*In memory of S. M. Nelson*

# Preparation and Spectroscopic Study of Functionally Substituted Cyclopentadienides of Thallium(I), Potassium, Rhodium(I), and Iridium(I)

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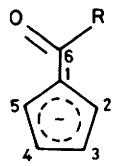
A $^{13}C$ and $^{1}H$ n.m.r. study has been carried out on a series of monosubstituted cyclopentadienide compounds of type $M^{I}(C_5H_4X)$ [M = K or Tl; X = Cl, COMe, $CO_2Me$, CHO, Ph, $COCO_2Et$, or $C(CN)=C(CN)_2$]. The different patterns observed for the ring nuclei reflect both the Lewis-acid character of the metal and the electronic effect of the substituent. Fluxional behaviour is observed for $K(C_5H_4COMe)$. Pseudo-first-order rate constants have been evaluated for hydrogen–deuterium exchange in several of the potassium compounds. The thallium(I) compounds generally exhibit greater synthetic utility than their potassium analogues and several have been used in the synthesis of new $[M(\eta^5\text{-}C_5H_4X)(\eta^2\text{-}C_2H_4)_2]$ (M = Rh or Ir) complexes. Activation barriers for alkene rotation and mass spectral fragmentation patterns are discussed for these compounds. The $^{1}H$ n.m.r. spectra found for the cyclopentadienyl ring indicate that the M–ring bonding is not fully delocalised. Analysis of the products resulting from reaction between methyl chloroformate and cyclopentadienide ion confirms the strongly electrophilic character of the former reagent.

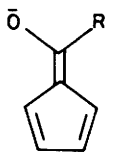
We have previously reported[1] the synthesis and isomerisation of many $[Rh(\eta^5\text{-}C_5H_4X)(\eta^4\text{-}L)]$ (L = diene) complexes and the activation energies for alkene rotation in analogous rhodium(I) and iridium(I) derivatives.[2] The $^{1}H$ and $^{13}C$ n.m.r. spectra of some of these compounds show unique behaviour which correlates with a contribution from an $\eta^3$-allyl–$\eta^2$-alkene rotamer to the metal–ring bonding scheme.[3] No systematic n.m.r. study has yet been undertaken of the thallium(I) and potassium cyclopentadienide precursors. Our results correlate with the nature of the metal and ring substituent. Some of these salts were subsequently used in the synthesis of new rhodium(I) and iridium(I) complexes $[M(\eta^5\text{-}C_5H_4X)(\eta^2\text{-}C_2H_4)_2]$ which were examined by variable-temperature n.m.r. spectroscopy and mass spectrometry.

## Results and Discussion

Table 1 gives the n.m.r. data for the main group cyclopentadienides. The two conformations which may be adopted are distinguished from the appearance of the $^{1}H$ or $^{13}C$ n.m.r. spectra. The orthogonal form (**I**) shows two pseudo-triplets for the two sets of ring hydrogen atoms whereas the planar form (**II**) gives a multiplet pattern characteristic of an ABCD spin system. The corresponding $^{13}C$ n.m.r. spectra give a single peak for each of the atom pairs C(2), C(5) and C(3), C(4) in the case of (**I**) whereas compounds in which form (**II**) predominates show four separate signals for the corresponding ring carbon atoms. Boche *et al.*[4] have suggested that form (**I**) is less stable than the planar conformation (**II**) by 17.6 kJ $mol^{-1}$ in the case of lithium acetylcyclopentadienide which did not show fluxional behaviour. We have found that the potassium analogue (**2**) gave one sharp signal for each of the atom pairs C(2), C(5) and C(3), C(4) at 373 K. Decrease in temperature results initially in broadening followed by splitting of each signal into two lines. This splitting is larger for the C(2) and C(5) signals which were employed in the estimation of the coalescence temperature (313 ± 3 K). The



(**I**)



(**II**)

constantly sharp signals due to C(1) and C(6) strongly indicate that the fluxional process only involves rotation about the C(1)–C(6) bond. The activation energy ($\Delta G^{\ddagger}$) for this process is estimated as 61.4 ± 1 kJ $mol^{-1}$.

The results for complexes (**3**), (**5**), and (**7**) suggest that the soft Lewis-acid character of thallium(I) stabilises the orthogonal form. However when the strongly electron-accepting tricyanovinyl group is present, as in (**9**), the pattern observed for the n.m.r. reflects a preference for the planar form. The $^{13}C$ n.m.r. signals for the ring carbon atoms in (**9**) did not show any significant change over the range 293—383 K. Hence, rotation about the C(1)–C(6) bond is slow on the n.m.r. time-scale. This behaviour was also found for the potassium salts (**4**) and (**6**) in which the ring carries more strongly electron-accepting substituents than COMe.

It has been suggested that compound (**9**) is more ionic than $Tl^{I}(C_5H_5)$.[5] We have compared the mass spectra of these thallium compounds with the parent system.[6] All confirm the monomeric nature of the sample in the vapour phase. The decreasing importance of covalent character as the electron-accepting nature of the ring substituent increases is reflected in the decrease in relative intensity of the parent (molecular) ion peak. Fragmentation of the ring or substituent while bonded to the metal was unimportant. The recent synthesis[7] of $Tl^{I}(C_5Me_5)$ suggests that electron-donating substituents cause increase in covalent character which is reflected in decreased

**Table 1.** Hydrogen-1 and carbon-13 chemical shifts (δ) for $M(C_5H_4X)$ compounds in $(CD_3)_2SO$ relative to dss (sodium 4,4-dimethyl-4-silapentanesulphonate) as internal standard at 304 K

| | | $^1H$ | | | $^{13}C$ | | | |
|---|---|---|---|---|---|---|---|---|
| | | H(2,5) | H(3,4) | X | C(1) | C(2,5) | C(3,4) | X |
| (1) | $Tl(C_5H_4Cl)$ | 5.76 (t) | 5.52 (t) | | 112.4 | 105.43 | 104.89 | |
| (2) | $K(C_5H_4COMe)$ | 6.55 (m) | 6.15 (m) | 2.15 (s) | 124.91 | 115.64 (br) | 111.98 (br) | 27.31 |
| | | | | | | 113.81 (br) | | 187.24 |
| (3) | $Tl(C_5H_4COMe)$ | 6.10 (t) | 5.64 (t) | 2.12 (s) | 126.60 | 113.63 | 113.23 | 28.10 |
| | | | | | | | | 191.47 |
| (4) | $K(C_5H_4CHO)$ | 6.66 (m) | 6.25 (m) | 8.60 (s) | 125.16 | 118.01 | 111.21 | 177.88 |
| | | | | | | 114.23 | 107.81 | |
| (5) | $Tl(C_5H_4CHO)$ | 6.25 (t) | 5.84 (t) | 9.25 (s) | 126.15 | 114.60 | 113.45 | 181.96 |
| (6) | $K(C_5H_4COCO_2Et)$ | 6.50 (m) | 6.16 (m) | 4.21 (q) | 128.64 | 118.46 | 114.83 | 174.63 |
| | | | | 1.26 (t) | | 117.16 | 113.24 | 170.51 |
| | | | | | | | | 60.79 |
| | | | | | | | | 15.83 |
| (7) | $Tl(C_5H_4CO_2Me)$ | 6.29 (t) | 5.66 (t) | 3.60 (t) | 116.50 | 116.21 | 114.30 | 57.40 |
| | | | | | | | | 168.51 |
| (8) | $Tl(C_5H_4Ph)$ | 6.36 (t) | 5.75 (t) | 7.07—7.49 (m) | 125.0 | 108.98 | 106.69 | 124.18 |
| | | | | | | | | 124.00 |
| | | | | | | | | 129.73 |
| (9) | $Tl[C_5H_4C(CN)=C(CN)_2]$ | 6.90 (m) | 6.28 (m) | | 113.30 | 129.05 | 122.63 | 118.69 |
| | | 6.14 (m) | | | | 124.50 | 116.31 | 123.00 (C=C) |
| | | | | | | | | 122.30 (br) (C=N) |

stability towards oxidation, and the observation of thallium–carbon coupling in the $^{13}C$ n.m.r. spectrum.

*Deuterium Exchange Experiments.*—A characteristic of the water-soluble potassium compounds (**2**), (**4**), and (**6**) is the ability to undergo slow exchange with $D_2O$. Although proton-transfer kinetics have been studied[8] in detail for related systems, no quantitative measurements have been carried out on hydrogen–deuterium exchange. When (**2**) and (**4**) (1—2 mol $dm^{-3}$) were dissolved in $D_2O$ the respective $K_{2,5}$ values were $8.66 \times 10^{-3}$ and $1.54 \times 10^{-3}$ $min^{-1}$ at 298 K. The corresponding $K_{3,4}$ values were $2.1 \times 10^{-3}$ and $2.2 \times 10^{-4}$ $min^{-1}$. The larger rate constant values for exchange involving the 2- and 5-positions stem from the intermediacy of a linearly conjugated diene as opposed to the less stable cross-conjugated isomer expected in the case of exchange involving the 3- and 4-positions. The differences between the two compounds apparently reflect their relative anion basicities. The large differences in rate constants for exchange involving (**2**) was employed in synthesis of 1-acetyl-2,5-dideuteriocyclopentadienyl derivatives of rhodium(I) and iridium(I) which enabled unambiguous assignment of ring hydrogen and carbon atom signals.[3]

*Reaction of* $K(C_5H_5)$ *with* $ClCO_2Me$.—In 1959 Peters[9] described the synthesis of sodium 1,2-di(methoxycarbonyl)-cyclopentadienide from reaction of methyl chloroformate and cyclopentadienide ion. Rausch *et al.*[10] subsequently outlined a mechanistic scheme involving sequential addition of ester groups to cyclopentadienide followed by deprotonation. Webster[11] had found, however, that cyanation of $C_5H_5^-$ with ClCN gave a mixture of isomeric 1,2- and 1,3-dicyano products. Our interest in the former reaction was the generation of $[Rh(\eta^5\text{-}C_5H_3X_2)(\eta^4\text{-}L)]$ (X = $CO_2Me$, L = diene) complexes to improve the catalytic behaviour of these systems.[12] Analogous cobalt complexes have recently been cited as effective catalysts in cyclocondensation of acrylonitrile with ethyne to give vinylpyridine.[13] We found that reaction of $K(C_5H_5)$ with $ClCO_2Me$ gave the reported[9] dicyclopentadiene dicarboxylic ester and the unreported dicyclopentadiene (3a,4,7,7a-tetrahydro-4,7-methanoindene) and dicyclopentadiene monocarboxylic ester as organic by-products. The main inorganic by-product was KCl but the 1,3-di(methoxycarbonyl)- and 1,2,3-tri(methoxycarbonyl)-cyclopentadienide salts are formed along with the reported 1,2-complex in a 2:1:7 ratio. Prolonged reaction time using 1:1 mole ratios of reactants led to the disappearance of disubstituted salts and formation of 1,2,3- and 1,2,4-tri(methoxycarbonyl) isomers in a 6:1 ratio.

The $^1H$ n.m.r. spectra of the 1,2- and 1,2,3-substituted salts in $D_2O$ gave time-independent signals for the ring hydrogens. In contrast, the poorly resolved triplet assigned to the single hydrogen atom on the ring carbon between the two ester groups in the 1,3-complex disappeared rapidly ($t_{\frac{1}{2}}$ *ca.* 5 min) due to deuterium exchange. In this case the intermediate diene can adopt a stable linear conjugated system. The preference found for isomers with adjacent ester groups is also explained by the intermediacy of the more stable linear conjugated forms which would suggest a lower transition-state energy compared to substitution of non-adjacent groups.[11] The products were inert towards $[\{RhCl(\eta^2\text{-}C_2H_4)_2\}_2]$ presumably as a consequence of reduction in the nucleophilic character of the cyclopentadienide group. The same results were achieved when the nitro- and tricyanovinyl-cyclopentadienide ions were employed.[14] The high reactivity and unselectivity of $ClCO_2Me$ towards cyclopentadienide compared to reagents such as dimethyl carbonate[15] is a consequence of the weak C–Cl bond and the absence of degenerate resonance stabilisation. We are currently studying the benzoylation of cyclopentadienide since it seems unlikely that this reaction should produce exclusively the 1,2-dibenzoyl product previously reported.[16] In view of our results, the method of Hafner *et al.*[17] may be more useful in the generation of di- and tri-substituted cyclopentadienide salts.

*Rhodium(I) and Iridium(I) Complexes.*—Table 2 gives the n.m.r. results found for some new complexes of the type $[M(\eta^5\text{-}C_5H_4X)(\eta^2\text{-}C_2H_4)_2]$ (M = Ir or Rh). Activation energies for alkene rotation ($\Delta G^{\ddagger}$) were estimated by the method of Cramer and Mrowca.[18] The results for complexes (**10**), (**11**), and (**13**) suggest that the increase in electron-accepting effect follows the sequence H < Ph ~ Cl < $CO_2R$ (R = Me, Et, or Pr) ~ CN < COMe < CHO < $COCO_2Et$.[2] The large chemical

**Table 2.** Hydrogen-1 and carbon-13 chemical shifts for $[M(\eta^5\text{-}C_5H_4X)(\eta^2\text{-}C_2H_4)_2]$ complexes in $CDCl_3$ with $^{103}Rh$ coupling constants [a] and $\Delta G^{\ddagger}$ values [b] for olefin rotation

| | | | $^1H$ | | | $^{13}C$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | M | $C_2H_4$ | X | H(2), H(5) | H(3), H(4) | C(1) | C(2), C(5) | C(3), C(4) | $C_2H_4$ | X |
| (**10**) | Rh | 2.03 | Cl | 4.98 (t) | 5.64 (td) | 100.09 | 81.75 | 85.88 | 40.52 | |
| | | (2.05) | | (0.4) | (0.8) | (4.6) | (3.8) | (3.8) | (13.4) | |
| | | [62.2] | | | | | | | | |
| (**11**) | Rh | 1.86 | Ph | 5.18 | 5.86 (td) | 104.8 | 87.47 | 84.76 | 39.21 | 125.42 |
| | | (2.0) | 7.15—7.40 (m) | (0.4) | (0.8) | (4.2) | (3.8) | (3.8) | (13.4) | 126.86 |
| | | [61.8] | | | | | | | | 128.64 |
| | | | | | | | | | | 133.05 |
| (**12**) | Ir | 1.81 | COMe | 5.29 (t) | 5.42 (t) | 95.49 | 82.51 | 87.44 | 22.64 | 26.85 |
| | | [76.0] | 2.34 (s) | | | | | | | 192.71 |
| (**13**) | Rh | 2.15 | COMe | 5.29 (t) | 5.45 (td) | 100.09 | 87.61 | 91.72 | 42.06 | 29.66 |
| | | (2.05) | 2.43 (s) | (0.4) | (0.8) | (4.4) | (3.8) | (3.4) | (13.1) | 194.00 |
| | | [56.02] | | | | | | | | |

[a] Values (Hz) given in parentheses. [b] Values ($\pm 1$ kJ mol$^{-1}$) given in square brackets.

**Table 3.** Relative abundances, principal positive ions, and metastable transitions in $[M(\eta^5\text{-}C_5H_4COMe)(\eta^2\text{-}C_2H_4)_2]$

| | Relative abundance | | | Neutral fragment | $M^{*a}$ | |
|---|---|---|---|---|---|---|
| Ion | M = Rh | M = Ir | Metastable transition | lost | Rh | Ir |
| $[M(C_5H_4COMe)(C_2H_4)_2]^+$ | 26.5 | 100.0 | | | | |
| $[M(C_5H_4COMe)(C_2H_4)]^+$ | 79.2 | 49.8 | $[M(C_5H_4COMe)(C_2H_4)_2]^+ \longrightarrow [M(C_5H_4COMe)(C_2H_4)]^+$ | $C_2H_4$ | 212.9 | 302.2 |
| $[M(C_5H_4COMe)(C_2H_2)]^+$ | *b* | 99.1 | $[M(C_5H_4COMe)(C_2H_4)]^+ \longrightarrow [M(C_5H_4COMe)(C_2H_2)]^+$ | $H_2$ | | 324.0 |
| $[M(C_5H_4COMe)]^+$ | 100.0 | *b* | $[M(C_5H_4COMe)(C_2H_4)]^+ \longrightarrow [M(C_5H_4COMe)]^+$ | $C_2H_4$ | 185.3 | |
| $[M(C_5H_4CO)(C_2H_2)]^+$ | *b* | 12.5 | $[M(C_5H_4COMe)(C_2H_2)]^+ \longrightarrow [M(C_5H_4CO)(C_2H_2)]^+$ | $CH_3$ | | 296.7 |
| $[M(C_6H_7)]^+$ | 33.4 | *b* | $[M(C_5H_4COMe)]^+ \longrightarrow [M(C_6H_7)]^+$ | CO | 157.7 | |
| $[M(C_6H_5)]^+$ | 39.3 | 11.8 | $[M(C_6H_7)]^+ \longrightarrow [M(C_6H_5)]^+$ | $H_2$ | 178.0 | |
| $[M(C_5H_4)(C_2H_2)]^+$ | *b* | 16.6 | $[M(C_5H_4CO)(C_2H_2)]^+ \longrightarrow [M(C_5H_4)(C_2H_2)]^+$ | CO | *b* | 257.6 |
| $[M(C_5H_5)]^+$ | 10.3 | 5.2 | | | | |
| $[M(C_5H_4)]^+$ | 23.6 | 10.1 | $[M(C_5H_4CO)]^+ \longrightarrow [M(C_5H_4)]^+$ | CO | 143.0 | |
| | | | $[M(C_5H_4)(C_2H_2)]^+ \longrightarrow [M(C_5H_4)]^+$ | $C_2H_2$ | | 233.4 |
| $M^+$ | 12.2 | *b* | | | | |

[a] Metastable ions. [b] Ions having relative abundance less than 3% are not recorded.

shift differences found for the ring hydrogen atom pairs in (**10**) and (**11**) have not previously been observed in similar rhodium complexes.[3] Assignment of nuclei was made with the aid of $[Eu(fod)_3]$ (fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione) as previously described.[3] The results found for (**12**) and (**13**) are entirely consistent with an increasing contribution from an $\eta^3$-allyl–$\eta^2$-alkene rotamer in solution as the electron-accepting nature of the ring substituent increases from X = $CO_2Me$ to X = CHO. However the separation and relative positions of the H(2,5) and H(3,4) ring nuclei in (**10**) and (**11**) is difficult to reconcile with the previous trend since the more weakly electron-accepting Cl and Ph groups might be expected to result in 'normal' n.m.r. behaviour.

We are currently carrying out a single-crystal *X*-ray study of (**11**) but in view of the results obtained by Bonnemann[19] on the conformation of $\eta^5$-chloro- and $\eta^5$-acetyl-cyclopentadienyl($\eta^4$-cyclo-octadiene)cobalt(I) systems it seems plausible that a contribution from a diolefin rotamer may apply to the rhodium complexes. In this case the 'terminal' diene hydrogens [H(2,5)] would be expected to resonate to high field of H(3,4) and the former nuclei would also be expected to exhibit a smaller $^{103}Rh$–$^1H$ coupling constant.[20]

The higher $\Delta G^{\ddagger}$ value for olefin rotation in (**12**) is expected from the stronger metal–alkene interaction in iridium(I) systems.[21] The value is intermediate between those observed[2] for the formyl and methoxycarbonyl complexes and suggests that steric contributions to the rotational barrier are similar for rhodium(I) and iridium(I). In the case of analogous cobalt(I) complexes the results demonstrate a major steric effect, however, presumably because of the closer proximity of the olefin groups.[22]

*Mass Spectra.*—The differences in stability between complexes formed by rhodium and iridium are demonstrated in the mass spectra of (**12**) and (**13**) (Table 3; the *m/z* values quoted here and in the text refer to $^{193}Ir$). All relative abundances refer to an arbitrary value of 100 chosen for the base peak in each spectrum.

The iridium complex shows the molecular ion as base peak which indicates a greater overall stability compared to (**13**). The

affinity of iridium for alkyne species is shown by initial olefin loss followed by dehydrogenation of the remaining alkene ligand. Compound (**13**) shows sequential alkene loss to give $[M(C_5H_4COMe)]^+$ as the base peak. This ion is, however, absent in the iridium complex since fragmentation of the ring side-chain is preferred to alkyne loss. Both complexes exhibit extrusion of CO to give species such as $[Ir(C_6H_7)(C_2H_2)]^+$ and $[Rh(C_6H_7)]^+$ in 3.8 and 33.4% abundance respectively. In the case of iridium a more favourable ring fragmentation involves loss of the methyl group to give $[Ir(C_5H_4CO)(C_2H_2)]^+$ (12.5% abundance). There was no evidence of migration of side-chain to metal[23] and the ions $[M(C_5H_5)]^+$, which are usually of high abundance in analogous complexes where the side-chain is an ester or aldehyde group,[24] were much less important in (**12**) and (**13**).

## Experimental

Experiments were performed under nitrogen in solvents freshly distilled from appropriate drying agents. Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. Hydrogen-1 and $^{13}C$ n.m.r. spectra were recorded on Bruker AW-60, WP 80, and AM-250 instruments equipped with variable-temperature accessories. Chemical shifts, coupling constants, and assignments are summarised in Tables 1 and 2 according to the labelling scheme given for form (**I**). Infrared spectra were measured in the range 4 000—250 $cm^{-1}$ (Perkin-Elmer 577 grating spectrophotometer) as KBr discs or thin films between KBr plates. Mass spectra were recorded using a Kratos MS-80 instrument. Metastable mapping techniques were employed for some of the complexes.

*Preparation of Cyclopentadienide Salts.*—Thallium(I) cyclopentadienide, thallium(I) methoxycarbonylcyclopentadienide, and potassium formylcyclopentadienide were prepared as described previously.[1]

*Thallium*(I) *chlorocyclopentadienide.* This was prepared by a modification of the method of Conway and Rausch.[25] Reaction of equimolar quantities of chlorocyclopentadiene monomer and thallium(I) ethoxide gave a 75% yield of product (Found: C, 20.05; H, 1.30%; $M^+$, 302/304/306. Calc. for $C_5H_4ClTl$: C, 20.50; H, 1.50%; *M*, 303.9).

*Thallium*(I) (*tricyanovinyl*)*cyclopentadienide.* This was synthesised by the method of Freeman and Sneddon[5] (Found: C, 32.85, H, 1.2%; $M^+$, 369/371. Calc. for $C_{10}H_4N_3Tl$: C, 32.40; H, 1.10%; *M*, 370.4).

*Thallium*(I) *phenylcyclopentadienide.* This was prepared in 60% yield by reaction of excess thallium(I) ethoxide with 5-phenylcyclopentadiene[26] (0.20 mol) in diethyl ether (75 $cm^3$) at 0 °C. Isolation of the precipitate and sublimation at 60 °C ($10^{-3}$ Torr, ≈0.13 Pa) using a solid $CO_2$ cooled probe gave a pale yellow solid (Found: C, 37.80; H, 2.55%; $M^+$, 333/335. $C_{11}H_9Tl$ requires C, 38.20; H, 2.60%; *M*, 334.4); $\nu_{max.}$ at 1 595 (C=C), 1 510, 760, 745, and 720 $cm^{-1}$.

*Potassium acetylcyclopentadienide.* This was synthesised by addition of methyl acetate (0.20 mol) to a solution of potassium cyclopentadienide prepared from cyclopentadiene (0.20 mol) and KOH (1.0 mol) in 1,2-dimethoxyethane (500 $cm^3$). The mixture was refluxed for 24 h and, on cooling, a white hygroscopic solid separated. This was washed with diethyl ether and dried *in vacuo* (Found: C, 56.80; H, 4.55. $C_7H_7KO$ requires C, 57.50; H, 4.80%).

*Thallium*(I) *acetylcyclopentadienide.* This was prepared in 90% yield by methatheses involving equimolar aqueous solutions of the potassium salt and thallium(I) acetate at 20 °C. The product was isolated by filtration and dried *in vacuo.* Recrystallisation of portions (3 g) from acetonitrile (250 $cm^3$) gave grey plates (*ca.* 2 g) melting at 145 °C (Found: C, 26.95; H, 2.25%; $M^+$, 310/312. $C_7H_7OTl$ requires C, 26.95; H, 2.25%; *M*, 311.4).

*Thallium*(I) *formylcyclopentadienide.* This was synthesised in 95% yield by addition of thallium(I) acetate (13.17 g, 0.05 mol) in water (100 $cm^3$) to potassium formylcyclopentadienide (6.60 g, 0.05 mol) in water (50 $cm^3$). Recrystallisation of the precipitate from acetonitrile gave an off-white microcrystalline product melting at 150—152 °C (Found: C, 24.00; H, 1.60%; $M^+$, 296/298. $C_6H_5OTl$ requires C, 24.20; H, 1.70%; *M*, 297.4).

*Potassium* (*ethoxycarbonylformyl*)*cyclopentadienide.* This was synthesised by extraction of the sodium salt into $CH_2Cl_2$ at pH 1.0, followed by separation of the organic layer and re-extraction with the stoicheiometric quantity of aqueous potassium hydroxide. Recrystallisation of the dried product from ethanol gave a pale brown solid (Found: C, 53.3; H, 4.60. $C_9H_9KO_3$ requires C, 52.90; H, 4.40%).

*Reaction of Methyl Chloroformate with Potassium Cyclopentadienide.*—Dropwise addition of $ClCO_2Me$ (2 mol) in 1,2-dimethoxyethane (200 $cm^3$) to $K(C_5H_5)$ (2 mol) in the same solvent (350 $cm^3$) at −10 °C gave a series of colour changes from pink *via* green to orange. Stirring was continued for 4 h and the mixture was allowed to reach 20 °C. The solvent was immediately removed under reduced pressure to give a brick-red residue. Separation of organic by-products was achieved by repeated extraction with ether (10 × 200 $cm^3$). T.l.c. (silica) on the organic extracts using dichloromethane–toluene (7:3 v/v) showed three components which were separated quantitatively by column chromatography. The u.v., i.r., n.m.r., and mass spectra and comparison with authentic samples showed that dicyclopentadiene (4.36 g, 0.033 mol), dicyclopentadiene monocarboxylic ester (6.27 g, 0.033 mol), and dicyclopentadiene dicarboxylic ester (23.0 g, 0.093 mol) were present. The main inorganic by-product was potassium chloride (46.0 g, 0.62 mol) which was shown to be 94% pure by Mohr titration after separation from the product by Soxhlet extraction using ethyl acetate. Subsequent extraction (Soxhlet) with trichloromethane for 3 d gave 9.7 g of orange residue (**A**) (Found: C, 48.60; H, 4.10%). The $^1H$ n.m.r. spectrum of (**A**) [in $D_2O$ with sodium 4,4-dimethyl-4-silapentanesulphonate (dss) as internal standard] gave peaks at δ 6.86 (d, 2 H, $J$ = 3.4 Hz) and 3.83 (s, 6 H) which were assigned to the 1,2-isomer.[8] The spectrum also gave peaks at δ 7.02 (t, 1 H), 6.58 (d, 2 H, $J$ = 2.1 Hz), and 3.83 (s, 6 H) which were assigned to the 1,3-isomer,[8] and a weak singlet at δ 7.20 which was assigned to the 1,2,3-tri(methoxycarbonyl)cyclopentadienide. The ratio of these compounds was 70:20:10 respectively. H.p.l.c. analysis of the residue using Lichrosorb RP18 and isocratic elution (methanol–water, 65:35) confirmed the presence of three components.

Extension of the reaction time between $ClCO_2Me$ (1 mol) and $K(C_5H_5)$ (1 mol) to 24 h at 20 °C, followed by separation of the by-products as before, gave only the 1,2,3- (85%) and 1,2,4- (15%) tri(methoxycarbonyl)cyclopentadienides. The $^1H$ n.m.r. spectrum ($D_2O$–dss) of the orange residue (**B**) gave δ 7.20 (s, 2 H), 3.63 (s, 9 H) (1,2,3-isomer); 7.30 (s, 2 H), 3.60 (s, 9 H) (1,2,4-isomer).

Reaction of (**A**) or (**B**) with $[\{RhCl(CO)_2\}_2]$ gave a 60% yield of the expected $\eta^5$-cyclopentadienyl derivatives. We were unable to effect a satisfactory separation of these rhodium(I) products but the $^1H$ and $^{13}C$ n.m.r. and mass spectra supported the formation of (**A**) and (**B**). There was no evidence for any mono-, tetra-, or penta-substituted cyclopentadienyl species.

*Rhodium*(I) *and Iridium*(I) *Derivatives.*—$[Rh(\eta^5\text{-}C_5H_4Cl)(\eta^2\text{-}C_2H_4)_2]$ was prepared by reaction of $Tl(C_5H_4Cl)$ with $[\{RhCl(\eta^2\text{-}C_2H_4)_2\}_2]$ in hexane by the previously described method for related systems.[1] Recrystallisation from hexane (−20 °C) gave a yellow solid melting at 60—63 °C (Found: C, 42.10; H,

4.80%; $M^+$, 258/260. $C_9H_{12}ClRh$ requires C, 41.80; H, 4.65%; $M$, 258.5).

$[Rh(\eta^5\text{-}C_5H_4Ph)(\eta^2\text{-}C_2H_4)_2]$ was prepared in 80% yield by reaction of thallium(I) phenylcyclopentadienide with $[\{RhCl(\eta^2\text{-}C_2H_4)_2\}_2]$ in hexane. Recrystallisation from hexane (−20 °C) gave a yellow solid melting at 79—80 °C (Found: C, 59.70; H, 5.75%; $M^+$, 300. $C_{15}H_{17}Rh$ requires C, 60.00; H, 5.70%; $M$, 300).

$[Ir(\eta^5\text{-}C_5H_4COMe)(\eta^2\text{-}C_2H_4)_2]$ was synthesised in 40% yield by reaction of $[\{IrCl(\eta^2\text{-}C_2H_4)_2\}_2]$[27] with thallium(I) acetylcyclopentadienide in hexane. The product is a beige solid melting at 71—72 °C (Found: C, 37.35; H, 4.25%; $M^+$, 354/356. $C_{11}H_{15}IrO$ requires C, 37.15; H, 4.20%; $M$, 355.2). The rhodium analogue $[Rh(\eta^5\text{-}C_5H_4COMe)(\eta^2\text{-}C_2H_4)_2]$ was obtained as a yellow solid (m.p. 65 °C) in 85% yield (Found: C, 50.10; H, 5.85%; $M^+$, 266. $C_{11}H_{15}ORh$ requires C, 49.60; H, 5.65%; $M$, 265).

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