*Journal of Organometallic Chemistry*, 429 (1992) 245–256
Elsevier Sequoia S.A., Lausanne
JOM 22462

# Substituted cyclopentadienyl compounds

# I. Formylation of methylcyclopentadienide and the synthesis and NMR study of some thallium(I) and rhodium(I) derivatives of cyano-, methyl-, methanoyl- and dimethylamidocyclopentadienes

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(Received August 7, 1991)

**Abstract**

Reaction of potassium methylcyclopentadienide with methyl methanoate yields the salts of 1-methanoyl-2-methylcyclopentadiene and 1-methanoyl-3-methylcyclopentadiene in a molar ratio of 1.3:1.0. At ambient temperature each isomer comprises two conformers. The identity of and relation between the products were confirmed by 2-*D* $^1$H NMR (COSY and NOESY). Thiele's acid (*endo*-tricyclo[5,2,1,$0^{2,6}$]-4,8-dicarboxylic acid-deca-3,8-diene) was converted into the thallium(I) salts of the monomeric dimethylamide and nitrile. The bis(ethene)–rhodium(I) derivatives were prepared in high yield by reaction of the thallium salts with Cramer's compound $\{(C_2H_4)_2RhCl\}_2$. The alkene rotational barriers ($\Delta G^{\neq}$) are compared and NMR evidence for ring slippage is discussed. The mixed compound $(CO)(C_2H_4)Rh(\eta^5\text{-}C_5H_4CHO)$ shows the lowest reported alkene rotational barrier for any simple rhodium(I)–monocyclic Cp system.

## Introduction

There is considerable interest in the synthesis of polysubstituted cyclopentadienyl systems and their applications as stabilising ligands in organometallic reactions [1–3]. The effectiveness of such ligands arises from a combination of steric and electronic factors with the former often predominant. Steric effects are also important in di- or tri-substituted cyclopentadienyls carrying the isopropyl or *t*-butyl group [4,5]. Our interest lies with those systems in which the influence of the ring substituent is mainly electronic. Apart from the pioneering synthetic work of Rausch [6], and the kinetic studies of Basolo [7], Delgado [8], Bönnemann [9], and Yamazaki [10], there has been little progress in the study of structure–activity

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relationships for mono-substituted cyclopentadienyls in which the substituent is an electron-accepting group. We have previously reported the synthesis of some mono- and di-substituted main group metal and rhodium cyclopentadienyl systems [11]. We noted [12] that electrophilic substitution of cyclopentadienide by chloromethyl methanoate gave a more elaborate product distribution than originally reported [13].

In an effort to expand the area of functionally substituted cyclopentadienyls of potassium, thallium(I), and rhodium(I), we now report on the reaction of methylcyclopentadienide with methyl methanoate and on the synthesis and characterisation of dimethylamido and cyanocyclopentadienyl thallium(I). The latter compounds were prepared from Thiele's dimeric acid [14]. The alkene rotational barriers and potential ring slippage of the bis(ethene)rhodium(I) derivatives are compared with analogous systems.

## Experimental

Reactions were performed under nitrogen in solvents freshly distilled from appropriate drying agents. Melting points were recorded on a Gallenkamp apparatus and are uncorrected. $^1H$ and $^{13}C$ NMR spectra were recorded on Bruker WH-400, AC-250 or Jeol FX-100 spectrometers fitted with variable temperature accessories. The probe temperature was calibrated using methanol below ambient, and ethylene glycol above it [15]. Free energies of activation were calculated from eq. 1 [16]

$$\Delta G^{\#} = -RT_c \ln \frac{\pi \Delta \nu h}{2^{1/2} k T_c} \quad (1)$$

where $\Delta\nu$ is the chemical shift of the coalescing resonances in the absence of exchange, $T_c$ is the coalescence temperature (K), and $R$, $h$ and $k$ have their usual thermodynamic significance. Microanalyses were performed by C.H.N. Analysis Ltd., Leicester. Infrared spectra were recorded over the range 4000–250 $cm^{-1}$ on a Perkin–Elmer 577 spectrophotometer as KBr discs or thin films between KBr plates. Mass spectra were recorded on a Kratos MS-80 instrument.

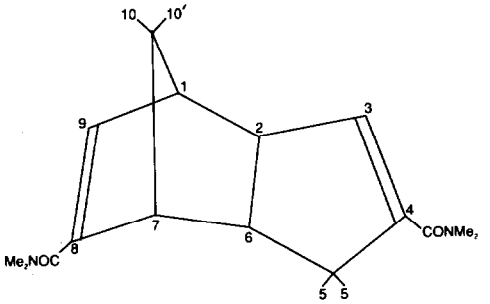
*Synthesis of dicyclopentadiene derivatives*

Dicyclopentadienedicarboxylic acid (Thiele's acid) was prepared as previously described [17].

Endo-*tricyclo[5,2,1,0$^{2,6}$]-4,8-dichloroformyldeca-3,8-diene.* This was prepared by a modification of Peters's method [18]. Pyridine (19.8 g, 0.25 mol) in ether (25 $cm^3$) was added dropwise to a stirred suspension of Thiele's acid (25 g, 0.12 mol) and thionyl chloride (39.3 g, 0.33 mol) in ether (100 $cm^3$) at 20°C. The mixture was stirred for 4 h and filtered, and the filtrate evaporated *in vacuo*. The brown residue was recrystallised from hexane (charcoal). White needles (13.5 g, 46%) of the dimeric acid chloride (m.p. 58–59°C; lit. 60–61°C) were obtained. Anal. Found: C, 56.40; H, 4.21%. $C_{12}H_{10}O_2Cl_2$ calc.: C, 56.03; H, 3.89%; $\nu_{max}$: 1730 (C=O) and 880 (C–Cl) $cm^{-1}$.

Endo-*tricyclo[5,2,1,0$^{2,6}$]-4,8-dimethylamidodeca-3,8-diene.* This was prepared in 65% yield from the dimeric acid chloride by Peters's method [18]. Crystallisation

from hexane gave a white solid melting at 95–96°C. Anal. Found: C, 70.04; H, 8.09, N, 10.22%; $M^+$, 274. $C_{16}H_{22}N_2O_2$ calc.: C, 70.05, H, 8.08, N, 10.21%. MS: $m/e$ 274.4 ($M^+$). The assignments of conformation and position of the amido substituents were made by analogy with the results obtained from the nOe difference and COSY NMR study of Thiele's ester [19]. Values in parentheses are resolved $J$ couplings (Hz, $\pm 0.1$); a dash indicates additional coupling which could not be resolved.




$^1$H NMR spectrum ($CDCl_3$/TMS) $\delta$: 6.14 (d, H(9), 3.2), 5.52 (q, H(3), 2.1), 3.43 (m, H(1), –); 3.22 (d, H(7), 4.0, –), 3.05 (m, H(6), –), 3.0 (s, $CH_3$(4), 2.90; m, H(2), –) 2.86 (d, $CH_3$(8)), 2.50 (dt, H(5), H(5'), 2.3), 1.67, (dt, H(10'), 8.5, 1.8), 1.39, (d, H(10), 8.5, –).

Approximate activation energies for rotation about the C–N bond ($\Delta G^{\#}$) were found to be 58.8 ± 1.0 kJ mol$^{-1}$ for $CH_3$(4) and 70.1 ± 1.0 kJ mol$^{-1}$ for $CH_3$(8). Inspection of molecular models reveals that rotation about the C–N bond is subject to a higher degree of steric hindrance in the latter case.

Endo-*tricyclo[5,2,1,0$^{2,6}$]4,8-dicyanodeca-3,8-diene.* This was prepared in 65% yield by reaction of the corresponding dimeric amide [18] with pyridine and benzenesulphonyl chloride in ether. Crystallisation of the lilac product from methylcyclohexane gave white needles melting at 60–62°C. (lit. 62–64°C) [18]. Anal. Found: C, 78.7; H, 5.8; N, 15.0%. $C_{12}H_{10}N_2$ calc.: C, 79.1; H, 5.5; N, 15.4%. MS: $m/e$ = 182.0 ($M^+$).

*Synthesis of cyclopentadienide salts*

The thallium salts of formylcyclopentadiene, methylcyclopentadiene, chlorocyclopentadiene and phenylcyclopentadiene were prepared as described previously [12,20].

*Thallium(I) dimethylamidocyclopentadienide.* The dimeric dimethylamide (5.0 g, 0.018 mol) was heated at 220°C under reduced pressure (≈ 3 kPa). The resulting monomeric amide was passed directly into a solution of thallium(I) ethoxide (0.036 mol) in benzene (100 cm$^3$). The white precipitate formed, was filtered off and washed successively with benzene (2 × 10 cm$^3$) and diethyl ether (2 × 5 cm$^3$). Recrystallisation of 3.0 g portions from acetonitrile (250 cm$^3$) gave 2.04 g, (37%) of white needles melting at 134–136°C. Anal. Found: C, 28.49; H, 2.97; N, 4.39%; $M^+$, 339/341. $C_8H_{10}NOTl$ calc.: C, 28.20; H, 2.94; N, 4.11%. MS: $m/e$ = 340.4 ($M^+$). $^1$H NMR spectrum (250 MHz, $(CD_3)_2SO$/DSS): $\delta$ 6.15 (t, H(2), H(5)), 5.68 (t, H(3), H(4)), 3.05 (s, Me).

*Thallium(I) cyanocyclopentadienide. Endo*-tricyclo[5,2,1,0$^{2,6}$]-4,8-dicyanodeca-3,8-diene (9.1 g, 0.05 mol) was heated at 200°C under reduced pressure (≈ 3 kPa).

The resulting monomer was passed directly into a stirred aqueous solution of thallium(I) sulphate, (50.5 g, 0.10 mol) and potassium hydroxide (5.6 g, 0.10 mol). The precipitate was washed with water ($4 \times 10$ cm$^3$) and diethyl ether ($2 \times 5$ cm$^3$). Recrystallisation from acetonitrile (1150 cm$^3$) gave 11.8 g (40%) of white needles melting at 150–152°C, lit. 150–152°C [21]. Anal. Found: C, 24.2; H, 1.6; N, 4.6%. $C_6H_4NTl$ calc.: C, 24.5; H, 1.4; N, 4.8%. $\nu_{max}$: 2200 (C≡N), and 740 (C–H) cm$^{-1}$. MS: $m/e$ = 294.4 ($M^+$). $^1$H NMR spectrum (250 MHz, $(CD_3)_2SO$/DSS): $\delta$ 6.34 (t, H(2), H(5)), 5.87 (t, H(3), H(4)).

*Reaction of potassium methyl cyclopentadienide with ethyl methanoate*

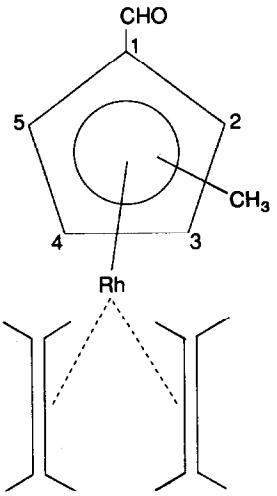
Powdered potassium hydroxide (50 g, 0.89 mol) was added with vigorous stirring to a solution of freshly purified [22] methylcyclopentadiene (16.0 g, 0.20 mol) in deoxygenated 1,2-dimethoxyethane (200 cm$^3$). The resulting pink suspension was filtered after 2 h. Freshly purified ethyl methanoate (14.8 g, 0.20 mol) was added to the filtrate and the solution was refluxed for 1 h. A slow precipitation of the off-white product commenced after 30 min. The solid was filtered off, washed with diethyl ether ($3 \times 25$ cm$^3$), and dried *in vacuo*. Anal. Found: C, 56.90; H, 4.4%. $C_7H_7OK$ requires C, 57.49; H, 4.79%. $\nu_{max}$: 2765, 2690, (CHO), 1600 (C=O), 791, 765, and 735 cm$^{-1}$. Increasing the reaction time and the proportion of ethyl methanoate had no effect on the relative amounts of 1,2- and 1,3-isomers present in the product and no higher substitution products could be identified.

*Thallium(I) 1,2- and 1,3-methylmethanoylcyclopentadienides.* To a saturated aqueous solution of thallium(I) ethanoate (13.1 g, 0.05 mol) was added a solution of the potassium salt, (7.4 g, 0.05 mol) in water (50 cm$^3$). The product precipitated at once and was washed with water ($3 \times 20$ cm$^3$), and dried *in vacuo*. Recrystallisation of 4.0 g portions from acetonitrile (250 cm$^3$) gave *ca.* 3.0 g of beige solid. Anal. Found: C, 26.70; H, 2.05%; $M^+$ 310/312. $C_7H_7O_2Tl$ calc.: C, 29.67; H, 2.25%. MS: $m/e$ 311.4 ($M^+$). $^1$H NMR spectrum (100 MHz $(CD_3)_2SO$/DSS): $\delta$ (1,2-isomer) 9.32 (br s, CHO), 6.07 (m, H(5)), 5.64 (m, H(4)), 5.59 (m, H(3)), 2.24 (s, Me); (1,3-isomer) 9.10 (s, CHO), 6.12 (m, H(5)), 5.72 (m, H(4)), 6.05 (m, H(2)), 2.04 (s, Me).

*Rhodium(I) complexes*

Ethylene complexes were prepared by reaction of Cramer's compound, $\{[C_2H_4]_2RhCl\}_2$ with an excess of the appropriate thallium salt at 20°C in diethyl ether. After 24 h, the ether was evaporated and the residue extracted repeatedly with pentane. Filtration and evaporation of the pentane extracts gave a yellow solid or oil which was purified by high vacuum sublimation. Compounds **5–9** have been reported previously [12,20].

*$\eta^5$-Methylmethanoylcyclopentadienylbis($\eta^2$-ethene)rhodium(I) (1 and 2).* A yellow oil was prepared in 65% yield. Anal. Found: C, 49.8; H, 5.8%. $C_{11}H_{15}ORh$ calc.: C, 49.6, H, 5.6%. MS: $m/e$ = 266 ($M^+$), 238 ($M^+ - C_2H_4$), 210 ($M^+ - 2C_2H_4$). ($\eta^5$-$C_5H_4CHO$)Rh(CO)($\eta^2$-$C_2H_4$) (**4**) was obtained as an orange oil by reaction of $[(\eta^2\text{-}C_2H_4)(CO)RhCl]_2$ (778 mg, 2.0 mmol) with K($C_5H_4CHO$) (790 mg, 6.0 mmol) in diethyl ether for 24 h at 20°C. The filtrate was evaporated and the residue distilled (≈ 100 Pa) on to a Drikold finger at −78°C; yield 520 mg (2.06 mmol, 52%). Anal. Found: C, 42.5; H, 4.0%. $C_9H_9O_2Rh$ calc.: C, 42.9; H, 3.6%. MS: $m/e$ 252 ($M^+$). Accurate mass analysis of fragment ion peaks at $m/e$



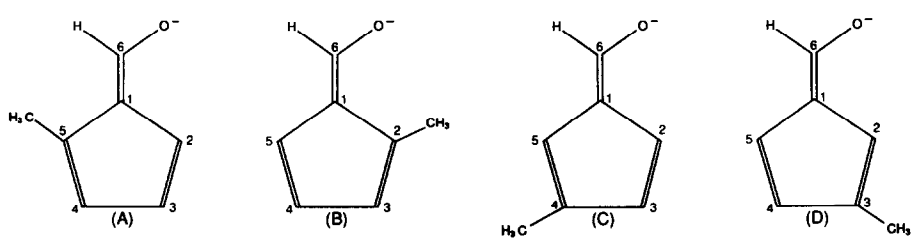

(1/2)

224 and 196 indicates that elimination of CO and $C_2H_4$ is competitive. Similarly, analysis of the related compound, $(C_5H_4CHO)Rh(C_2H_4)_2$ shows that the peak at *m/e* 196 arises from loss of two ethene groups and competitive loss of ethene then CO [23].

*$\eta^5$-Dimethylamidocyclopentadienylbis($\eta^2$-ethene)rhodium(I) (3).* A yellow solid melting at 67°C was prepared in 76% yield by reaction of $Tl(C_5H_4CONMe_2)$ with $[RhCl(\eta^2\text{-}C_2H_4)_2]_2$. Anal. Found: C, 49.04; H, 6.17; N, 4.82%. $C_{12}H_{18}ORh$ calc.: C, 48.83; H, 6.15; N, 4.75. MS: *m/e* 295 ($M^+$).

## Results and discussion

Figure 1 shows the 400 MHz $^1H$ NMR spectrum of the products resulting from reaction of $K^+[C_5H_4Me]^-$ and $C_2H_5OCHO$. Since Hafner found [24] that reaction of sodium cyclopentadienide with ethyl methanoate gave only sodium methanoylcyclopentadienide, we anticipated a similar result for the anion of methylcyclopentadiene. However, structural elucidation using 2-*D* NMR techniques was required in this case owing to the complex pattern shown by the ring nuclei.




An excerpt from the contour plots of the COSY spectrum of the reaction products is shown in Fig. 2. This shows the *J* coupling interactions between the

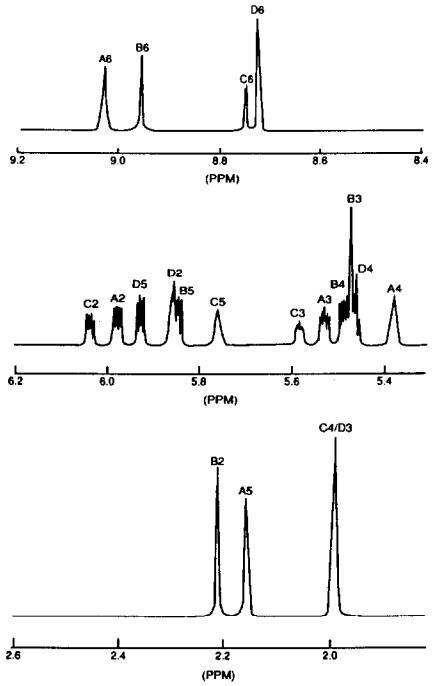



Fig. 1. 400 MHz $^1$H NMR spectrum of $K^+[C_5H_3(CHO)CH_3]^-$. Chemically nonequivalent cyclopentadienide species are labelled A, B, C, and D.

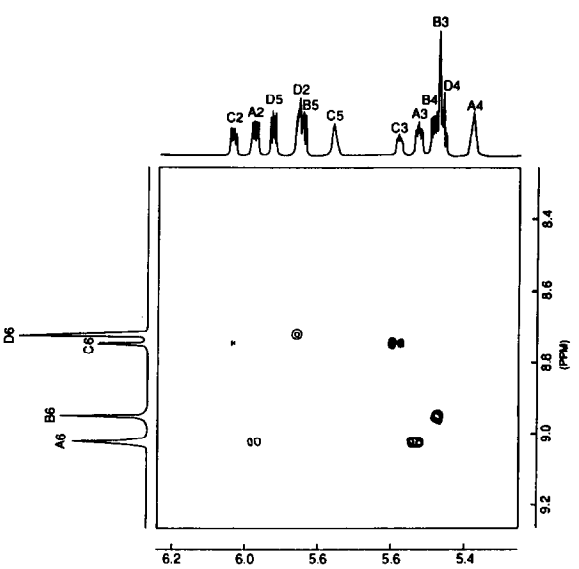



Fig. 2. Excerpt from 400 MHz COSY spectrum of $K^+[C_5H_3(CHO)CH_3]^-$ showing the $J$ coupling interactions between H(6) and the ring nuclei, H(2)–H(5).

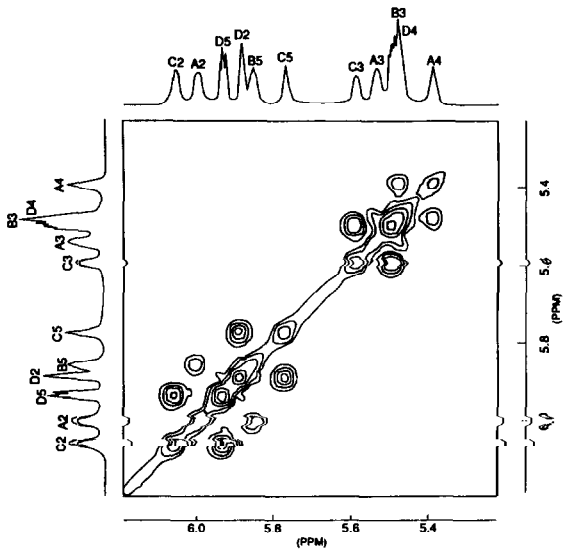



Fig. 3. Excerpt from 400 MHz NOESY spectrum of $K^+[C_5H_4(CHO)CH_3]^-$ at 324 K showing exchange-related hydrogen nuclei directly bonded to the Cp ring.

aldehydic and ring nuclei. The five bond (*trans*) coupling from the aldehyde hydrogen H(6) to H(3) is larger than the corresponding four bond coupling between H(6) and H(2) and there is no coupling resolved between H(6) and H(4) or H(6) and H(5). This extended W effect is consistent with previous NMR analyses of related compounds [11,25].

COSY contour plots for the aldehyde–methyl, methyl–ring, and ring nuclei enabled the assignment of four chemically non-equivalent species, A, B, C and D but do not provide evidence for any relationship between them. On warming a deuteriodimethylsulphoxide solution of the sample to 324 K, the resonances assigned to the ring hydrogens showed a pronounced broadening. NOESY spectra were recorded at this temperature and these provide evidence that the two isomers each have a set of exchange-related pairs, A ↔ B, and C ↔ D. An excerpt from the NOESY spectrum showing the exchange-related peaks for the three ring hydrogens of each conformer is shown in Fig. 3. For example, ring nuclei D2 and D5 and A2 and B5, are exchange related.

At ambient temperature there is a significant barrier to rotation about the C(1)–C(6) bond in each conformer. This contrasts with the NMR results found for the thallium(I) analogue which indicate that there is free rotation about the C(1)–C(6) bond. The energy difference between the fulvene (planar) and cyclopentadienyl (orthogonal) structures has been estimated at 17.6 kJ $mol^{-1}$ for the ethanoylcyclopentadienide ion. The term "orthogonal" has been used [26] to describe the structure in which there is free rotation about the ring–substituent bond. This does not imply that a static structure exists in this case. The fulvene structure is slightly more stable than the orthogonal one and Boche concluded that systems of this type should be conformationally labile [26]. Our studies of the variable temperature NMR spectra of $(CD_3)_2S{=}O$ solutions of the lithium, potas-

Table 1

$^1$H NMR data (400 MHz) for the isomers of $K^+[C_5H_3(CHO)(CH_3)]^-$. Chemical shift assignments of A, B, C, and D in $(CD_3)_2SO$ with DSS (sodium 4,4-dimethyl-4-silapentanesulphonate) as internal standard at 294 K [a]

| Isomer | $^1$H Assignment | | | | |
|---|---|---|---|---|---|
| | H(2) | H(3) | H(4) | H(5) | H(6) |
| A | 5.98 | 5.53 | 5.38 | 2.16 | 9.02 |
| | (dd 4.2, 2.0) | (m, –) | (m, –) | (Me, d, 0.4) | (–) |
| B | 2.21 | 5.47 | 5.49 | 5.84 | 8.95 |
| | (Me, d, 0.4) | (m, –) | (dd, 3.9, 1.9) | (dd, 4.0, 2.4) | (d, 0.7) |
| C | 6.04 | 5.58 | 1.99 | 5.76 | 8.74 |
| | (dd, 4.0, 2.2) | (m, –) | (Me, t, 0.4) | (m, –) | (d, 1.0) |
| D | 5.85 | 1.99 | 5.46 | 5.93 | 8.72 |
| | (m, –) | (Me, t, 0.4) | (m, –) | (dd, 3.9, 2.2) | (s) |

[a] Values in parentheses are resolved $J$ couplings (Hz, ±0.1); a dash indicates additional coupling which could not be measured; the numbering system for the ring nuclei is clockwise from the nodal carbon which carries the methanoyl group as shown in the text.

sium and thallium(I) salts of methanoylcyclopentadiene show that the Lewis nature of the cation has an important role in controlling the preference for a specific conformer; *e.g.* the lithium salt is non-fluxional and prefers the fulvene structure. The potassium salt prefers the fulvene structure at 294 K and is fluxional with an activation energy ($\Delta G^{\#}$) for rotation about the C(1)–C(6) bond of approximately 67 kJ mol$^{-1}$) while the thallium salt prefers the orthogonal conformation over the temperature range 294–373 K [27]. Corresponding variable temperature NMR spectra of $K^+[C_5H_3(Me)(CHO)]^-$ suggest that $\Delta G^{\#}$ is very similar to the value obtained for $K^+[C_5H_4CHO]^-$.

Table 1 shows the $^1$H NMR data for the conformers of $K^+[C_5H_3(Me)(CHO)]^-$. The molar ratio of the two isomers is 1.3 (1,2-):1.0 (1,3-) which shows that adjacent substitution is marginally more favourable. Formylation of alkyl-ferrocenes has been reported to afford mainly the 3-isomer [28], a result consistent with Slocum's proposal that the alkyl group interacts with the cyclopentadienyl ring predominantly by a resonance mode at the 3,4 positions [29].

The results of several electrophilic substitutions on ionic cyclopentadienides suggest that the 2 position is more favoured; for example, Webster [30] noted that cyanation of sodium cyclopentadienide gave a 6:1 molar ratio of isomeric 1,2- and 1,3-dicyanocyclopentadienides. He suggested that the relative stabilities of the intermediate di-substituted cyclopentadienes determined the product ratio. Thus, the incorporation of two adjacent cyano groups permits linear conjugation between the group and the olefin functions of the ring whereas 1,3-substitution results in a less stable cross-conjugated structure.

The stereochemical disposition of the cyano groups prevents inclusion of fulvene intermediates in this case. However, Linn and Sharkey found that benzoylation of lithium cyclopentadienide gave only a 1,2-disubstituted product which was isolated as 1-benzoyl-6-hydroxy-6-phenylfulvene [31]. They proposed that the bonding in the lithium salt of the product fulvene involves a strong interaction between the oxygen atoms of adjacent benzoyl substituents and the metal. This results in an especially stable structure. Alternatively, kinetic control may be involved in this

reaction since adjacent benzoyl groups permit intramolecular hydrogen bonding and extensive electron delocalisation within the fulvene itself [32].

We found that carboxylation of potassium cyclopentadienide with chloromethyl methanoate gave a 3.5:1 ratio of 1,2- and 1,3-dimethoxycarbonylcyclopentadienides [12]. The differing stabilities of the fulvene intermediates [32] or the products could account for this ratio. McLean and Haynes observed a similar ratio of isomers in the methylation of sodium cyclopentadienide with dimethyl sulphate [33]. Their finding that 1,2- and 1,3-dimethylcyclopentadienes were formed in a 3.5:1 ratio was explained by the assumption that a methyl substituent activates the 2 position towards electrophilic attack. We might therefore have anticipated a significantly higher proportion of 1,2- isomer in the formylation of methylcyclopentadienide. However, the 2 position is only marginally preferred in this case which suggests that the relative stabilities of either the cyclopentadiene intermediates or the potassium salts of the fulvene products are probably more important.

*Thallium salts of dimethylamido- and cyanocyclopentadiene*

These were readily prepared by initial conversion of Thiele's dimeric acid into the reactive acid chloride. Subsequent conversion to the dimethylamide followed by vacuum distillation into a solution of thallium(I) ethoxide in benzene gave off-white needles of the air-stable thallium salt in high yield. Similarly, the cyano derivative was obtained after conversion of the acid chloride to the amide and nitrile followed by vacuum distillation of the monomer into an aqueous solution of thallium(I) hydroxide. Cyanocyclopentadiene dimer has been previously synthesised via reaction of cyanogen chloride with sodium hydride and cyclopentadiene [30]. The apparent simplicity of this alternative route is marred by the requirement that ClCN, a rather hazardous material, must also be synthesised. The thallium salts have extended shelf-lives and are undoubtedly superior precursors for the synthesis of a variety of cyclopentadienyl compounds [34]. We were interested in the study of some mono- and di-substituted cyclopentadienyl-rhodium(I) derivatives with particular emphasis on spectroscopic evidence for ring slippage.

*Rhodium complexes*

Table 2 gives the $^{1}H$ and $^{13}C$ NMR data for the bis(ethene)rhodium(I) derivatives **1–4**, and Table 3 compares the free energies of activation ($\Delta G^{\#}$) for olefin rotation with some previously characterised analogues, **5–9** [12,20]. The relative positions of H(2,5) and H(3,4) in **3** parallel those in related ferrocene derivatives. On cooling a $CDCl_3$ solution of **3**, the signals assigned to H(2,5) move slightly upfield while those assigned to H(3,4) move downfield. The degree of movement is linearly dependent on temperature and is of the same type as discussed previously [20]. The extrapolated signal coincidence point is 94 K in **3**. This compares with the experimental value of 273 K in **5** and the extrapolated value of 530 K in **6**.

The relative positions of H(2,5) and H(3,4) in **1**, **2**, **4** and **6** at ambient temperature are the reverse of those observed for ferrocene analogues. Our assignments of the various sets of ring resonances in **1–9** involved use of nOe difference spectra [37], selective deuterium labelling and lanthanide shift reagents [20]. These variable temperature $^{1}H$ NMR spectra may be explained by a temperature dependent, thermodynamic equilibrium between all possible rotamers of the type discussed by Byers and Dahl for related 18*e* compounds, $\{(\eta^5\text{-}C_5R_5)MLL'\}$

Table 2

$^1$H NMR [a] (250 MHz) and $^{13}$C NMR [b] (62.8 MHz) chemical shifts for [$\eta^5$-$C_5H_3$(CHO)Me]Rh($\eta^2$-$C_2H_4$)$_2$] isomers and [($\eta^5$-$C_5H_4$X)Rh($\eta^2$-$C_2H_4$)$_2$] compounds in $CDCl_3$, relative to $Me_4Si$ at 294 K

| | $^1$H | | | | | | | | $^{13}$C | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | X [c] | H(2) | H(5) | H(3) | H(4) | $C_2H_4$ | Other | | C(1) | C(2) | C(5) | C(3) | C(4) | $C_2H_4$ | Other | |
| 1 | Me/CHO | | | | | | | | | | | | | | | |
| | (1,2-isomer) | – | 5.07 | 5.51 | 5.48 | 2.20 | Me | 1.88 | 108.72 | 102.82 | 88.29 | 95.65 | 90.54 | 45.01 | Me | 11.03 |
| | | | (dd, 2.8, 1.8) | (m) | (td, 2.8, 1.0) | | CHO | 9.84 | (5.7) | (4.0) | (5.0) | (3.8) | (4.2) | | CHO | 183.96 |
| 2 | Me/CHO | | | | | | | | | | | | | | | |
| | (1,3-isomer) | 5.23 | 5.01 | – | 5.67 | 2.20 | Me | 1.98 | 102.28 | 90.47 | 86.21 | 101.10 | 93.92 | 45.00 | Me | 13.55 |
| | | (br t, 1.8) | (dd, 2.8, 1.8) | – | (m) | | CHO | 9.67 | (5.7) | (4.2) | (4.7) | (4.1) | (3.6) | | CHO | 183.64 |
| 3 | $CONMe_2$ | | 5.38 | 5.24 | | 2.10 | Me | 1.17 | 98.62 | 87.82 | | 89.47 | | 39.72 | Me | 37.86 |
| | | | (t) | (td) | | | $C_2H_4$ | 2.10 | (4.4) | (4.0) | | (3.6) | | | | |
| 4 | CHO [d] | | 5.57 | 5.79 | | 2.97 | CHO | 9.69 | 106.39 | 88.28 | | 94.03 | | 39.70 | CHO | 183.65 |
| | | | (t) | (tq) | | | | | (4.2) | (3.6) | | (3.6) | | | CO | 188.05 |

[a] Values in parentheses are resolved vicinal and cross ring $J$ couplings. $^{103}$Rh–Cp couplings in **1**–**4** are 0.7–0.8 Hz for H(3),H(4) and 0.4 Hz for H(2),H(5). Long range couplings occur from the Me group in **1** and **2**: $^4J$(Me–H) = 0.7 Hz; similarly $^5J$(CHO–H) in **1**, **2** and **4** = 0.8 Hz. [b] Values in parentheses are $^{103}$Rh–Cp carbon couplings; $J(^{103}Rh–C_2H_4)$ = 13.2 Hz. [c] The numbering system is clockwise from the nodal carbon carrying the CHO group in **1** and **2** and clockwise from the X group in **3** and **4**. [d] Data refer to ($\eta^5$-$C_5H_4$CHO)Rh(CO)($C_2H_4$); $^1J(^{103}Rh–CO)$ = 85.9 Hz.

Table 3

Free energies of activation ($\Delta G^{\#}$) [a] for olefin rotation in [$\eta^5$-($C_5H_3$(CHO)Me)Rh($\eta^2$-$C_2H_4$)$_2$] isomers and [($\eta^5$-$C_5H_4X$)Rh($\eta^2$-$C_2H_4$)$_2$] compounds

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| X | Me/CHO | Me/CHO | $CONMe_2$ | CHO [b] | CN | CHO | Me | $C_6H_5$ | Cl |
| $\Delta G^{\#}$ | 53.3 | 53.3 | 60.0<br>56.4 [c] | 49.1 | 58.9 | 54.5 | 65.7 | 61.8 | 62.0 |

[a] $\pm 1.0$ kJ mol$^{-1}$. [b] Data refer to [($\eta^5$-$C_5H_4$CHO)Rh(CO)($\eta^2$-$C_2H_4$)]. [c] Refers to rotation about the C–N bond.

[38]. However, it is not expected that the relative energies of the thermodynamic wells should remain the same when L ≠ L′ or when the ring is unsymmetrically substituted. It is clear that the 'allyl–ene' rotamer form predominates in the thermodynamic mixture in the case of the carboxyl substituted Cp–Rh derivatives [20,36]. Table 3 suggests that the extent of this slippage directly affects $\Delta G^{\#}$ in the cases of **1**, **2**, **3**, **5**, and **6**. Compound **4** is [(CO)($\eta^2$-$C_2H_4$)Rh($\eta^5$-$C_5H_4$CHO)] which shows the smallest $\Delta G^{\#}$ value of $49.1 \pm 1.0$ kJ mol$^{-1}$. This compares with $\Delta G^{\#}$ values of 54.5 kJ mol$^{-1}$ in **6** and 54.0 kJ mol$^{-1}$ in the related complex [(CO)($\eta^2$-$C_2H_4$)Rh($\eta^5$-$C_5H_5$)] [23]. Since the corresponding value for [($\eta^2$-$C_2H_4$)$_2$Rh($\eta^5$-$C_5H_5$)] is 65.7 kJ mol$^{-1}$, the combined effects of the CO group and the CHO ring substituent are, as anticipated, competitive. However, Shapley recently found that the rotational barrier for ethene in [(CO)($\eta^2$-$C_2H_4$)Ir($\eta^5$-$C_5H_5$)] is actually higher than the value obtained for the analogous bis(ethene) complex [35] which implies that the electronic effects of CO and $C_2H_4$ are rather similar in this case. We find this puzzling in view of our previous study of alkene rotation in analogous rhodium(I) and iridium(I) compounds [23].

**7** shows the same $\Delta G^{\#}$ value as the unsubstituted compound which is in accord with the weak electron releasing properties of the alkyl group. This is seen again in the results for **1** and **2** which are very similar to that of **6**. The positions of the H(2,5) and H(3,4) resonances in **7** are similar to the ferrocene analogue but some slippage is indicated by the differing rhodium–hydrogen coupling constants, *i.e.* $^{103}$Rh–H(2,5) = 0.8 Hz and $^{103}$Rh–(H3,4) = 0.4 Hz. Again the signal with the smaller metal coupling moves upfield with decreasing temperature and *vice versa*. This is the reverse of that observed for the carboxyl substituted derivatives and may reflect the relative stabilities of allyl–ene rotamers in which the 'allyl' carries electron accepting or donating substituents. The $\Delta G^{\#}$ values for **8** and **9** are very similar and indicate that each ring substituent is quite weakly accepting. Nevertheless, the relative positions and large separation of H(2,5) and H(3,4) again suggest some degree of slippage in these compounds. The nature of this rotamer is discussed in Part II [39].

**Acknowledgments**

We thank Dr. O.W. Howarth for the 400 MHz NMR spectra and Johnson Matthey for the generous loan of rhodium trichloride.

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