCOCHCOR)(CO)(PPh<sub>3</sub>)] and [Rh(FcCOCHCOR)(CO)(PPh<sub>3</sub>)(CH<sub>3</sub>)(I)] were synthesised and characterised. Equilibrium constants between two possible isomers of a large number of unsymmetrical rhodium(I) phosphine complexes have been determined, and the influence of temperature and solvent on this equilibrium was quantified. The influence that  $pK'_{a}$ values of β-diketone ligands and group electronegativities of substituents R on  $\beta$ -diketonato ligands has on d(Rh-P) or v(CO) stretching frequencies was demonstrated and a relationship between d(Rh-P), and <sup>31</sup>P NMR peak positions as well as coupling constants  ${}^{1}J({}^{31}P-{}^{103}Rh)$  have been quantified.

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