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Reactions of cationic (η^6-chloroarene) complexes of iron and ruthenium with some *O*-silyl and *C*-silyl compounds

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Abstract

The introduction of an alkylcarbonyl side chain into the aromatic ring of some chloro-substituted benzenes has been achieved under mild conditions by the Yanovsky-type reaction of (η^6-chloroarene)(η^5-cyclopentadienyl) cationic complexes of iron or ruthenium with silyl enol ethers. An ester side chain has been introduced similarly using ethyl trimethylsilylacetate. The resulting (η^5-chlorocyclohexadienyl)(η^5-cyclopentadienyl) adducts derived from the ruthenium salts are more stable than their iron analogues. Treatment of the neutral ruthenium adducts with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone gives moderate yields of the [η^6-(substituted chloroarene)(η^5-Cp)]Ru^+ PF_6^- salt, together with the decomplexed substituted chloroarene.

Introduction

In an earlier communication we reported [1] the reaction of a carbanion derived from 3-ethoxy-6-methylpyridazine-N-oxide (**1**) with (η^5-2,4-cyclopentadien-1-yl)(η^6-1,4-dichlorobenzene)iron(1 +) hexafluorophosphate(1 −) (**2**) to give the neutral Yanovsky-type adduct **3** via *ortho* attack. However, rigorous control of the experimental conditions was required to generate the carbanion (BuLi/THF/ − 100 °C/5 min) and then to effect its reaction with the (η^6-dichlorobenzene) salt (−78 °C/15 min, then warmed to room temperature). Moreover, brief treatment of the adduct **3** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) returned only the decomplexed substituted arene **4**; none of its cationic FeCp complex was recovered. In an extension of this work directed at generating a carbanion under less stringent conditions we have investigated the reaction of some (η^6-chloroarene)iron(1 +) salts with some silyl enol ethers and with ethyl trimethylsilylacetate; the adduct derived from attachment of the latter is capable of potential elaboration into a pyridazinone (cf. [1]). Furthermore, we have prepared the analogous (η^6-chloroarene)ruthenium salts and investigated their reactions with the silylated carbanion precursors, since the adducts derived from the second row transition metal are expected to be kinetically more stable than their iron analogues.

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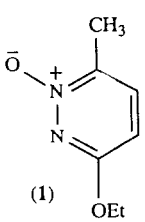
Results and discussion

The Yanovsky-type attachment of an alkylcarbonyl side chain to an arene has been carried out in concentrated aqueous hydroxide by the direct reaction of a simple water-soluble ketone with (η^6-arene)(η^5-cyclopentadienyl)iron cationic complexes in which the arene contains an electron-withdrawing substituent [2,3]. In related work [4–8], reactions of η^5-tricarbonylcyclohexadienyliron salts with silyl enol ethers, silyl ketene acetals, or stannyl enol ethers have been shown to be advantageous in allowing the use of non-aqueous media, in minimizing side-reactions often associated with the relatively high basicity of lithio or potassio enolates, and in affording greater regioselection during adduct formation.

The (η^6-arene)(η^5-cyclopentadienyl)iron(1 +) salts **2**, **5**, and **6** derived from 1,4-dichlorobenzene, 1,2-dichlorobenzene, and chlorobenzene were prepared as the hexafluorophosphates by ligand exchange from ferrocene using the method of Khand et al. [9]. The silyl enol ethers **7**–**9** derived from 3-pentanone (65%) ($Z:E = 11.5:1$) [10], cyclohexanone (53%), and butanal (46%) ($Z:E = 3.35:1$) were prepared using Me_3SiCl–NaI–Et_3N in acetonitrile according to Cazeau et al. [11]. Although potassium fluoride–Celite [12] in THF proved ineffective as a source of fluoride ion to promote reaction between the ArCpFe salts and these silyl enol ethers (cf. ref. 13), one molar equivalent of tetrabutylammonium fluoride caused reaction to occur rapidly in THF at room temperature. The results obtained from these reactions, as well as from those using ethyl trimethylsilylacetate (10) are given in Table 1. All of the adducts gave NMR and IR data which were consistent with their structures. However, they were isolated as acid-sensitive (eg. to $CDCl_3$) unstable orange oils (particularly so in the case of the adduct **19** from chlorobenzene) for which satisfactory elemental analyses could not be obtained, decomposition occurring within 24 h at room temperature. The stereochemistry of the entering nucleophile was *exo* to the FeCp moiety [14]. In the cases of the adducts derived



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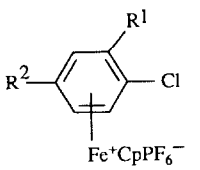
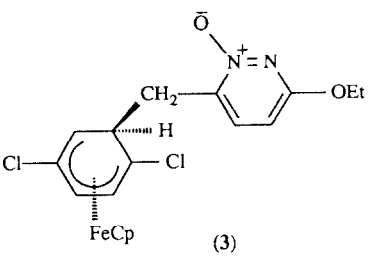


(2; R^1=H;R^2=Cl
5; R^1=Cl;R^2=H
6; R^1=R^2=H)



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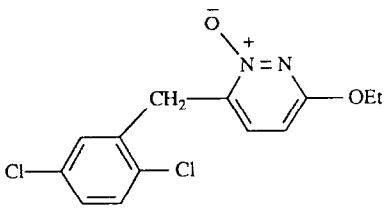

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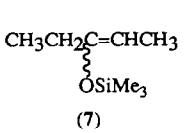
Table 1

Reactions of (η^6-chloroarene)$CpFe^+ PF_6^-$ salts with silylated reagents

Iron(1 +)salt	Silyl reagent	Adduct(s)	Diastereomeric ratio	Yield (%)
2	**7**	**11**	1.5 : 1.0	67
2	**10**	**12**	–	56
5	**7**	**13**	1.5 : 1.0	72
5	**8**	**14** (trace *meta* isomer)	1.2 : 1.0	41
5	**9**	**15**	2.0 : 1.0	27
		16	1.0 : 1.0	3
5	**10**	**17**	–	70
		18	–	18
6	**7**	**19**, very unstable		

from **7–9** the generation of a new stereocentre in the alkylcarbonyl side chain was reflected in the formation of inseparable mixtures of diastereomers. If the carbon–carbon bond formation step resulting from nucleophilic attack on the (η^6-chloroarene)iron(1 +) salt was stereospecific, the ratio of the diastereomers of each *exo* adduct should reflect the *Z*/*E* ratio of the precursor silyl enol ether. However, the ratios of the pairs of diastereomeric adducts recorded in Table 1 clearly differ from the *Z*/*E* ratios of the appropriate silyl reagent, suggesting either that epimerization occurs via fluoride-catalyzed enolate formation in the adduct subsequent to nucleophilic attack, or that equilibration occurs in the enolate/carbanion prior to its attack on the η^6-chloroarene salt. In an attempt to minimize the loss of stereochemistry 0.33 molar equivalents of $Bu_4N^+F^-$ were used in a reaction of the (η^6-1,2-dichlorobenzene)iron salt **5** with the silyl enol ether **7**. However, conversion into both diastereomers **13** again occurred, and in the same ratio (1.5 : 1.0), although the yield of the adducts was decreased correspondingly to 33%. In another attempt to avoid this loss of stereochemistry the fluoride source was omitted and acetonitrile was used as solvent in place of THF (cf. ref. 4); however, no reaction occurred after 68 h at room temperature. In the case of the cyclohexanone derivatives **14** the favoured (albeit slightly) diastereomer is presumably **20**, in which the (η^5-4,5-dichlorocyclohexadienyl) ring is equatorial on the cyclohexyl ring. Although reaction of the (η^6-1,2-dichlorobenzene)iron salt **5** with **7** afforded only the epimeric adducts **13** resulting from *ortho* attack, mixtures of regioisomeric adducts **14** + trace *meta* isomer, **15**, **16**, and **17**, **18** resulting from both *ortho* and *meta* attack were formed from **8**, **9**, and **10**, respectively.



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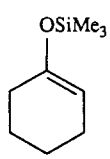

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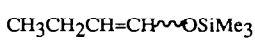

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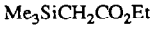

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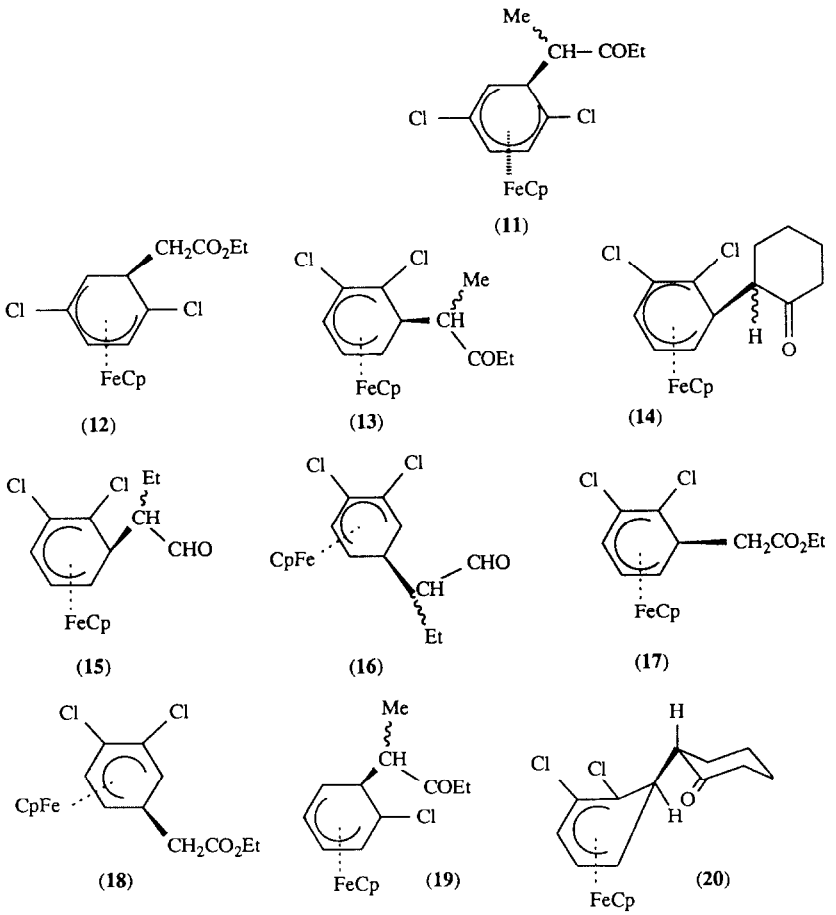
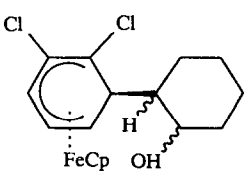
In an attempt to increase the stability of the alkylcarbonyl adducts by decreasing their susceptibility to acid-catalyzed reversion to the parent (η^6-chloroarene)iron-



(1 +) salt, the crude cyclohexanone derivatives **14** were treated directly with $NaBH_4$-ethanol. The major product was a mixture of the isomeric alcohols **21** (53%) which, however, was not significantly more stable than the precursor ketones **14**. A minor product from the reduction was the monocyclic η^5-complex **22** (32%) resulting from base-promoted loss of the cyclohexanone substituent to regenerate the η^6-salt, followed by *ortho* attack of hydride (cf. ref. 15). Treatment of the 2-hydroxycyclohexyl adducts **21** with DDQ–K_2CO_3 in acetonitrile resulted in oxidative demetallation to afford the diastereomers **23** (25%). Similarly, treatment of the alkylcarbonyl adducts **11** with DDQ in dichloromethane resulted in oxidative demetallation to afford the functionalized 1,4-dichlorobenzene **24** in low yield (16% as the 2,4-dinitrophenylhydrazone).

As a consequence of the relatively low stability of the (η^5-substituted chlorocyclohexadienyl)CpFe adducts, and of the inability to effect oxidative aromatization without concomitant decomplexation, the metal was changed from iron to ruthenium



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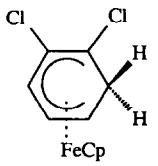

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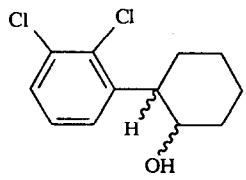

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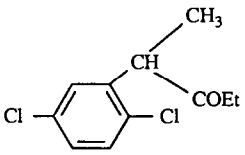
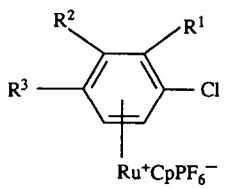


(24)

to take advantage not only of the milder conditions used for formation of the cationic (η^6-arene)ruthenium com[plexes [16] but also of the expected enhanced kinetic stability of their (η^5-alkylcarbonylcyclohexadienyl) adducts.



(**25**: R^1=R^2=R^3=H

26: R^1=Cl; R^2=R^3=H

27: R^1=R^2=H; R^3=Cl

28: R^1=R^2=H; R^3=OMe

29: R^1=Cl; R^2=OMe; R^3=H)

The (η^6-chloroarene)(cyclopentadienyl)ruthenium(1 +) hexafluorophosphates **25–29** were prepared by thermally-promoted ligand exchange between tris-(acetonitrile)(η^5-cyclopentadienyl)ruthenium(1 +) hexafluorophosphate(1 −) [17–19] and the appropriate chloroarene in refluxing 1,2-dichloroethane. The direct complexation of the chloroanisole derivatives **28** and **29** is particularly noteworthy since their iron analogues cannot be made in good yield directly by the usual ligand exchange from ferrocene; in the context of the eventual synthesis of functionalized diphenyl ethers (cf. ref. 1) the availability of cationic complexes of chloroanisoles is advantageous. The ruthenium salts **25–29** were pale brown solids which had a tendency to form solvates. Their ^{1}H and ^{13}C NMR spectra were as expected. Particularly noteworthy was the observation that although the ^{1}H signal due to the Cp protons occurred at significantly lower field in a ruthenium salt than in its iron analogue (cf. **5**, δ(H) 5.38; **26**, 5.72), the chemical shifts of the signals due to the arene ring protons were very similar (cf. **5**, 6.58 and 7.02; **26**, 6.49 and 7.03). A similarity in the reactivity of the arene rings towards nucleophilic addition was therefore expected. In the event, the η^5-cyclohexadienyl adducts of the (η^6-chloro-arene)ruthenium(1 +) salts **25–29** were prepared under the same conditions as for the iron complexes, using the silyl reagents **7–10**. The results are summarized in Table 2.

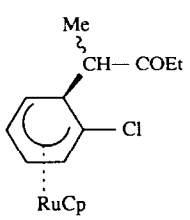
The neutral η^5 ruthenium complexes generally could be stored as yellow oils at room temperature under argon for several weeks without decomposition. This

Table 2

Reactions of (η^6-chloroarene)CpRu$^+$ PF_6^- salts with silylated reagents

Ruthenium(1 +) salt	Silyl reagent	Adduct(s)	Diastereomeric ratio	Yield (%)
25	**7**	**30**	2.0:1.0	70
		31	1.0:1.0	17
25	**8**	**32**	2.0:1.0	66
		33	1.0:1.0	16
25	**10**	**34**	–	45
		35	–	15
26	**7**	**36**	1.7:1.0	60
		37	1.0:1.0	15
26	**8**	**38**	1.3:1.0	68
		39	1.0:1.0	22
26	**10**	**40**	–	74
		41	–	15
27	**7**	**42**	1.8:1.0	56
27	**8**	**43**	1.6:1.0	87
27	**10**	**44**	–	62
28	**10**	**45**	–	42
		46	–	9
29	**10**	**47**	–	14
		48	–	14
		49	–	9

enhanced stability due to the second-row metal was particularly evident in the adducts **30** and **31** derived from the (η^6-chlorobenzene) salt **25** relative to the iron analogue **19**, which itself was less stable than is dichloro congeners. The products showed the expected ^1H and ^{13}C NMR spectra. Mixtures of diastereomers again formed when a new chiral centre was generated in the alkylcarbonyl substituent. Although the adducts resulting from *ortho* attack on the complexes **25** and **26** were predominant, a significant proportion of the corresponding *meta* regioisomer was also present; the isomers were not separable chromatographically. In the case of the isomers **45** and **46**, the regiochemistry of the major isomer **45** was proved by the observation of a nuclear Overhauser enhancement of the signal due to the methoxy group in the ^1H NMR spectrum when the signals due to H(1) and H(3) were irradiated separately. All three possible regioisomers **47**–**49** (1.0 : 1.0 : 0.6) were formed in the reaction of **29** with **10**.



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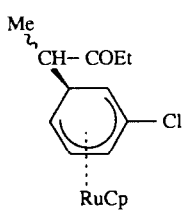
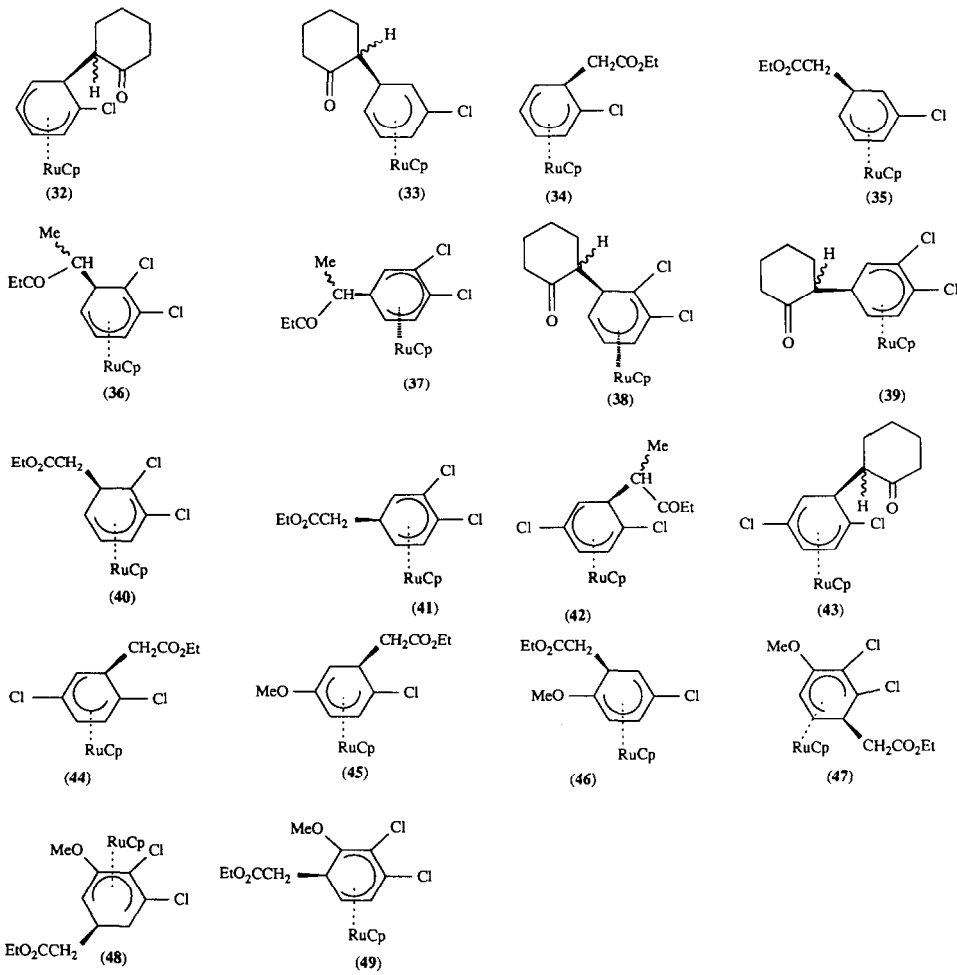
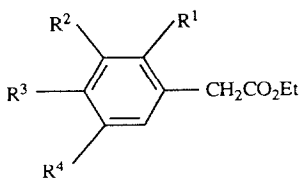


(31)

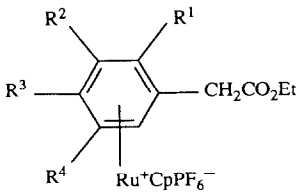
Since the anticipated utilization of these adducts required oxidative aromatization, the reaction of the regioisomerically pure adduct **44** with DDQ was investi-



gated. In order to be able to identify possible products from **44** (and from **40**, **41**) unequivocally the ethyl (chloroarene)acetates **50–53** were synthesized by Arndt–Eistert homologation of the appropriate chlorobenzoic acid. The corresponding cationic ruthenium complexes **54–57** were synthesized from $(MeCN)_3CpRu^+PF_6^-$ as before. The monochloro esters **50** and **51** and their ruthenium(1 +) salts **54** and **55** were also synthesized since an initial reaction on the adduct **44** with DDQ in acetonitrile suggested the possibility of some dechlorination. Further work, however, showed that the products from the oxidation reaction of **44** with DDQ were the arene **53** (15%) and, gratifyingly, its ruthenium(1 +) complex **57** (53%). Although the latter salt can be formed by direct complexation of ethyl (2,5-dichlorobenzene)acetate (**53**) (22%), the yield of **57** is higher (33%) via the addition–oxidation sequence. Similar treatment of the mixture of adducts **40** and **41** with DDQ afforded (53%) the free arenes **52** and **58**, and the cationic complex **56** (17%) which did not show any evidence of contamination by the regiosomeric salt derived from **41**. The mixture of adducts **45**, **46** underwent oxidative aromatization to afford only



(**50**: R^1=Cl; R^2=R^3=R^4=H
51: R^2=Cl; R^1=R^3=R^4=H
52: R^1=R^2=Cl; R^3=R^4=H
53: R^1=R^4=Cl; R^2=R^3=H
58: R^1=R^4=H; R^2=R^3=Cl)



(**54**: R^1=Cl; R^2=R^3=R^4=H
55: R^2=Cl; R^1=R^3=R^4=H
56: R^1=R^2=Cl; R^3=R^4=H
57: R^1=R^4=Cl; R^2=R^3=H
59: R^1=Cl; R^2=R^3=H; R^4=OMe
60: R^1=OMe; R^2=R^3=H; R^4=Cl)

a mixture of the ethoxycarbonylmethyl-substituted η^6-arene cationic complexes **59**, **60** (40%).

Thus, O-silyl or C-silyl reagents undergo Yanovsky-type additions to (η^6-chloroarene)Cp salts of both iron and ruthenium under mild conditions. The adducts of the ruthenium salts offer significant advantages in terms of improved stability, and in the subsequent oxidative generation of a (η^6-functionalized chloroarene) salt activated towards further nucleophilic addition or to nucleophilic aromatic substitution by *ipso* displacement of chloride.

Experimental

Unless otherwise indicated, ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AM-400 spectrometer, as solutions in $CDCl_3$ pre-filtered through K_2CO_3. Chemical shifts are given in δ(ppm) downfield from TMS. Multiplicities of the ^{13}C NMR signals were determined from DEPT spectra. The assignments of pairs of hydrogens or carbons labelled * or # may be interchanged. IR spectra were recorded on Shimadzu IR-27G or Perkin–Elmer 1600 FT–IR spectrometers. Unless otherwise indicated, the spectra of solids were recorded as KBr discs, and the spectra of oils and liquids as films between NaCl plates. Low resolution mass spectra (MS) were recorded on a VG-7070 mass spectrometer operating at a nominal accelerating voltage of 70 eV. High resolution MS were recorded on the same instrument operating at 5000 or 10000 nominal resolution; perfluorokerosene was used as the internal standard. Melting points were determined on a Reichert–Kofler block and are uncorrected. Column chromatography was performed using Al_2O_3 90 (70–230 mesh, Merck) and an Al_2O_3 : sample ratio (w/w) of 29 : 1. Solvents were degassed prior to use. Tetrahydrofuran (THF) was distilled from sodium-benzophenone, and acetonitrile and 1,2-dichloroethane were distilled from CaH_2. Tetrabutylammonium fluoride (1 mol L^{-1} in THF) was supplied by Aldrich. All cationic complexes were purified immediately prior to use by rapid filtration through alumina in dichloromethane.

(η^5-2,4-Cyclopentadien-1-yl)(η^6-1,2-dichlorobenzene)iron(1 +) hexafluorophosphate(1 −) (5)

Ferrocene (14.17 g, 76 mmol), aluminium powder (1.67 g, 62 mmol) and aluminium trichloride (29.27 g, 219 mmol) were added successively to degassed 1,2-dichlorobenzene (230 mL, 2.04 mol) and water (1.4 mL). The mixture was stirred vigorously for 5.5 h at 150 °C under nitrogen. The red-brown mixture was cooled on ice, then ice-cold water (a portion from 670 mL) was added carefully with stirring. When the vigorous reaction subsided the mixture was poured into a separatory funnel and the remaining water added. The organic layer was separated, and the aqueous layer was washed with hexanes until the washings were colourless. The aqueous layer was filtered, and a solution of ammonium hexafluorophosphate (18.63 g, 0.11 mol) in water (30 mL) was added slowly with stirring, which was continued for a further 20 min to complete the precipitation of a yellow-green solid (14.47 g, 46%). Chromatography through a short alumina column (CH_2Cl_2–EtOH, 10 : 1) yielded (η^5-2,4-cyclopentadien-1-yl)(η^6-1,2-dichlorobenzene)iron(1 +) hexafluorophosphate(1 −) (**5**) (12.89g, 41%) as a yellow crystalline solid, m.p. 232–235 °C (dec) (lit. [9] 199–201 °C as the tetrafluoroborate salt). IR: ν_{max} (KBr) 1425 (aryl C=C), 8.30 (P–F), 740 (aryl), and 552 cm^{-1} (P–F). ^1H NMR (CD_3COCD_3): δ 5.38 (5, C_5H_5); 6.60 (dxd, J 2.7, 4.5 Hz, H(4 and 5); 7.06 (dxd, J 2.7, 4.5 Hz, H(3 and 6). ^{13}C NMR (CD_3COCD_3): δ 81.8 (C_5H_5); 88.4 (C(4,5)); 89.6 (C(3,6)); 107.7 (C(1,2)).

(η^6-Chlorobenzene)(η^5-2,4-cyclopentadien-1-yl)iron(1 +) hexafluorophosphate(1 −) (6)

A mixture of chlorobenzene (14 mL, 0.14 mol), ferrocene (1.0 g, 5.38 mmol) and aluminium powder (0.15 g, 5.38 mmol) was degassed with nitrogen. Aluminium trichloride (1.43 g, 10.75 mmol) was added and the mixture was heated under reflux with vigorous stirring for 14.5 h. Workup as above yielded (η^6-chlorobenzene)(η^5-2,4-cyclopentadien-1-yl)iron(1 +) hexafluorophosphate(1 −) (**6**) (0.42 g, 21%) as yellow crystals, m.p. 228–233 °C. IR: ν_{max} (KBr) 1438 (aryl C=C), 817 and 548 cm^{-1} (P–F). ^1H NMR (CD_3COCD_3): δ 5.29 (s, C_5H_5); 6.44 (t, J_{obs} 5.9, 6.1 Hz, H(4)); 6.56 (t, J 6.3 Hz, H(3,5)); 6.80 (d, J 6.3 Hz, H(2,6)). ^{13}C NMR (CD_3COCD_3): δ 79.8 (C_5H_5); 88.1 (C(4); 89.15 (C(2,6); 89.7 (C(3,5)); 108.1 (C(1)).

(η^5-2,4-Cyclopentadien-1-yl)(η^6-1,4-dichlorobenzene)iron(1 +) hexafluorophosphate(1 −) (2)

Ferrocene (4.0 g, 22 mmol), aluminium powder (0.58 g, 22 mmol), and aluminium trichloride (5.74 g, 43 mmol) were added to a degassed solution of 1,4-dichlorobenzene (31.6 g, 0.22 mmol) in octane (25 mL) and the mixture was vigorously stirred and heated under reflux for 6 h. Workup as above gave a crude yellow solid (3.0 g, 34%). Additional product (0.23 g, 3%) was isolated by extracting the aqueous mother liquor with dichloromethane. Chromatography on alumina gave (η^5-2,4-cyclopentadien-1-yl)(η^6-1,4-dichlorobenzene)iron(1 +) hexafluorophosphate(1 −) (**2**) (2.27 g, 26%) as a yellow crystalline solid, m.p. 218.5–222 °C (dec.) (lit [20] 213–217 °C (dec)). IR: ν_{max} (KBr) 1450 (aryl C=C), 817 and 550 cm^{-1} (P–F). ^1H NMR (CD_3COCD_3): δ 5.47 (s, C_5H_5); 7.01 (s, H(2,3,5,6). ^{13}C NMR (CD_3COCD_3): δ 82.3 (C_5H_5); 89.5 (C(2,3,5,6)); 107.35 (C(1,4)).

Trimethyl(2-penten-3-yloxy)silane (7)

Reaction of 3-pentanone (4.31 g, 50 mmol), triethylamine (6.26 g, 62 mmol), chlorotrimethylsilane (6.72 g, 62 mmol), and sodium iodide (9.3 g, 62 mmol) in acetonitrile (62 mL) as described [11] gave trimethyl(2-penten-3-yloxy)silane (**7**) (5.16 g, 65%), b.p. 136–139 °C (lit. [11] b.p. 139 °C) as a mixture of the *Z*-isomer (92%) and the *E*-isomer (8%). IR: ν_{max} 1678 cm^{-1} (C=C). *Z*-isomer: ^1H NMR: δ 0.19 (s, $SiMe_3$); 1.02 (t, *J* 7.4 Hz, CH_3CH_2); 1.51 (dt, *J* 6.6, 1.3 Hz, CH_3CH=); 2.02 (qqd, *J* 7.4, 1.3, 0.9 Hz, $MeCH_2$); 4.52 (qt, *J* 6.6, 0.9 Hz, MeCH=). ^{13}C NMR: δ 0.3 ($SiMe_3$); 11.4 (CH_3CH_2); 29.2 ($MeCH_2$); 100.6 (=CHMe); 152.4 (C=CHMe). *E*-isomer: ^1H NMR: δ 0.17 (s, $SiMe_3$); 1.00 (t, *J* 7.4 Hz, CH_3CH_2); 1.53 (d, *J* 7.1 Hz, CH_3CH=); 2.07 (q, *J* 7.5 Hz, $MeCH_2$); 4.59 (q, *J* 6.9 Hz, MeCH). ^{13}C NMR: δ 1.6 ($SiMe_3$); 7.5 (=$CHCH_3$); 11.3 (CH_3CH_2); 23.8 ($MeCH_2$); 100.0 (=CHMe); 153.2 (C=CHMe).

(1-Cyclohexen-1-yloxy)trimethylsilane (8)

Reaction of cyclohexanone (2.45 g, 25 mmol), triethylamine (3.14 g, 31 mmol), chlorotrimethylsilane (3.37 g, 31 mmol), and sodium iodide (4.65 g, 31 mmol) in acetonitrile (31 mL) as described [11] gave (1-cyclohexen-1-yloxy)trimethylsilane (**8**) (2.25 g, 53%) as a colourless liquid, b.p. 120–122 °C, 180 mmHg (lit. [11] 76 °C, 30 mmHg). IR: ν_{max} 1668 cm^{-1} (C=C). ^1H NMR: δ 0.17 (s, $SiMe_3$); 1.51 (m, H(4*); 1.65 (m, H(5*); 1.96–2.03 (m, H(3,6); 4.87 (t, *J* 3.8 Hz, =CH). ^{13}C NMR: δ 22.4 (CH_2); 23.2 (CH_2); 23.8 (CH_2); 29.9 (CH_2); 104.3 (=CH); 150.3 (=COSi).

(1-Buten-1-yloxy)trimethylsilane (9)

Reaction of chlorotrimethylsilane (7.28 g, 67 mmol), butanal (2.67 g, 37 mmol), triethylamine (3.74 g, 37 mmol) and sodium iodide (5.55 g, 37 mmol) as described [11] gave (1-buten-1-yloxy)trimethylsilane (2.46 g, 46%), b.p. 110–120 °C, 760 mmHg (lit. [11] 48 °C, 50 mmHg), as a mixture of the *Z*-isomer (77%) and the *E*-isomer (23%). IR: ν_{max} 1655 cm^{-1} (C=C). *Z*-isomer: ^1H NMR: δ 0.07 (s, $SiMe_3$); 0.95 (t, *J* 7.6 Hz, CH_2CH_3); 2.08 (qdd, *J* 7.6, 7.1, 1.4 Hz, CH_2Me); 4.49 (td, *J* 7.1, 5.9 Hz, CH_2CH=); 6.11 (dt, *J* 5.9, 1.5 Hz, =CHO). ^{13}C NMR: δ 2.5 ($SiMe_3$); 15.0 (CH_2CH_3); 17.7 (CH_2CH_3); 114.2 (=$CHCH_2$); 137.8 (=CHO). *E*-isomer: ^1H NMR: δ 0.17 (s, $SiMe_3$); 0.96 (t, *J* 7.4 Hz, CH_2CH_3); 1.91 (qdd, *J* 7.4, 7.2, 1.3 Hz, CH_2Me); 5.03 (dt, *J* 12.0, 7.2 Hz, CH_2CH=); 6.20 (dt, *J* 12.0, 1.4 Hz, =CHO). ^{13}C NMR: δ 0.6 ($SiMe_3$); 15.7 (CH_2CH_3); 21.4 (CH_2Me); 114.4 (=$CHCH_2$); 139.4 (=CHO).

*(η^5-2,4-Cyclopentadien-1-yl)[(1,2,3,4,5-η)-2,5-dichloro-6-*exo*-(1ξ-methyl-2-oxobutyl)-2,4-cyclohexadien-1-yl]iron (11)*

A solution of the complex **2** (50 mg, 0.12 mmol) in tetrahydrofuran (11 mL) was treated successively under nitrogen with trimethyl(2-penten-3-yloxy)silane (58 mg, 0.36 mmol) and a solution of tetrabutylammonium fluoride in tetrahydrofuran (0.12 mL, 0.12 mmol). The mixture was stirred for 10 min, solvent was removed *in vacuo*, and the resulting oil chromatographed on alumina. Elution with hexanes/dichloromethane/triethylamine (30 : 10 : 1) gave (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η)-2,5-dichloro-6-*exo*-(1ξ-methyl-2-oxobutyl)-2,4-cyclohexadien-1-yl]iron (**11**) (30 mg, 67%) as an orange oil containing a mixture (1.5 : 1.0) of two diastereomers. IR: ν_{max} 1705 (CO), 812 cm^{-1} (C–Cl). Major diastereomer: ^1H NMR: δ 0.62 (d, *J* 6.9 Hz,

CHCH_3); 0.95 (t, J 7.2 Hz, CH_2CH_3); 1.48 (dq, J 8.7, 7.0 Hz, CHMe); 2.25 (dq, J 18, 7.2 Hz, CH_AH$_B$Me); 2.34 (dq, J 18, 7.2 Hz, CH$_A$$H_B$Me); 3.12 (ddd, J 8.7, 7.0, 1.5 Hz, H(6)); 3.35 (dd, J 7.0, 1.8 Hz, H(1)); 4.43 (s, C_5H_5); 4.61 (dd, J 5.2, 1.5 Hz, H(4); 6.07 (dd, J 5.3, 1.8 Hz, H(3)). ^{13}C NMR: δ 7.7 (CH_2CH_3); 13.8 (CHCH_3); 33.6 (CHMe); 36.6 (CH_2Me); 52.1 (C(1*); 53.1 (C(6*); 62.6 (C(5)); 74.4 (C(4)); 77.7 (C(3)); 78.4 (C_5H_5)); 101.5 (C(2)); 213.4 (CO). Minor diastereomer: ^{1}H NMR: δ 0.78 (d, J 7.0 Hz, CHCH_3); 0.9 (t, J 7.3 Hz, CH_2CH_3); 1.56 (dq, J 9.2, 7.0 Hz, CHMe); 2.18 (dq, J 17, 7.2 Hz, CH_AH$_B$Me); 2.24 (dq, J 17, 7.2 Hz, CH$_A$$H_B$Me); 3.11 (ddd, J 8.7, 7.0, 1.5 Hz, H(6)); 3.26 (dd, J 6.9, 1.8 Hz, H(1); 4.42 (s, C_5H_5); 4.62 (dd, J 6.1, 1.6 Hz, H(4)); 6.05 (dd, J 5.3, 1.9 Hz, H(3)). ^{13}C NMR: δ 7.55 (CH_2CH_3); 14.1 (CHCH_3); 33.8 (CHMe); 36.8 (CH_2Me); 50.9 (C(1*); 54.3 (C(6*); 60.6 (C(5)); 74.3 (C(4)); 77.6 (C(3)); 78.5 (C_5H_5); 101.5 (C(2)); 213.2 (CO).

*(η^5-2,4-Cyclopentadien-1-yl)[1,2,3,4,5-η)-2,5-dichloro-6-*exo*-(ethoxycarbonylmethyl)-2,4-cyclohexadien-1-yl]iron (**12**)*

A solution of the complex **2** (50 mg, 0.12 mmol) in tetrahydrofuran (13 mL) under nitrogen was treated successively with ethyl trimethylsilylacetate (21 mg, 0.13 mmol) and a solution of tetrabutylammonium fluoride in tetrahydrofuran (0.12 mL, 0.12 mmol). The solution was stirred for 25 min, solvent was removed under reduced pressure, and the residue was extracted with pentane to give (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η)-2,5-dichloro-6-*exo*-(ethoxycarbonylmethyl)-2,4-cyclohexadien-1-yl]iron (**12**) (24 mg, 56%). IR: ν_{max} 1714 (CO), 813 cm^{-1} (C–Cl). ^{1}H NMR: δ 1.20 (dd, J 14.4, 8.5 Hz, CH_AH$_B$CO); 1.21 (t, J 7.2 Hz, CH_2CH_3); 1.65 (dd, J 14.6, 4.8 Hz, CH$_A$$H_B$CO); 3.37 (dddd, J 8.5, 6.9, 4.8, 1.6 Hz, H(6)); 3.41 (dd, J 6.9, 1.8 Hz, H(1)); 4.02 (dq, J 15.4, 7.2 Hz, CH_AH$_B$Me); 4.05 (dq, J 15.4, 7.2 Hz, CH$_A$$H_B$Me); 4.43 (s, C_5H_5)); 4.56 (dd, J 5.3, 1.6 Hz, H(4)); 6.10 (dd, J 5.3, 1.8 Hz, H(3)). ^{13}C NMR: δ 14.2 (CH_2CH_3); 35.6 (C(1)); 41.4 (CH_2CO); 45.9 (C(6)); 60.3 (CH_2Me); 6.18 (C(5)); 74.1 (C(4)); 77.5 (C(3)); 78.2 (C_5H_5); 101.4 (C(2)); 170.5 (CO).

*(η^5-2,4-Cyclopentadien-1-yl)[(1,2,3,4,5-η)-4,5-dichloro-6-*exo*-(1ξ-methyl-2-oxobutyl)-2,4-cyclohexadien-1-yl]iron (**13**)*

A solution of the complex **5** (50 mg, 0.12 mmol) in tetrahydrofuran (6 mL) under nitrogen was treated successively with trimethyl(2-penten-3-yloxy)silane (58 mg, 0.36 mmol) and a solution of tetrabutylammonium fluoride in tetrahydrofuran (0.12 mL, 0.12 mmol). The mixture was stirred for 15 min, solvent was removed under reduced pressure, and the resulting oil chromatographed on alumina. Elution with hexanes/dichloromethane/triethylamine (25 : 25 : 1) gave (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η)-4,5-dichloro-6-*exo*-(1ξ-methyl-2-oxobutyl)-2,4-cyclohexadien-1-yl]-iron (**13**) (31 mg, 72%) as an orange oil containing a mixture (ca. 1.5 : 1.0) of two diastereomers. IR: ν_{max} 1705 (CO), 810 cm^{-1} (C–Cl). Major diastereomer: ^{1}H NMR: δ 0.54, (d, J 6 Hz, CHCH_3); 0.97 (s, CH_2CH_3); 1.45 (m, CHMe); 2.19 (m, CH_2Me); 2.89 (m, H(1*); 3.11 (m, H(6*); 4.26 (s, H(2)); 4.40 (s, C_5H_5); 6.18 (s, H(3)). ^{13}C NMR: δ 7.1 (CH_2CH_3); 11.4 (CHCH_3); 32.3 (CHMe); 37.2 (CH_2Me); 51.7 (C(1*); 52.5 (C(6*); 61.9 (C(5)); 75.0 (C(2,3)); 78.5 (C_5H_5); 101.3 (C(4)); 213.6 (CO). Minor diastereomer: ^{1}H NMR: δ 0.78 (d, J 6 Hz, CHCH_3); 0.91 (brs, CH_2CH_3); 1.54 (m, CHMe); 2.32 (m, CH_2Me); 2.84 (m, H(1*); 3.19 (m, H(6*); 4.17 (brs, H(2)); 4.40 (s, C_5H_5); 6.13 (s, H(3)). ^{13}C NMR: δ 7.5 (CH_2CH_3); 13.8

($CHCH_3$); 32.8 ($CHMe$); 36.2 (CH_2Me); 50.4 (C(1*); 53.9 (C(6*); 62.0 (C(5)); 75.0 (C(2)); 77.6 (C(2,3)); 78.4 (C_5H_5); 101.3 (C(4)); 213.6 (CO). MS: *m/z* 267 (100%, M^+-C_5H_9O), 231 (41, 267-HCl and *M*-FeCp), 121 (42, FeCp).

*(η^5-2,4-Cyclopentadien-1-yl)[(1,2,3,4,5-η)-4,5-dichloro-6-*exo*-(1ξ-2-oxocyclohexyl)-2,4-cyclohexadien-1-yl]iron (**14**)*

A solution of the complex **5** (0.10 g, 0.24 mmol) in tetrahydrofuran (12 mL) under nitrogen was treated successively with (1-cyclohexen-1-yloxy)trimethylsilane (0.12 g, 0.73 mmol) and a solution of tetrabutylammonium fluoride in tetrahydrofuran (0.24 mL, 0.24 mmol). The mixture was stirred for 20 min, solvent was removed *in vacuo*, and the residue was chromatographed on alumina. Elution with dichloromethane/pentane/triethylamine (25 : 25 : 1) gave (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η)-4,5-dichloro-6-*exo*-(1ξ-2-oxocyclohexyl)-2,4-cyclohexadien-1-yl]iron (**14**) as an orange oil containing a mixture (1 : 2 : 1.0) of two diastereomers (36 mg, 41%). IR: ν_{max} 1700 (CO), 808 cm^{-1} (C–Cl). Major diastereomer: ^1H NMR: δ 0.8–2.3 (CH_2, CH); 3.12 (t, *J* 6.2 Hz, H(1)); 3.29 (m, H(6)); 4.10 (t, *J* 5.4 Hz, H(2)); 4.40 (s, C_5H_5); 6.11 (d, *J* 4.6 Hz, H(3)). ^{13}C NMR: δ 24.4 (CH_2); 28.0 (CH_2); 30.3 (CH_2); 35.0 ($CHCO$); 42.1 (CH_2CO); 47.8 (C(1)); 58.7 (C(5)); 59.4 (C(6)); 74.4 (C(2)); 78.4 (C(3)); 78.5 (C_5H_5); 100.9 (C(4)); 211.5 (CO). Minor diastereomer: ^1H NMR: δ 0.8–2.3 (CH_2, CH); 2.91 (t, *J* 6.3 Hz, H(1)); 3.29 (m, H(6)); 4.24 (t, *J* 5.5 Hz, H(2)); 4.40 (s, C_5H_5); 6.12 (d, *J* 4.6 Hz, H(3)). ^{13}C NMR: δ 23.4 (CH_2); 27.2 (CH_2); 27.7 (CH_2); 34.1 ($CHCO$); 41.5 (CH_2CO); 47.8 (C(1)); 55.3 (C(6)); 58.7 (C(5)); 76.1 (C(2*)); 77.7 (C(3*)); 78.2 (C_5H_5)); 101.4 (C(4)); 211.5 (CO).

*(η^5-2,4-Cyclopentadien-1-yl)[(1,2,3,4,5-η)-4,5-dichloro-6-*exo*-(1ξ-formyl-1-propyl)-2,4-cyclohexadien-1-yl]iron (**15**) and regioisomer **16***

A solution of complex **5** (0.19 g, 0.47 mmol) in tetrahydrofuran (12 mL) under nitrogen was treated successively with (1-buten-1-yloxy)trimethylsilane (0.14 g, 0.94 mmol) and a solution of tetrabutylammonium fluoride in tetrahydrofuran (0.47 mL, 0.47 mmol). The mixture was stirred for 25 min, the solution was decanted from an oily solid, and the solvent was removed *in vacuo*. Extraction of the residue with pentane gave a mixture (10 : 1) containing (i) (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η)-4,5-dichloro-6-*exo*-(1ξ-formyl-1-propyl)-2,4-cyclohexadien-1-yl]iron (**15**) as a mixture (2 : 1) of two diastereomers, and (ii) (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η)-3,4-dichloro-6-*exo*-(1ξ-formyl-1-propyl)-2,4-cyclohexadien-1-yl]iron (**16**) as a mixture (1 : 1) of two diastereomers. IR: ν_{max} 1700 (CO), 750 cm^{-1} (C–Cl). (i) Major diastereomer of **15**: ^1H NMR: δ 0.65 (t, *J* 7.2 Hz, Me); 1.17 (m, CH_2CH_3); 1.33 (m, $CHCH_2$); 2.89 (td, *J* 7.0, 1.0 Hz, H(1); 3.22 (t, *J* 7.4 Hz, H(6)); 4.29 (dd, *J* 6, 5 Hz, H(2); 4.42 (s, C_5H_5); 6.20 (dd, *J* 4.9, 1.0 Hz, H(3)); 9.37 (d, *J* 3.6 Hz, CHO). ^{13}C NMR: δ 11.5 (Me); 17.2 (CH_2Me); 32.1 ($CHCH_2$); 49.0 (C(1)); 61.5 (C(5)); 62.2 (C(6)); 75.2 (C(2)); 78.5 (C_5H_5); 78.7 (C(3)); 101.4 (C(4)); 203.2 (CO). Minor diastereomer of **15**: ^1H NMR: δ 0.71 (t, *J* 7.1 Hz, Me); 1.21 (m, CH_2Me); 1.33 (m, $CHCH_2$); 2.89 (td, *J* 7.0, 1.0 Hz, H(1)); 3.32 (t, *J* 6.9 Hz, H(6)); 4.26 (dd, *J* 6, 5 Hz, H(2)); 4.41 (s, C_5H_5); 6.17 (dd, *J* 4.7, 1.0 Hz, H(3)); 9.17 (d, *J* 2.6 Hz, CHO). ^{13}C NMR: δ 11.4 (Me); 18.2 (CH_2Me); 32.7 ($CHCH_2$); 47.9 (C(1)); 61.1 (C(6)); 61.5 (C(5)); 75.6 (C(2)); 78.5 (C_5H_5); 78.7 (C(3)); 101.4 (C(4)); 203.5 (CO). (ii) **16**: ^1H NMR: δ 2.37, 2.44 (td, *J* 6.4, 1.5 Hz, H(6)); 2.61, 2.63 (t, *J* 6.4 Hz, H(1)); 2.97

(dd, *J* 6.5, 1.5 Hz, H(5)); 4.39 (s, C_5H_5); 4.81 (dd, *J* 6.4, 2.5 Hz, H(2)); 9.27, 9.30 (d, *J* 3.0 Hz, CHO). ^{13}C NMR: δ 77.6 (C_5H_5).

*(η^5-2,4-Cyclopentadien-1-yl)[(1,2,3,4,5-η)-4,5-dichloro-6-*exo*-(ethoxycarbonylmethyl)-2,4-cyclohexadien-1-yl]iron (**17**) and regioisomer **18***

A solution of complex **5** (50 mg, 0.12 mmol) in tetrahydrofuran (6 mL) under nitrogen was treated successively with ethyl trimethylsilylacetate (58 mg, 0.36 mmol) and a solution of tetrabutylammonium fluoride in tetrahydrofuran (0.12 mL, 0.12 mmol). The solution was stirred for 30 min, solvent was removed *in vacuo*, and the resulting oil was chromatographed on alumina. Elution with dichloromethane/pentane/triethylamine (50 : 50 : 1) gave a mixture (4 : 1) (28 mg, 88%) of (i) (η^5-2,4-cyclopentadien-1-yl)-[(1,2,3,4,5-η)-4,5-dichloro-6-*exo*-(ethoxycarbonylmethyl)-2,4-cyclohexadien-1-yl]iron (**17**) and (ii) (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η)-3,4-dichloro-6-*exo*-(ethoxycarbonylmethyl)-2,4-cyclohexadien-1-yl]iron (**18**) as an orange oil. IR: ν_{max} 1726 (CO), 808 cm^{-1} (C–Cl). (i): ^{1}H NMR: δ 1.12 (dd, *J* 14.4, 9.5 Hz, CH_AH_BCO); 1.19 (t, *J* 7 Hz, CH_2CH_3); 1.66 (dd, *J* 14.6, 4.4 Hz, CH_AH_BCO); 2.96 (brs, $W_{1/2}$ 15 Hz, H(1)); 3.40 (m, H(6)); 4.01 (q, *J* 6.8 Hz, CH_2Me); 4.21 (m, H(2)); 4.41 (s, C_5H_5); 6.21 (d, *J* 4.1 Hz, H(3)). ^{13}C NMR: δ 14.2 (CH_2CH_3); 34.2 (C(1)); 41.1 (CH_2CO); 45.4 (C(6)); 60.3 (CH_2Me); 61.8 (C(5)); 76.7 (C(2$^\#$)); 77.5 (C(3$^\#$)); 78.2 (C_5H_5); 100.7 (C(4)); 170.5 (CO); and (ii): ^{1}H NMR: δ 2.45 (brs, H(1*); 2.80 (brs, H(5*); 4.38 (s, C_5H_5); 4.77 (d, *J* 5.8 Hz, H(2)). ^{13}C NMR: δ 28.6 (C(5)); 35.0 (C(1)); 44.9 (CH_2CO); 60.1 (CH_2Me); 78.3 (C_5H_5).

*Reduction of (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η)-4,5-dichloro-6-*exo*-(1ξ-2-oxocyclohexyl)-2,4-cyclohexadien-1-yl]iron) (**14**) with sodium borohydride*

A solution of the adducts **14** (prepared from complex **5** (0.19 g, 0.47 mmol), (1-cyclohexen-1-yloxy)trimethylsilane (87 mg, 0.51 mmol) and tetrabutylammonium fluoride (0.47 mL, 0.47 mmol) in tetrahydrofuran) was treated with sodium borohydride (88 mg, 2.3 mmol) and ethanol (3 mL). The mixture was stirred for 20 h, solvent was removed under reduced pressure, and the resulting oil triturated with pentane. The pentane extracts were chromatographed on alumina using pentane/dichloromethane/triethylamine (60 : 20 : 1) as eluent to give, in order of elution: (i) (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η)-4,5-dichloro-2,4-cyclohexadien-1-yl]iron (**22**) (22 mg, 32%). IR: ν_{max} 811 cm^{-1} (C–Cl). ^{1}H NMR: δ 2.05 (d, *J* 12.7 Hz, H(6 *exo*); 2.60 (brs, $W_{1/2}$ 17 Hz, H(1)); 2.98 (dd, *J* 12.4, 6.8 Hz, H(6 *endo*); 4.24 (brs, $W_{1/2}$ 15 Hz, H(2)); 4.40 (s, C_5H_5); 6.30 (d, *J* 3.6 Hz, H(3)). ^{13}C NMR: δ 28.1 (C(1)); 38.7 (C(6)); 77.0 (C(2*)); 78.0 (C(3*)); 78.2 (C_5H_5); and (ii) (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η)-4,5-dichloro-6-*exo*-(1ξ-2-hydroxycyclohexyl)-2,4-cyclohexadien-1-yl]iron (**21**) (91 mg, 53%) as a mixture of stereoisomers. IR: ν_{max} 3350 (br, OH), 1053 (C–O), 806 cm^{-1} (C–Cl). ^{1}H NMR: δ 0.8–2.6 (CH_2, CH); 2.89 (t, *J* 6 Hz, H(1)); 3.0–3.15 (m, CHOH); 3.48 (t, *J* 6 Hz, H(6)); 4.27 (t, *J* 6 Hz, H(2)); 4.40 (s, C_5H_5); 4.42 (s, C_5H_5); 4.43 (s, C_5H_5); 4.78 (t, *J* 6 Hz, (*meta* attack product?); 6.12 (d, *J* 5 Hz, H(3)). ^{13}C NMR: δ 24.4 (CH_2); 24.7 (CH_2); 25.5 (CH_2); 33.4 (CHCOH); 35.1 (CH_2COH); 49.9 (C(1*); 50.5 (C(6*); 69.6 (CHOH); 75.8 (C(2$^\#$)); 77.4 (C_5H_5); 77.7 (C_5H_5); 78.2 (C_5H_5); 78.35 (C(3$^\#$)); 78.4 (C(3$^\#$)).

*Treatment of (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η)-4,5-dichloro-6-*exo*-(1ξ-2-hydroxycyclohexyl)-2,4-cyclohexadien-1-yl]iron (**21**) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)*

A mixture of the adduct **21** (91 mg, 0.25 mmol) in dry acetonitrile (5 mL), potassium carbonate (5 mg), and DDQ (62 mg, 0.27 mmol) in acetonitrile was stirred at 0 °C for 30 min. Solvent was removed *in vacuo* and the solid chromatographed on alumina. Elution with dichloromethane/pentane (1 : 4) gave an unidentified oil (4 mg), and a mixture of metal-free aromatic products **23** (15 mg, 25%). ^{1}H NMR: δ 1.2–2.5 ($(CH_2)_n$); 3.17 (m, C*H*OH); 3.80 (m, C*H*OH); 7.15–7.40 (m, aromatic H).

*Treatment of (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η)-2,5-dichloro-6-*exo*-(1ξ-methyl-2-oxobutyl)-2,4-cyclohexadien-1-yl]iron (**11**) with DDQ*

A solution of the complex **11** (57 mg, 0.14 mmol) and DDQ (31 mg, 0.14 mmol) in dichloromethane (5 mL) was stirred under nitrogen at room temperature for 30 min. The suspension was filtered, solvent was removed from the filtrate *in vacuo*, and the residue was chromatographed on alumina. Elution with dichloromethane afforded a mixture (TLC) containing (IR, ^{1}H NMR) an aromatic ketone. A solution of 2,4-dinitrophenylhydrazine (25 mg, 0.13 mmol) in methanol (3 mL) and conc. hydrochloric acid (ca. 0.2 mL) was added. Extraction with dichloromethane and chromatography on alumina and then PLC (alumina) gave 2-[2-(1,4-dichloro)phenyl]-3-pentanone (**24**) 2,4-dinitrophenylhydrazone (5 mg, 16%) as an orange solid (Found: $M^{+\cdot}$ 410.0544. $C_{17}H_{16}{}^{35}Cl_2N_4O_4$ calcd.: $M^{+\cdot}$ 410.0549). IR: ν_{max} 1619 (C=N), 1519 (asymm. NO_2), 1372 (symm. NO_2), 739 cm^{-1} (C–Cl). ^{1}H NMR: δ 1.14 (t, J 7.7 Hz, CH_2CH_3); 1.53 (d, J 6.9 Hz, $CHCH_3$); 2.25 (dq, J 14.9, 7.6 Hz, CH_AH_BMe); 2.45 (dq, J 14.9, 7.6 Hz, CH_AH_BMe); 4.36 (q, J 6.9 Hz, C*H*Me); 7.19 (d, J 1.6 Hz, H(3)); 7.20 (d, J 7.2 Hz, H(6′)); 7.36 (dd, J 7.2, 1.7 Hz, H(5′)); 7.85 (brs, NH); 7.97 (d, J 9.6 Hz, H(6)); 8.35 (dd, J 9.6, 2.6 Hz, H(5)); 9.16 (d, J 2.6 Hz, H(3). MS: m/z 410 (22%, M^+), 375 (100, M-Cl), 193 (46, M-$C_6H_3(NO_2)_2NH$).

*(η^6-Chlorobenzene)(η^5-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphate(1 −) (**25**)*

Nitrogen was bubbled for 10 min through a solution of chlorobenzene (0.39 g, 3.5 mmol) and tris(acetonitrile)(η^5-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphate(1 −) [17–19] (1.0 g, 2.3 mmol) in dry 1,2-dichloroethane which was then refluxed for 16 h. Workup as before gave a solid (0.81 g, 84%) which was dissolved in acetone and precipitated with ether to afford (η^6-chlorobenzene)(η^5-2,4-cyclopentadien-1-yl)ruthenium(1 +)hexafluorophosphate(1 −) (**25**) (0.40 g, 38%) as an off-white powder, m.p. 175–179 °C(dec.) (Found: C, 3.19; H, 2.45. $C_{11}H_{10}ClF_6PRu \cdot 0.16Me_2CO$ calcd.: C, 31.9; H, 2.6%). ^{1}H NMR (CD_3COCD_3): δ 5.64 (s, C_5H_5); 6.35 (t, J 6.0 Hz, H(4)); 6.47 (br t, J 6.0 Hz, H(3,5)); 6.80 (brd, J 5.9 Hz, H(2,6)). ^{13}C NMR(CD_3COCD_3): δ 83.4 (C_5H_5); 86.5 (C(4)); 86.9 (C(3,5)); 87.0 (C(1); 88.6 C(2,6)).

*(η^5-2,4-Cyclopentadien-1-yl)(η^6-1,2-dichlorobenzene)ruthenium(1 +) hexafluorophosphate(1 −) (**26**)*

A solution of 1,2-dichlorobenzene (0.51 g, 3.5 mmol) and $(MeCN)_3CpRu^+PF_6^-$ (1.0 g, 2.3 mmol) in dry 1,2-dichloroethane (40 mL) was degassed with nitrogen and

refluxed for 16 h. Solvent was removed under reduced pressure to afford a solid which was washed with hexanes and chromatographed on alumina. Elution with acetone gave (η^5-2,4-cyclopentadien-1-yl)(η^6-1,2-dichlorobenzene)ruthenium(1 +) hexafluorophosphate(1 −) (**26**) (0.76 g, 72%) which was dissolved in acetone and precipitated with ether to give the salt (0.51 g, 48%) as a fawn powder, m.p. 236–238 °C(dec.) (Found: C, 29.5; H, 2.1. $C_{11}H_9Cl_2F_6PRu \cdot 0.16Me_2CO$ calcd.: C, 29.5; H, 2.15%). ^{1}H NMR (CD_3COCD_3): δ 5.72 (s, C_5H_5); 6.49 (m, H(4,5)); 7.03 (m, H(3,6). ^{13}C (CD_3COCD_3): δ 85.2 (C_5H_5); 86.8 (C(4,5)); 87.0 (C(1,2)); 88.5 (C(3,6)).

*(η^5-2,4-Cyclopentadien-1-yl)(η^6-1,4-dichlorobenzene)ruthenium(1 +) hexafluorophosphate(1 −) (**27**)*

Reaction of 1,4-dichlorobenzene (0.45 g, 3.0 mmol) and $(MeCN)_3CpRu^+PF_6^-$ (0.88 g, 2.0 mmol) in dry refluxing 1,2-dichloroethane (35 mL) for 16 h followed by chromatography on alumina and elution with acetone gave (η^5-2,4-cyclopentadien-1-yl)(η^6-1,4-dichlorobenzene)ruthenium(1 +) hexafluorophosphate(1 −) (**27**) (0.60 g, 66%) which was dissolved in acetone and precipitated with ether to give the salt (0.48 g, 52%) as a fawn powder, m.p. 246–249 °C (dec.) (lit. [17] 248–250 °C (dec.)). ^{1}H NMR (CD_3COCD_3, 60 MHz): δ 5.80 (s, C_5H_5); 6.96 (s, C_6H_4).

*(η^6-1-Chloro-4-methoxybenzene)(η^5-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphate(1 −) (**28**)*

Reaction of 1-chloro-4-methoxybenzene (0.31 g, 2.18 mmol) with $(MeCN)_3CpRu^+PF_6^-$ (0.50 g, 1.17 mmol) in refluxing 1,2-dichloroethane (30 mL) for 16 h followed by workup and chromatography on alumina in dichloromethane gave (η^6-1-chloro-4-methoxybenzene)(η^5-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphate(1 −) (**28**) (0.35 g, 67%) as a cream powder, m.p. 175 °C (CH_2Cl_2–hexanes) (Found: C, 32.0; H. 2.6. $C_{12}H_{12}ClF_6OPRu$ calcd.: C, 31.75; H, 2.7%). ^{1}H NMR (CD_3COCD_3): δ 3.85 (s, OMe); 5.62 (s, C_5H_5); 6.44 (d, *J* 6.5 Hz, H(1,6); 6.68 (d, *J* 6.5 Hz, H(3,5)). ^{13}C NMR (CD_3COCD_3): δ 58.1 (OMe); 75.1 (C(3,6)); 82.95 (C_5H_5); 86.4 (C(2,5)); 102.9 (C(1)); 135.1 (C(4)).

*(η^5-2,4-Cyclopentadien-1-yl)[η^6-(1,2-dichloro-3-methoxybenzene)]ruthenium(1 +) hexafluorophosphate(1 −) (**29**)*

Reaction of $(MeCN)_3CpRu^+PF_6^-$ (0.61 g, 1.41 mmol) with 1,2-dichloro-3-methoxybenzene (0.27 g, 1.52 mmol) in 1,2-dichloroethane (35 mL) followed by triturating the crude product with hexanes and then chromatography of the residual salt on alumina in dichloromethane afforded (η^5-2,4-cyclopentadien-1-yl)[η^6-(1,2-dichloro-3-methoxybenzene)](ruthenium(1 +) hexafluorophosphate(1 −) (**29**) (0.53 g, 76%) as a cream solid, m.p. 164–165 °C (CH_2Cl_2–hexanes) (Found: C, 30.1; H, 2.3. $C_{12}H_{12}Cl_2F_6OPRu$ calcd.: C, 29.5; H, 2.3%). IR: ν_{max} 1642 (C=C), 1277 (C–O), 836 cm^{-1} (P–F). ^{1}H NMR (CD_3COCD_3): δ 4.07 (s, OCH_3); 5.62 (s, C_5H_5); 6.36 (t, *J* 6.1 Hz, H(5)); 6.67 (d, *J* 6.2 Hz, H(4)); 6.75 (d, *J* 5.7 Hz, H(6)). ^{13}C NMR (CD_3COCD_3): δ 59.4 (OCH_3); 71.9 (C(4)); 83.1 (C(6)); 83.75 (C_5H_5); 85.0 (C(5)); 88.1 (C(2)); 105.9 (C(1)); 132.5 (C(3)).

*Reaction of (η^6-chlorobenzene)(η^5-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphate(1 −) (**25**) with trimethyl(2-penten-3-yloxy)silane*

Trimethyl(2-penten-3-yloxy)silane (29 mg, 0.18 mmol) and a solution of tetrabutylammonium fluoride (0.17 mL, 0.17 mmol) in tetrahydrofuran were added dropwise to a solution of the complex **25** (70 mg, 0.18 mmol) in tetrahydrofuran. The mixture was stirred for 30 min, solvent was removed *in vacuo*, and the residue was extracted with pentane to give a semi-solid (52 mg, 87%); IR: ν_{max} 1705(CO), 796 cm^{-1} (C–Cl)), containing a mixture (4 : 1) of (i) [(1,2,3,4,5-η)-5-chloro-6-*exo*-(1ξ-methyl-2-oxobutyl)-2,4-cyclohexadien-1-yl](η^5-2,4-cyclopentadien-1-yl)ruthenium (**30**) as a mixture (2 : 1) of two diastereomers. Major diastereomer: ^{1}H NMR: δ 0.69 (d, *J* 6.8 Hz, $CHCH_3$); 0.99 (t, *J* 7.0 Hz, CH_2CH_3); 1.89 (dq, *J* 8.6, 6.9 Hz, CHMe); 2.33 (dq, *J* 18.1, 7.2 Hz, CH_AH_BMe); 2.46 (dd, *J* 18.1, 7.2 Hz, CH_AH_BMe); 3.10 (t, *J* 7 Hz, H(6)); 3.28 (td, *J* 5.7, 1 Hz, H(1)); 4.39 (br t, *J* 5.2 Hz, H(2)); 4.83 (s, C_5H_5); 4.89 (br d, *J* 4.7 Hz, H(4)); 5.60 (td, *J* 4.7, 1 Hz, H(3)). ^{13}C NMR: δ 7.8 (CH_2CH_3); 11.7 ($CHCH_3$); 31.6 (CHMe); 36.3 (CH_2Me); 53.8 (C(1*)); 54.6 (C(6*)); 61.0 (C(5)); 75.1 (C(2#)); 76.5 (C(4#)); 77.9 (C(3#)); 78.6 (C_5H_5)); 213.9 (CO). Minor diastereomer: ^{1}H NMR: δ 0.90 (d, *J* 7.0 Hz, $CHCH_3$); 0.97 (t, *J* 7.4 Hz, CH_2CH_3); 1.99 (dq, *J* 8.6, 7.0 Hz, $CHCH_3$); 2.26 (q, *J* 7.2 Hz, CH_2Me); 3.1 (m, H(6)); 3.21 (br t, *J* 5.8 Hz, H(1)); 4.31 (br t, *J* 5.2 Hz, H(2)); 4.82 (s, C_5H_5); 4.89 (br d, *J* 4.7 Hz, H(4)); 5.57 (td, *J* 5.1, 1 Hz, H(3)). ^{13}C NMR: δ 7.6 (CH_2CH_3); 13.9 ($CHCH_3$); 32.1 (CHMe); 37.6 (CH_2Me); 52.7 (C(1)); 55.8 (C(6)); 59.1 (C(5)); 77.4 (C(2*); 78.6 (C_5H_5); 81.2 (C(3*)); 213.4 (CO); and (ii) [(1,2,3,4,5-η)-2-chloro-6-*exo*-(1ξ-methyl-2-oxobutyl)-2,4-cyclohexadien-1-yl](η^5-2,4-cyclopentadien-1-yl)ruthenium (**31**) as a mixture (1 : 1) of two diastereomers. ^{1}H NMR: δ 0.66, 0.72 (d, *J* 6.7 Hz, $CHCH_3$); 0.95, 0.96 (t, *J* 7.2 Hz, CH_2CH_3); 1.7–1.8 (m, CHMe); 2.5 (m, CH_2Me); 2.78, 2.83 (br t, *J* 6 Hz, H(6)); 3.1 (m, H(5)); 3.30, 3.40 (br d, *J* 6.3 Hz, H(1)); 4.43, 4.47 (td, *J* 5.3, 1 Hz, H(4)); 4.81 (s, C_5H_5); 6.08, 6.09 (d, *J* 6.1 Hz, H(3)). ^{13}C NMR: δ 7.5 (CH_2CH_3); 11.4, 11.7 ($CHCH_3$); 29.5, 29.7 (CHMe); 36.3, 36.8 (CH_2Me); 45.9, 46.1 (C(5)); 56.2, 56.5, C(6); 74.4, 74.6, C(4); 78.4, C_5H_5.

*Reaction of (η^6-chlorobenzene)(η^5-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphate(1 −) (**25**) with (1-cyclohexen-1-yloxy)trimethylsilane*

(1-Cyclohexen-1-yloxy)trimethylsilane (31 mg, 0.18 mmol) and a solution of tetrabutylammonium fluoride (0.17 mL, 0.17 mmol) in tetrahydrofuran were added to a solution of the complex **25** (70 mg, 0.17 mmol) in tetrahydrofuran (15 mL). The mixture was stirred for 30 min, solvent was removed *in vacuo*, and the residue was extracted with pentane to give a pale yellow semi-solid (51 mg, 82%; IR: ν_{max} 1700 (CO), 797 cm^{-1} (C–Cl)), containing a mixture (4 : 1) of (i) [(1,2,3,4,5-η)-5-chloro-6-*exo*-(1ξ-2-oxocyclohexyl)-2,4-cyclohexadien-1-yl](η^5-2,4-cyclopentadien-1-yl)ruthenium (**32**) as a mixture of two diastereomers. Major diastereomer: ^{1}H NMR: δ 0.8–2.8 (CH_2, CH); 3.33 (td, *J* 6.3, 1 Hz, H(6)); 3.64 (br t, *J* 6.7 Hz, H(1)); 4.37 (br dd, *J* 5.7, 4.8 Hz, H(2)); 4.83 (s, C_5H_5); 4.91 (dd, *J* 4.8, 1 Hz, H(4)); 5.55 (td, *J* 4.7, 1.1 Hz, H(3)). ^{13}C NMR: δ 22.5 (CH_2); 27.5 (CH_2); 28.0 (CH_2); 32.4 ($CHCO$); 41.1 (CH_2CO); 49.9 (C(1)); 57.9 (C(6)); 60.6 (C(5)); 75.6 (C2*)); 77.0 (C(4*)); 78.0 (C(3*)); 78.5 (C_5H_5); 212.4 (CO). Minor diastereomer: ^{1}H NMR: δ 0.8–2.8 (CH_2, CH); 3.00 (t, *J* 6 Hz, H(6*)); 3.44 (td, *J* 6, 1 Hz, H(1*)); 4.24 (br dd, *J* 5.8, 4.6 Hz, H(2)); 4.83 (s, C_5H_5); 4.88 (dd, *J* 4.8, 1 Hz, H(4)); 5.56 (t, *J* 4.6 Hz, H(3)). ^{13}C NMR: δ 24.1 (CH_2); 27.9 (CH_2); 30.4 (CH_2); 31.6 ($CHCO$); 42.1 (CH_2CO); 49.6

(C(1)); 60.6 (C(5)); 61.3 (C(6)); 74.8 (C(2*)); 76.2 C(4*)); 77.8 (C_5H_5); 78.3 (C(3*)); 212.4 (CO); and (ii) [(1,2,3,4,5-η)-2-chloro-6-*exo*-(1ξ-2-oxocyclohexyl)-2,4-cyclohexadien-1-yl](η^5-2,4-cyclopentadien-1-yl)ruthenium (**33**) as a mixture of two diastereomers. ^{1}H NMR: δ 0.8–2.8 (CH_2, CH); 3.56 (br d, J 6.3 Hz, H(1)); 4.39, 4.44 (ddd, J 5.7, 4.9, 0.8 Hz, H(4)); 4.81 (s, C_5H_5); 6.04 (d, J 4.6 Hz, H(3)). ^{13}C NMR: δ 23.8 (CH_2); 27.2 (C(1)); 27.5 (CH_2); 28.0 (C(1)); 33.2, 33.8 (CHMe); 42.0, 42.2 (CH_2CO) 42.5, 42.7 (C(5)); 60.5, 60.7 (C(6)); 77.3 (C(4)); 78.7 (C_5H_5); 80.9 (C(3)).

*Reaction of (η^6-chlorobenzene)(η^5-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphate(1 −) (**25**) with ethyl trimethylsilylacetate*

Ethyl trimethylsilylacetate (29 mg, 0.18 mmol) and a solution of tetrabutylammonium fluoride (0.17 mL, 0.17 mmol) in tetrahydrofuran were added dropwise to a solution of the complex **25** (70 mg, 0.17 mmol) in tetrahydrofuran (15 mL) under nitrogen. The mixture was stirred under nitrogen for 30 min, solvent was removed *in vacuo*, and the residue was extracted with pentane to give a mixture (3 : 1) (36 mg, 60%) of (i) [(1,2,3,4,5-η)-5-chloro-6-*exo*-(ethoxycarbonylmethyl)-2,4-cyclohexadien-1-yl](η^5-2,4-cyclopentadien-1-yl)ruthenium (**34**), and (ii) [(1,2,3,4,5-η)-2-chloro-6-*exo*-(ethoxycarbonylmethyl)-2,4-cyclohexadien-1-yl](η^5-2,4-cyclopentadien-1-yl)ruthenium (**35**). IR: ν_{max} 1725 (CO), 798 cm^{-1} (C–Cl). Isomer **34**: ^{1}H NMR: δ 1.22 (t, J 7.1 Hz, CH_2CH_3); 1.51 (dd, J 14.4, 8.5 Hz, CH_AH_BCO); 1.90 (dd, J 14.3, 4.5 Hz, CH_AH_BCO); 2.86 (m, H(6)); 3.36 (m, H(1)); 4.05 (q, J 7.1 Hz, CH_2Me); 4.37 (dd, J 5.7, 4.7 Hz, H(2)); 4.8 (br, H(4)); 4.84 (s, C_5H_5); 5.61 (t, J 4.7 Hz, H(3)). ^{13}C NMR: δ 14.3 (CH_2CH_3); 33.7 (C(1)); 43.2 (CH_2C=O); 47.6 (C(6)); 60.1 (CH_2Me); 60.2 (C(5)); 75.3 (C(2*)); 76.2 (C(4*)); 78.2 (C(3*)); 78.4 (C_5H_5); 171.1 (C=O). Isomer **35**: ^{1}H NMR: δ 1.21 (t, J 7.1 Hz, CH_2CH_3); 1.53 (dd, J 14.3, 7 Hz, CH_AH_BCO); 1.59 (dd, J 14.3, 6.8 Hz, CH_AH_BCO); 2.90 (m, H(6)); 3.36 (d, J 5.5 Hz, H(1)); 3.40 (m, H(5)); 4.03 (q, J 7.0 Hz, CH_2Me); 4.45 (td, J 5.3, 0.9 Hz, H(4)); 4.82 (s, C_5H_5); 6.10 (dd, J 4.4, 0.4 Hz, H(3)). ^{13}C NMR: δ 14.2 (Me); 27.7 (C(1*)); 31.4 (C(5*)); 39.6 (C(6)); 46.6 (CH_2CO); 60.0 (CH_2Me); 74.6 (C(4)); 77.3 (C(3)); 78.2 (C_5H_5); 99.1 (C(2)); 171.1 (CO).

*(η^5-2,4-Cyclopentadien-1-yl)[(1,2,3,4,5-η)-4,5-dichloro-6-*exo*-(1ξ-methyl-2-oxobutyl)-2,4-cyclohexadien-1-yl]ruthenium (**36**) and regioisomer **37***

Trimethyl(2-penten-3-yloxy)silane (27 mg, 0.17 mmol) and a solution of tetrabutylammonium fluoride (0.15 mL, 0.15 mmol) in tetrahydrofuran were added successively via syringe to a solution of the complex **26** (70 mg, 0.15 mmol) in tetrahydrofuran (10 mL) under nitrogen. The solution was stirred for 20 min, solvent was removed *in vacuo*, and the residue extracted with pentane to give a mixture (4 : 1) (46 mg, 75%) of (i) (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η)-4,5-dichloro-6-*exo*-(1ξ-methyl-2-oxobutyl)-2,4-cyclohexadien-1-yl]ruthenium (**36**) containing a mixture (1.7 : 1.0) of two diastereomers, and (ii) (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η)-2,3-dichloro-6-*exo*-(1ξ-methyl-2-oxobutyl)-2,4-cyclohexadien-1-yl]-ruthenium (**37**) as a yellow oil. IR: ν_{max} 1710 (C=O), 803 cm^{-1} (C–Cl). Isomer **36**, major diastereomer: ^{1}H NMR: δ 0.67 (d, J 6.7 Hz, $CHCH_3$); 1.00 (t, J 7.2 Hz, CH_2CH_3); 1.90 (dq, J 8.5, 6.9 Hz, CHMe); 2.31 (dq, J 18, 7.2 Hz, CH_AH_BMe); 2.44 (dq, J 18, 7.2 Hz, CH_AH_BMe); 3.20 (m, H(1,6); 4.45 (dd, J 6.5, 4.5 Hz, H(2)); 4.87 (s, C_5H_5); 6.07 (d, J 4.5 Hz, H(3)). ^{13}C NMR: δ 7.8 (CH_2CH_3); 11.5

($CHCH_3$); 31.7 ($CHMe$); 37.2 (CH_2Me); 53.7 (C(1*)); 56.0 (C(6*)), 59.0 (C(5)); 74.3 (C(2)); 79.8 (C(3)); 81.0 (C_5H_5); 98.1 (C(4)); 213.6 (CO). Minor diastereomer: ^{1}H NMR: δ 0.89 (d, J 7.1 Hz, $CHCH_3$); 0.97 (t, J 7.3 Hz, CH_2CH_3); 2.01 (dq, J 8.6, 7.1 Hz, $CHMe$); 2.28 (q, J 7.2 Hz, CH_2CH_3); 3.20 (m, H(1)); 3.30 (dd, J 8.6, 6.3 Hz, H(6)); 4.37 (dd, J 5.8, 4.6 Hz, H(2)); 4.87 (s, C_5H_5); 6.02 (dd, J 4.5, 0.9 Hz, H(3)). ^{13}C NMR: δ 7.55 (CH_2CH_3); 13.7 ($CHCH_3$); 32.3 ($CHMe$); 36.3 (CH_2Me); 54.85 (C(1*)); 54.9 (C(6*)); 57.3 (C(5)); 74.4 (C(2)); 80.1 (C(3)); 81.0 (C_5H_5); 98.1 (C(4)); 213.6 (CO). Isomers **37**: ^{1}H NMR: δ 0.66 (d, J 6.8 and 0.73, d, J 7.0 Hz, $CHCH_3$); 0.95, 0.99 (t, J 7.3 Hz, CH_2CH_3); 2.5 (m, CH_2CH_3); 2.79, 2.83 (td, J 6.1, 1.3 Hz, H(5)); 3.23 (m, H(6)); 3.34, 3.42 (dd, J 6.1, 1.3 Hz, H(1)); 4.85 (s, C_5H_5); 4.98, 5.02 (dd, J 6.0, 0.6 Hz, H(4)). ^{13}C NMR: δ 11.8 ($CHCH_3$); 37.5, 36.8 (CH_2Me); 46.1, 46.0 (C(5)); 56.5, 56.7 (C(6)); 81.0 (C_5H_5). MS: m/z 397 (0.2%, $M^+ - H$), 313 (100, $M - C_5H_{10}O$), 167 (30, C_5H_5Ru).

*(η^5-2,4-Cyclopentadien-1-yl)[(1,2,3,4,5-η)-4,5-dichloro-6-*exo*-(1ξ-2-oxocyclohexyl)-2,4-cyclohexadien-1-yl]ruthenium (**38**) and regioisomer **39***

(1-Cyclohexen-1-yloxy)trimethylsilane (29 mg, 0.17 mmol) and a solution of tetrabutylammonium fluoride (0.15 mL, 0.15 mmol) in tetrahydrofuran were added successively via syringe to a solution of the complex **26** (70 mg, 0.15 mmol) in tetrahydrofuran (6 mL) under nitrogen. The solution was stirred for 20 min, solvent was removed under reduced pressure, and the resulting oil extracted with pentane to give a mixture of (3 : 1) (57 mg, 90%) of (i) (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η)-4,5-dichloro-6-*exo*-(1ξ-2-oxocyclohexyl)-2,4-cyclohexadien-1-yl]ruthenium (**38**) containing a mixture (1.3 : 1) of two diastereomers, and (ii) (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η)-2,3-dichloro-6-*exo*-(1ξ-2-oxocyclohexyl)-2,4-cyclohexadien-1-yl]ruthenium (**39**) as a pale yellow oil. IR: ν_{max} 1705 cm^{-1} (CO). Isomer **38**, major diastereomer: ^{1}H NMR: δ 0.8–2.8 (m, 9H, CH_2, CH); 3.43 (t, J 6.0 Hz, H(1); 3.43 (m, H(6)); 4.44 (dd, J 5.9, 4.6 Hz, H(2)); 4.88 (s, C_5H_5); 5.99 (dd, J 4.5, 0.7 Hz, H(3)). ^{13}C NMR: δ 23.4 (CH_2); 27.2 (CH_2); 28.1 (CH_2); 33.5 ($CHCO$); 41.6 (CH_2CO); 52.1 (C(1)); 56.4 (C(6)); 58.8 (C5)); 75.3 (C(2)); 79.7 (C(3)); 80.8 (C_5H_5); 98.6 (C(4)); 211.5 (CO). Minor diastereomer: ^{1}H NMR: δ 0.8–2.8 (9H, CH_2, CH); 3.43 (m, H(6)); 3.87 (t, J 6.0 Hz, H(1)); 4.29 (dd, J 6.5, 4.4 Hz, H(2); 4.87 (s, C_5H_5); 6.02 (dd, J 4.6, 0.6 Hz, H(3)). ^{13}C NMR: δ 24.1 (CH_2); 28.0 (CH_2); 31.8 (CH_2); 34.4 ($CHCO$); 42.2 (CH_2CO); 52.0 (C(1)); 55.3 (C(5)); 60.9 (C(6)); 73.9 (C(2)); 79.7 (C_5H_5); 80.0 (C(3)); 98.3 (C(4)); 211.5 (CO). Isomers **39**: ^{1}H NMR: δ 0.8–2.8 (CH_2, CH); 3.04 (td, J 6.1, 1.2 Hz, H(5)); 3.43 (m, H(6)); 3.62 (dd, J 6.1, 1.4 Hz, H(1)); 4.86 (s, C_5H_5); 4.92 (d, J 6.1 Hz, H(4)); 4.99 (d, J 5.9 Hz, H(4)). ^{13}C NMR: δ 24.1 (CH_2); 24.3 (CH_2); 26.1, 27.1 (C(1)); 28.1 (CH_2); 29.7 (CH_2); 30.9, 31.8 ($CHMe$); 42.3 (CH_2CO); 42.9, 43.1 (C(5)); 60.5, 60.8 (C(6)); 76.9, 77.3 (C(4)); 81.1 (C_5H_5). MS: m/z 409 (0.4%, $M^+ - H$), 313 (100, $M - C_6H_9O$), 167 (29, C_5H_5Ru).

*(η^5-2,4-Cyclopentadien-1-yl)[(1,2,3,4,5-η)-4,5-dichloro-6-*exo*-(ethoxycarbonylmethyl)-2,4-cyclohexadien-1-yl]ruthenium (**40**) and regioisomer **41***

Ethyl trimethylsilylacetate (22 mg, 0.14 mmol) and then a solution of tetrabutylammonium fluoride in tetrahydrofuran (0.05 ml, 0.05 mmol) were added to a solution of the complex **26** (22 mg, 0.048 mmol) in tetrahydrofuran (3 mL) under nitrogen. The solution was stirred for 25 min, solvent was removed under reduced

pressure, and the oil extracted with pentane to afford a mixture (ca. 5 : 1) (17 mg, 89%) of (i) (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η)-4,5-dichloro-6-*exo*-(ethoxycarbonylmethyl)-2,4-cyclohexadien-1-yl]ruthenium (**40**), and (ii) (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η)-2,3-dichloro-6-*exo*-(ethoxycarbonylmethyl)-2,4-cyclohexadien-1-yl]ruthenium (**41**) as a pale yellow oil. IR: ν_{max} 1727 (CO), 804 cm^{-1} (C–Cl). Isomer **40**: ^{1}H NMR: δ 1.20 (t, J 7.1 Hz, CH_2CH_3); 1.52 (dd, J 14.5, 9.4 Hz, CH_AH_BCO); 1.91 (dd, J 14.5, 4.8 Hz, CH_AH_BCO); 3.32 (br t, J 6.1 Hz, H(1)); 3.49 (ddd, J 9.4, 6.1, 4.8 Hz, H(6)); 4.05 (q, J 7.1 Hz, CH_2Me); 4.42 (br t, J 5.2 Hz, H(2)); 4.88 (s, C_5H_5); 6.08 (d, J 4.5 Hz, H(3)). ^{13}C NMR: δ 14.2 (CH_2CH_3); 33.8 (C(1)); 42.5 (CH_2CO); 49.8 (C(6)); 58.5 (C(5)); 60.3 (CH_2Me); 75.6 (C(2)); 79.9 (C(3)); 80.8 (C_5H_5); 97.6 (C(4)); 170.8 (CO). Isomer **41**: ^{1}H NMR: δ 1.00 (t, J 7 Hz, CH_2CH_3); 1.56 (d, J 7 Hz, CH_2CO_2); 2.85 (m, H(1)); 2.90 (t, J 7 Hz, H(5)); 3.43 (m, H(6)); 4.86 (s, C_5H_5); 5.00 (br d, J 7 Hz, H(4)); CH_2CH_3 could not be assigned. ^{13}C NMR: δ 14.3 (CH_2CH_3); 28.8 (C(1)); 39.9 (C(6)); 46.8 (CH_2CO); 60.2 (CH_2Me); 75.2 (C(4)); 79.7 (C_5H_5); C(2), C(3) and C(5) could not be assigned.

*(η^5-2,4-Cyclopentadien-1-yl)[(1,2,3,4,5-η)-2,5-dichloro-6-*exo*-(1ξ-methyl-2-oxobutyl)-2,4-cyclohexadien-1-yl]ruthenium] (**42**)*

Trimethyl(2-penten-3-yloxy)silane (27 mg, 0.17 mmol) and a solution of tetrabutylammonium fluoride in tetrahydrofuran (0.15 mL, 0.15 mmol) were added successively via syringe to a solution of the complex **27** (70 mg, 0.15 mmol) in tetrahydrofuran (10 mL) under nitrogen. The mixture was stirred for 20 min, solvent was removed under reduced pressure and the residue was extracted with pentane to give (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η)-2,5-dichloro-6-*exo*-(1ξ-methyl-2-oxobutyl)-2,4-cyclohexadien-1-yl]ruthenium (**42**) (34 mg, 56%) as a yellow oil containing a mixture (1.8 : 1.0) of two diastereomers. IR: ν_{max} 1710 (CO), 803 cm^{-1} (C–Cl). Major diastereomer. ^{1}H NMR: δ 0.76 (d, J 6.9 Hz, $CHCH_3$); 0.98 (t, J 7.1 Hz, CH_2CH_3); 1.92 (dq, J 8.6, 6.9 Hz, $CHMe$); 2.33 (dq, J 18.2, 7.1 Hz, CH_AH_BMe); 2.43 (dq, J 18.2, 7.2 Hz, CH_AH_BMe); 3.21 (dd, J 8.6, 6.7 Hz, H(6)); 3.76 (dd, J 6.7, 1.6 Hz, H(1)); 4.90 (s, C_5H_5); 4.92 (dd, J 4.9, 1.6 Hz, H(4)); 5.97 (dd, J 4.8, 1.6 Hz, H(3)). ^{13}C NMR: δ 7.7 (CH_2CH_3); 11.9 ($CHCH_3$); 33.5 ($CHMe$); 39.5 (CH_2Me); 54.3 (C(1*)); 55.2 (C(6*)); 59.8 (C(5)); 74.7 (C(4)); 79.6 (C(3)); 80.9 (C_5H_5); 97.8 (C(2)); 213.4 (CO). Minor diastereomer: ^{1}H NMR: δ 0.9 (d, J 7.0 Hz, $CHCH_3$); 1.00 (t, J 6.8 Hz, CH_2CH_3); 2.03 (dq, J 9.0, 7.0 Hz, $CHMe$); 2.32 (q, J 7.2 Hz, CH_2Me); 3.21 (br dd, J 9.0, 6.5 Hz, H(6)); 3.66 (br d, J 6.5 Hz, H(1)); 4.89 (s, C_5H_5); 4.92 (dd, J 4.9, 1.6 Hz, H(4)); 5.95 (dd, J 4.8, 1.6 Hz, H(3)). ^{13}C NMR: δ 7.6 (CH_2CH_3); 13.8 ($CHCH_3$); 33.9 ($CHMe$); 36.9 (CH_2Me); 55.2 (C(1*)); 55.5 (C(6*)); 59.7 (C(5)); 74.8 (C(4)); 79.4 (C(3)); 8.10 (C_5H_5); 97.8 (C(2)); 213.2 (CO).

*(η^5-2,4-Cyclopentadien-1-yl)[(1,2,3,4,5-η)-2,5-dichloro-6-*exo*-(1ξ-2-oxocyclohexyl)-2,4-cyclohexadien-1-yl]ruthenium (**43**)*

(1-Cyclohexen-1-yloxy)trimethylsilane (66 mg, 0.39 mmol) and a solution of tetrabutylammonium fluoride in tetrahydrofuran (0.13 mL, 0.13 mmol) were introduced successively via a syringe to a solution of the complex **27** (60 mg, 0.13 mmol) in tetrahydrofuran (10 mL) and the solution was stirred for 30 min. Solvent was removed *in vacuo* and the oily residue was extracted with pentane to give (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η-2,5-dichloro-6-*exo*-(1ξ-2-oxocyclohexyl)-2,4-cyclo-

hexadien-1-yl]ruthenium (**43**) (47 mg, 87%) as a pale yellow oil, consisting of a mixture (1.6 : 1.5) of two diastereomers. IR: ν_{max} 1701 (CO), 800 cm^{-1} (C–Cl). Major diastereomer: ^1H NMR: δ 1.2–2.5 (m, 9H, CH_2, CH); 3.37 (ddd, *J* 9.4, 6.7, 1.6 Hz, H(6)); 3.77 (dd, *J* 6.8, 1.3 Hz, H(1)); 4.90 (s, C_5H_5); 4.92 (dd, *J* 4.8, 1.2 Hz, H(4)); 5.90 (dd, *J* 4.8, 1.2 Hz, H(3)). ^{13}C NMR: δ 23.2 (CH_2); 28.0 (CH_2); 29.7 (CH_2); 34.6 (*C*HCO); 41.4 (*C*H_2CO); 52.4 (C(1)); 57.2 (C(6)); 59.4 (C(5)); 75.3 (C(4)); 79.0 (C(3)); 80.8 (C_5H_5); 98.5 (C(2)); 211.6 (CO). Minor diastereomer: ^1H NMR: δ 1.2–2.5 (m, CH_2, CH); 3.78 (ddd, *J* 9.8, 6.6, 1.3 Hz, H(6)); 3.97 (dd, *J* 6.7, 1.5 Hz, H(1)); 4.89 (s, C_5H_5); 4.92 (dd, *J* 4.8, 1.2 Hz, H(4)); 5.92 (dd, *J* 4.7, 1.6 Hz, H(3)). ^{13}C NMR: δ 24.5 (CH_2); 27.4 (CH_2); 30.5 (CH_2); 36.1 (*C*HCO); 42.3 (*C*H_2CO); 52.3 (C(1)); 59.4 (C(5)); 60.6 (C(6)); 74.6 (C(4)); 79.5 (C(3)); 81.1 (C_5H_5); 98.5 (C(2)); 211.0 (CO).

*(η^5-2,4-Cyclopentadien-1-yl)[(1,2,3,4,5-η)-2,5-dichloro-6-*exo*-(ethoxycarbonylmethyl)-2,4-cyclohexadien-1-yl]ruthenium) (**44**)*

Ethyl trimethylsilylacetate (27 mg, 0.17 mmol) was added via a syringe to a solution of the complex **27** (70 mg, 0.15 mmol) (purified immediately before use by rapid filtration through alumina in CH_2Cl_2) in tetrahydrofuran (13 mL) under nitrogen at room temperature. Tetrabutylammonium fluoride in tetrahydrofuran (0.15 mL, 0.15 mmol) was added dropwise and the mixture was stirred for 20 min. Solvent was removed *in vacuo* and the residue extracted into pentane to give (η^5-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η)-2,5-dichloro-6-*exo*-(ethoxycarbonylmethyl)2,4-cyclohexadien-1-yl]ruthenium (**44**) (38 mg, 62%) as a yellow oil (Found: C, 45.2; H, 4.3. $C_{15}H_{16}Cl_2O_2Ru$ calcd.: C, 45.0; H, 4.0%). IR: ν_{max} 1725 (CO), 799 cm^{-1} (C–Cl). ^1H NMR: δ 1.24 (t, *J* 7.1 Hz, CH_2CH_3); 1.59 (dd, *J* 14.5, 8.9 Hz, CH_AH_BCO); 1.90 (dd, *J* 14.5, 5.1 Hz, CH_AH_BCO); 3.44 (ddd, *J* 8.9, 6.6, 5.1, 1.6 Hz, H(6)); 3.83 (dd, *J* 6.6, 1.6 Hz, H(1)); 4.05 (dq, *J* 16.1, 7.1 Hz, CH_AH_BMe); 4.09 (dq, *J* 16.1, 7.1 Hz, CH_AH_BMe); 4.86 (dd, *J* 4.8, 1.6 Hz, H(4)); 4.90 (s, C_5H_5); 5.98 (dd, *J* 4.8, 1.6 Hz, H(3)). ^{13}C NMR: δ 14.2 (CH_2CH_3); 35.6 (C(1)); 42.8 (*C*H_2CO); 50.2 (C(6)); 58.9 (C(5)); 60.4 (*C*H_2Me); 74.5 (C(4)); 79.4 (C(3)); 80.7 (C_5H_5); 97.8 (C(2)); 170.7 (CO). MS: *m/z* 399 (1%, $M^+ - H$), 313 (100, $M^+ - C_4H_7O_2$), 167 (33, C_5H_5Ru).

*(η^5-2,4-Cyclopentadien-1-yl)[(1,2,3,4,5-η)-5-chloro-2-methoxy-6-*exo*-(ethoxycarbonylmethyl)-2,4-cyclohexadien-1-yl]ruthenium (**45**) and regioisomer **46***

Ethyl trimethylsilylacetate (28 mg, 0.18 mmol) was added via a syringe to a solution of the complex **28** (84 mg, 0.18 mmol) (purified immediately prior to use by chromatography on alumina in CH_2Cl_2) in tetrahydrofuran (13 mL) under nitrogen at room temperature. A solution of tetrabutylammonium fluoride in tetrabutylammonium fluoride in tetrahydrofuran (0.18 mL, 0.18 mmol) was added dropwise with stirring. After 30 min the solvent was removed and the brown oil was extracted into pentane to give an inseparable mixture (4.5 : 1) (32 mg, 51%) of [(1,2,3,4,5-η)-5-chloro-2-methoxy-6-*exo*-(ethoxycarbonylmethyl)-2,4-cyclohexadien-1-yl](η^5-2,4-cyclopentadien-1-yl)ruthenium (**45**) and [(1,2,3,4,5-η)-2-chloro-5-methoxy-6-*exo*-(2,4-cyclohexadien-1-yl)](η^5-2,4-cyclopentadien-1-yl)ruthenium (**46**) as a yellow oil (Found: C, 48.3; H, 5.0. $C_{16}H_{19}ClO_3Ru$ calcd.: C, 48.5; H, 4.8%). IR: ν_{max} 1731 (CO), 809 cm^{-1} (C–Cl). Major isomer **45**: ^1H NMR: δ 1.22 (t, *J* 7.14 Hz, CH_2CH_3); 1.56 (dd, *J* 14.3, 9.0 Hz, $CH_AH_BCO_2$); 1.93 (dd, *J* 14.3, 4.9 Hz,

$CH_AH_BCO_2$); 3.29 (s, OMe); 3.38 (br s, H(6)); 3.66 (dd, *J* 6.68, 1.88 Hz, H(1)); 4.06 (q, *J* 7.1 Hz, CH_2CH_3); 4.77 (dd, *J* 5.00, 1.43 Hz, H(4)); 4.81 (s, C_5H_5); 5.68 (dd, *J* 5.00, 1.8 Hz, H(3)). ^{13}C NMR: δ 13.9 (CH_2CH_3); 24.4 (C(1)); 42.8 (CH_2CO_2); 48.6 (C(6)); 55.0 (OMe); 58.3 (C(5)); 60.0 (CH_2CH_3); 66.6 (C(4)); 7.17 (C(3)); 77.2 (C_5H_5); 127.8 (C(2)); 170.45 (CO). Minor isomer **46**: ^{1}H NMR: δ 1.25 (t, CH_2CH_3); 1.62 (m, $CH_AH_BCO_2$); 1.80 (dd, *J* 14.04, 5.9 Hz); $CH_AH_BCO_2$); 3.24 (s, OMe); 3.48 (m, H(6)); 3.95 (q, CH_2CH_3); 4.51 (dd, *J* 6.92, 1.2 Hz, H(1)); 4.86 (s, C_5H_5); 5.08 (dd, *J* 5.0, 1.2 Hz, H(3)); 5.76 (dd, *J* 5.0, 1.3 Hz, H(4)); 4.86 (s, C_5H_5). ^{13}C NMR: δ 14.2 (CH_2CH_3); 34.4 (C(1)); 43.9 (CH_2CO_2); 55.3 (C(6)); 56.0 (OMe); 63.4 (OCH_2CH_3); 67.2 (C(3)); 67.45 (C(2)); 74.1 (C(4)); 77.9 (C_5H_5); 128.1 (C(5)); 171 (CO).

*Reaction of (η⁵-2,4-cyclopentadien-1-yl)[(η⁶-(1,2-dichloro-3-methoxybenzene)]ruthenium(1 +) hexafluorophosphate(1 −) (**29**) with ethyl trimethylsilylacetate*

The cationic complex **29** (220 mg, 0.45 mmol) was dissolved in tetrahydrofuran (30 mL) under nitrogen at room temperature. A solution of tetrabutylammonium fluoride in tetrahydrofuran (0.5 mL, 0.5 mmol) was added dropwise with stirring. After 25 min the solvent was removed and the residue triturated with pentane (3 × 10 mL). Removal of the pentane gave a yellow oil (72 mg, 37%) which was an inseparable mixture (1.0 : 1.0 : 0.6) of (η⁵-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η)-4,5-dichloro-3-methoxy-6-*exo*-(ethoxycarbonylmethyl)-2,4-cyclohexadien-1-yl]ruthenium
(**47**) (η⁵-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η)-2,3-dichloro-4-methoxy-6-*exo*-(ethoxycarbonylmethyl)-2,4-cyclohexadien-1-yl]ruthenium (**48**), and (η⁵-2,4-cyclopentadien-1-yl)[(1,2,3,4,5-η)-3,4-dichloro-5-methoxy-6-*exo*-(ethoxycarbonylmethyl)-2,4-cyclohexadien-1-yl]ruthenium (**49**). IR: ν_{max} 1728 cm^{-1} (CO) (Found: C, 45.4; H, 4.15, Cl, 16.4. $C_{16}H_{18}Cl_2O_3Ru$ calcd.: C, 44.7; H, 4.2; Cl, 16.5%. Isomer **47**. ^{1}H NMR: δ 1.20 (t, *J* 7.1 Hz, CH_3); 1.91 (dd, *J* 14.6, 4.7 Hz, $CH_AH_BCO_2$); 3.12 (t, *J* 6.2 Hz, H(1)); 3.19 (dd, *J* 6.2, 0.7 Hz, H(2)); 3.77 (s, OMe); 4.90 (s, C_5H_5); CH_2CH_3, $CH_AH_BCO_2$ and H(6) could not be assigned. Isomer **48**. ^{1}H NMR: δ 1.20 (t, *J* 7.1 Hz, CH_3); 3.30 (dd, *J* 5.2, 0.9 Hz, H(5)); 3.34 (s, OMe); 4.02 (q, *J* 7.1 Hz, CH_2CH_3); 4.83 (s, C_5H_5); H(1) and H(6) could not be assigned. Isomer **49**. ^{1}H NMR: δ 1.22 (t, *J* 7.1 Hz, CH_3); 3.09 (t, *J* 6.2 Hz, H(1)); 3.54 (s, OMe); 3.69 (q, *J* 7.0 Hz, CH_2CH_3); 4.90 (s, C_5H_5); $CH_AH_BCO_2$, H(2), and H(6) could not be assigned unequivocally: a series of overlapping multiplets occurred between 1.45–1.60. Isomer **47**: ^{13}C NMR: δ 14.1 (CH_3); 27.8 (C(1)); 42.2 (CH_2CO_2); 50.5 (C(6)); 55.9 (C(5)); 58.95 (OMe); 60.25 (OCH_2); 61.8 (C(2)); 79.5 (C_5H_5); 85.0 (C(4)); 128.0 (C(3)); 170.5 (CO). Isomer **48**. ^{13}C NMR: δ 17.5 (CH_3); 29.5 (C(1)); C(5) not resolved; 40.8 (C(6)); 46.75 (CH_2CO_2); 56.5 (OMe); 60.1 (OCH_2); 81.1 (C_5H_5); 96.9 (C(2)); C(3) not resolved; 124.8 (C(4)); 170.7 (CO). Isomer **49**. ^{13}C NMR: δ 14.2 (CH_3); 30.8 (C(1)); 41.4 (C(6)); 43.65 (CH_2CO_2); 58.2 (OMe); 60.3 (OCH_2); 74.96 (C(2)); 79.7 (C_5H_5); 92.2 (C(4)); 99.1 (C(3)); 124.8 (C(5)); 170.5 (CO).

*Ethyl (2-chlorobenzene)acetate (**50**)*

This compound, b.p. 118°C, 0.3 mmHg (lit. [2] 143°C, 6 mmHg) was synthesized from 2-chlorobenzoic acid via the acid chloride (71%, b.p. 64°C, 4 mmHg), the diazoketone (100%), and a Wolff rearrangement as described below for the dichloro analog **53**. IR: ν_{max} 1736 cm^{-1} (CO). ^{1}H NMR: δ 1.24 (t, *J* 7.1 Hz, CH_2CH_3); 3.65 (s, CH_2CO_2); 4.20 (q, *J* 7.1 Hz, CH_2CH_3); 7.19 (m, H(4)); 7.20 (m,

H(5)); 7.26 (m, H(6)); 7.35 (m, H(3)). ^{13}C NMR: δ 14.2 (CH_3); 38.9 (CH_2CO_2); 60.6 (CH_2CH_3); 126.8 (C(5)); 128.4 (C(4)); 129.3 (C(3)); 131.25 (C(6)); 132.2 (C(1)); 135.7 (C(2)); 170.3 (CO). MS: *m/z* 198/200 (6/2, M^+), 163 (55), 139/141 (11/4), 125/127 (100/34), 89 (10), 63 (5).

*Ethyl (3-chlorobenzene)acetate (**51**)*

This compound, b.p. 105 °C, 0.33 mmHg, was synthesized from 3-chlorobenzoic acid via the acid chloride (70%, b.p. 80 °C, 23 mmHg), the diazoketone (93%), and a Wolff rearrangement as described below for the dichloro analogue **53**. IR: ν_{max} 1736 cm^{-1} (CO). ^{1}H NMR: δ 1.27 (t, *J* 7.1, CH_2CH_3); 3.58 (s, CH_2CO_2); 4.19 (q, *J* 7.1, CH_2CH_3); 7.14 (m, H(6)); 7.22 (m, H(4)); 7.23 (m, H(5)); 7.27 (br s, H(2)). ^{13}C NMR: δ 14.1 (CH_3): 41.2 (CH_2CO_2); 50.6 (CH_2CH_3); 127.2 (C(4)); 127.4 (C(6)); 129.3 (C(2)); 129.7 (C(5)); 134.5 (C(3)); 136.6 (C(1)); 171.4 (CO). MS: *m/z* 198/200 (18/6, M^+), 170/172 (9/3), 165 (20), 139/141 (42/24), 125/127 (100/33), 111/113 (18/10), 92 (12), 89 (16), 77 (10), 75 (8), 63 (7).

*Ethyl (2,3-dichlorobenzene)acetate (**52**)*

Reaction of 2,3-dichlorobenzoic acid with thionyl chloride gave the acid chloride (IR: ν_{max} 1772 cm^{-1} (CO), b.p. 100 °C, 1.5 mmHg) which was treated with diazomethane to afford the diazoketone as a yellow solid (100%, IR: ν_{max} 2108 (N_2), 1623 cm^{-1} (CO)). Wolff rearrangement as for the dichloro isomer **53** gave ethyl (2,3-dichlorobenzene)acetate (**52**) (49%) as a pale yellow oil, b.p. 188 °C, 2 mmHg (Found: C, 51.1; H, 4.3. $C_{10}H_{10}Cl_2O_2$ calcd.: C, 5.15; H, 4.3%). IR: ν_{max} 1722 cm^{-1} (CO). ^{1}H NMR: δ 1.25 (t, *J* 7.1 Hz, CH_3); 3.78 (s, CH_2CO_2); 4.19 (q, *J* 7.1 Hz, CH_2CH_3); 7.16 (t, *J* 7.6 Hz, H(5)); 7.19 (dd, *J* 7.6, 2.1 Hz, H(6)); 7.39 (dd, *J* 7.5, 2.1 Hz, H(4)). ^{13}C NMR: δ 14.1 (CH_3); 40.0 (CH_2CO_2); 61.1 (CH_2CH_3); 127.2 (C(5)); 129.4 (C(4,6)); 129.6 (C(6,4)); 133.1 (C(1,3)); 133.2 (C(3,1)); 134.8 (C(2)); 170.1 (CO). MS: *m/z* 232/234/236 (5/3/< 1, M^+), 197/199 (42/14), 169/171 (14/5), 159/161/163 (100/67/12), 123/125 (15/10), 89 (17), 73 (5), 63 (10).

*Ethyl (2,5-dichlorobenzene)acetate (**53**)*

Treatment of 2,5-dichlorobenzoic acid (2.12 g, 11 mmol) with thionyl chloride (4.1 g, 34 mmol) gave 2,5-dichlorobenzoyl chloride (1.57 g, 69%) as a colourless oil, b.p. 81 °C, 2.2 mmHg. IR: ν_{max} 1771 cm^{-1} (COCl). A cold solution of diazomethane (ca. 3 molar equiv.) in ether was added to the acid chloride (1.0 g, 4.7 mmol) dissolved in ether (100 mL) and the solution was stood at room temperature for 2 h. Workup gave the diazoketone (1.01 g, 100%) as a yellow solid. IR: ν_{max} 2108 (N_2), 1622 cm^{-1} (CO). ^{1}H NMR: δ 5.86 (s, CHN_2); 7.38 (br s, H(3,4)); 7.58 (br s, H(6)). The crude diazoketone (1.01 g, 4.7 mmol) was dissolved in ethanol (60 mL) and a slurry of silver(I) oxide (0.82 g, 5.9 mmol) in ethanol was added in portions over 2 h; nitrogen evolution occurred. The mixture was heated under reflux for 30 min, treated with charcoal, and the solvent removed to give ethyl (2,5-dichlorobenzene)acetate (**53**) (0.78 g, 72%) as a pale yellow oil, b.p. 186 °C, 2.5 mmHg (Found: C, 51.2; H, 4.0. $C_{10}H_8Cl_2O_2$ calcd.: C, 51.5; H, 4.3%). IR: ν_{max} 1737 cm^{-1} (CO). ^{1}H NMR: δ 1.25 (t, *J* 7.2 Hz, CH_2CH_3); 3.72 (s, CH_2CO_2); 4.18 (q, *J* 7.2 Hz, CH_2CH_3); 7.2 (dd, *J* 8.5, 2.5 Hz, H(4)); 7.28 (d, *J* 2.5 Hz, H(6)); 7.31 (d, *J* 8.5 Hz, H(3)). ^{13}C NMR: δ 12.8 (CH_3); 38.0 (CH_2CO_2); 60.6 (CH_2CH_3); 129.0 (C(4)); 130.7 (C(3)); 131.8 (C(6)); 133.0 (C(5)); 133.5 (C(2)); 134.8 (C(1)); 170.0 (CO). MS:

m/z 232/234/236 (12/8/2, M^+), 197/199 (48/14), 169/171 (16/5), 159/161/163 (100/67/12), 123/125 (15/11), 89 (16), 73 (6), 63 (12).

*(η^5-2,4-Cyclopentadien-1-yl)[η^6-(ethyl (2-chlorobenzene)acetate)]ruthenium(1 +) hexafluorophosphate(1 −) (**54**)*

Reaction of $(MeCN)_3CpRu^+PF_6^-$ (**5**) (0.45 g, 1.0 mmol) with ethyl (2-chlorobenzene)acetate (0.18 g, 0.9 mmol) in 1,2-dichloroethane (10 mL) followed by chromatography as before afforded (η^5-2,4-cyclopentadien-1-yl)[η^6-(ethyl (2-chlorobenzene)acetate)]ruthenium(1 +) hexafluorophosphate(1 −) (**54**) (0.3 g, 71%) as an off-white powder, m.p. 126–127 °C (CH_2Cl_2–hexanes) (Found: C, 35.1; H, 3.1; Cl, 6.5. $C_{15}H_{16}ClF_6O_2PRu$ calcd.: C, 35.3; H, 3.2; Cl, 6.95%). IR: ν_{max} 1744 (CO), 839 cm^{-1} (P–F). ^1H NMR (CD_3COCD_3): δ 1.25 (t, *J* 7.1 Hz, CH_3); 3.94 (d, *J* 17.2 Hz, $CH_AH_BCO_2$); 4.09 (d, *J* 17.2 Hz, $CH_AH_BCO_2$); 4.18 (q, *J* 7.1 Hz, CH_2CH_3); 5.62 (s, C_5H_5); 6.37 (dd, J_{obs} 5.75 Hz, H(4)); 6.47 (d, J_{obs} 5.8 Hz, H(5)); 6.59 (d, *J* 5.7 Hz, H(6)); 6.84 (d, *J* 6.0 Hz, H(3)). ^{13}C NMR (CD_3COCD_3): δ 14.35 (CH_3); 38.2 (CH_2CO_2); 61.8 (CH_2CH_3); 83.45 (C_5H_5); 86.39 (C(4,5)); 86.43 (C(5,4)); 88.90 (C(3,6)); 88.95 (C(6,3)); 98.9 (C(1)); 107.8 (C(2)); 178.5 (CO).

*(η^5-2,4-Cyclopentadien-1-yl)[η^6-(ethyl (3-chlorobenzene)acetate)]ruthenium(1 +) hexafluorophosphate(1 −) (**55**)*

Reaction of $(MeCN)_3CpRu^+PF_6^-$ (**5**) (0.19 g, 0.43 mmol) with ethyl (3-chlorobenzene)acetate (60 mg, 0.3 mmol) in 1,2-dichloroethane (10 mL) followed by chromatography as before gave (η^5-2,4-cyclopentadien-1-yl)[η^6-ethyl (3-chlorobenzene)acetate)]ruthenium(1 +) hexafluorophosphate(1 −) (**55**) (73 mg, 47%) as a pale brown powder (Found: C, 34.9; H, 2.8; Cl, 6.4. $C_{15}H_{16}ClF_6O_2PRu$ calcd.: C, 35.3; H, 3.2; Cl, 6.95%). IR: ν_{max} 1732 (CO), 838 cm^{-1} (P–F). ^1H NMR (CD_3COCD_3): δ 1.25 (t, *J* 7.1 Hz, CH_3); 3.66 (s, CH_2CO_2); 4.20 (q, *J* 7.1 Hz, CH_2CH_3); 5.63 (s, C_5H_5); 64.1 (d, *J* 5.8 Hz, H(6)); 6.48 (t, *J* 5.9 Hz, H(5)); 6.79 (d, *J* 5.4 Hz, H(4)); 6.9 (s, H(2)). ^{13}C NMR (CD_3COCD_3): δ 14.4 (CH_3); 38.4 (CH_2CO_2); 61.7 (CH_2CH_3); 84.2 (C_5H_5); 86.0 (C(4)); 87.4 (C(6)); 87.5 (C(2)); 90.0 (C(5)); 99.5 (C(3)); 105.9 (C(1)); 169.9 (CO).

*(η^5-2,4-Cyclopentadien-1-yl)[η^6-(ethyl (2,3-dichlorobenzene)acetate)]ruthenium(1 +) hexafluorophosphate(1 −) (**56**)*

Reaction of $(MeCN)_3CpRu^+PF_6^-$ (**5**) (0.31 g, 0.72 mmol) with ethyl (2,3-dichlorobenzene)acetate (0.22 g, 0.94 mmol) in 1,2-dichloroethane (30 mL) followed by chromatography using dichloromethane and then dichloromethane–ethanol (5 : 1) gave (η^5-2,4-cyclopentadien-1-yl)[η^6-(ethyl (2,3-dichlorobenzene)acetate)]ruthenium (1 +) hexafluorophosphate(1 −) (**56**) (188 mg, 48%) as a brown solid, m.p. 300–303 °C (dec.) (Found: C, 33.75; H, 2.8. $C_{15}H_{15}Cl_2F_6O_2PRu$ calcd.: C, 33.1; H, 2.8%). IR: ν_{max} 1732 (CO), 838 (P–F), 737 cm^{-1} (C–Cl). ^1H NMR (CD_3COCD_3): δ 1.22 (t, *J* 7.2 Hz, CH_3); 4.03 (d, *J* 17.3 Hz, $CH_AH_BCO_2$); 4.17 (d, J_{obs} 16.0 Hz, $CH_AH_BCO_2$); 4.18 (q, *J* 7.2 Hz, CH_2CH_3); 5.72 (s, C_5H_5); 6.50 (t, *J* 5.8 Hz, H(5)); 6.62 (d, *J* 5.8 Hz, H(6)); 7.13 (d, *J* 5.8 Hz, H(4)). ^{13}C NMR (CD_3COCD_3): δ 14.3 (CH_3); 39.2 (CH_2CO_2); 62.25 (CH_2CH_3); 85.7 (C_5H_5); 86.1 (C(5)); 88.2 (C(4)); 88.6 (C(6)); 99.25 (C(3)); 106.8 (C(2)); 108.3 (C(1)); 168.9 (CO).

(η^5-2,4-Cyclopentadien-1-yl)[η^6-(ethyl (2,5-dichlorobenzene)acetate)]ruthenium(1 +) hexafluorophosphate(1 −) (57)

Tris(acetonitrile)(η^5-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphate(1 −) (134 mg, 0.31 mmol) and ethyl (2,5-dichlorobenzene)acetate (54 mg, 0.23 mmol) were heated under reflux in 1,2-dichloroethane (20 mL) for 16 h. Chromatography of the crude product on alumina in hexanes–dichloromethane (5 : 1, to remove neutral compounds) and then dichloromethane gave (η^5-2,4-cyclopentadien-1-yl)[η^6-(ethyl (2,5-dichlorobenzene)acetate)]ruthenium(1 +) hexafluorophosphate(1 −) (**57**) (28 mg, 22%). IR: ν_{max} 1732 (CO), 839 cm^{-1} (P–F). ^1H NMR (CD_3COCD_3): δ 1.24 (t, J 7.1 Hz, CH_2CH_3); 4.01 (d, J 17.4 Hz, $CH_AH_BCO_2$); 4.13 (d, $CH_AH_BCO_2$); 4.19 (q, J 7.1 Hz, CH_2CH_3); 5.72 (s, C_5H_5); 6.93 (dd, J 6.2, 1.4 Hz, H(4)); 6.97 (d, J 6.2 Hz, H(3)); 7.09 (d, J 1.4 Hz, H(6)). ^{13}C NMR (CD_3COCD_3): δ 14.3 (CH_3); 37.7 (CH_2CO_2); 62.0 (CH_2CH_3); 85.05 (C_5H_5); 87.6 (C(3,4); 87.7 (C(4,3)); 90.0 (C(6)); 98.2 (C(5)); 104.9 (C(2)); 106.6 (C(1)); 168.5 (CO).

*Treatment of **44** with DDQ*

DDQ (60 mg, 0.26 mmol) was added over 20 min to a solution of the adduct **44** (89 mg, 0.22 mmol) in acetonitrile (30 mL). The red solution was stirred at room temperature for 2 h, and a solution of ammonium(1 +) hexafluorophosphate(1 −) (877 mg, 0.47 mmol) in water (5 mL) was then added. After a further 15 min the solvents were removed under reduced pressure to give a brown solid which was extracted with dichloromethane (20 mL). The extract was washed with water (3 × 3 mL), dried, and the solvent removed to give a yellow oil which was chromatographed on alumina. Elution with dichloromethane-pentane (3 : 1) gave ethyl (2,5-dichlorobenzene)acetate (**53**) (8 mg, 15%), identical with an authentic sample. Elution with dichloromethane and then dichloromethane–ethanol (9 : 1) gave (η^5-2,4-cyclopentadien-1-yl)[μ^6-(ethyl (2,5-dichlorobenzene)acetate)]ruthenium(1 +) hexafluorophosphate(1 −) (**57**) (65 mg, 53%) as a pale brown solid, identical with an authentic sample.

*Treatment of **40**, **41** with DDQ*

DDQ (56 mg, 0.25 mmol) was added over 20 min to a solution of the adducts **40** and **41** (ca 5 : 1) (82 mg, 0.2 mmol) in acetonitrile (30 mL) under nitrogen at room temperature. Workup as above gave a green-brown oil which was chromatographed on alumina. Elution with dichloromethane–hexanes (7 : 3) gave a mixture (ca 3.8 : 1) (25 mg, 53%) of (i) ethyl (2,3-dichlorobenzene)acetate (**52**) identical with an authentic sample; and (ii) ethyl (3,4-dichlorobenzene)acetate (**58**) (Found: $M^{+\cdot}$ 232.0058. $C_{10}H_{10}{}^{35}Cl_2O_2$ calcd.: $M^{+\cdot}$ 232.0057). IR: ν_{max} 1737 (CO), 746 cm^{-1} (C–Cl). ^1H NMR: δ 1.26 (t, CH_2CH_3); 3.56 (s, CH_2CO); 4.16 (q, J 7.1 Hz, CH_2CH_3); 7.13 (dd, J 8.3, 2.0 Hz, H(6)); 7.19 (d, J 2.6 Hz, H(2)); 7.39 (d, J 8.2 Hz, H(5)). Elution with dichloromethane gave (η^5-2,4-cyclopentadien-1-yl)[η^6-(ethyl(2,3-dichlorobenzene)acetate)]ruthenium(1 +) hexafluorophosphate(1 −) (**56**) (19 mg, 17%), identical with an authentic sample.

*Treatment of **45**, **46** with DDQ*

DDQ (63 mg, 0.28 mmol) was added over 10 min to a solution of the adducts **45** and **46** (4.5 : 1) in acetonitrile (30 mL) under nitrogen at room temperature. The red

solution was stirred for 2 h and a solution of ammonium(1 +) hexafluorophosphate(1 −) (124 mg, 0.76 mmol) in water (5 mL) was then added. After a further 15 min, workup gave a brown oil which was chromatographed on alumina. Elution with dichloromethane and then dichloromethane–ethanol (9 : 1) gave a mixture (ca. 3.8 : 1) (44 mg, 40%) of (η^5-2,4-cyclopentadien-1-yl)[η^6-ethyl(2-chloro-5-methoxybenzene)acetate)]ruthenium(1 +) hexafluorophosphate(1 −) (**59**) and (η^5-2,4-cyclopentadien-1-yl)[η^6-(ethyl(5-chloro-2-methoxybenzene) acetate)]ruthenium(1 +) hexafluorophosphate(1 −) (**60**) as a yellow oil. IR: ν_{max} 1732 (CO), 838 cm^{-1} (P–F). Major isomer **59**: ^{1}H NMR (CD_3COCD_3): δ 1.23 (t, J 7.1 Hz, CH_3); 3.80 (s, OMe); 3.91 (d, J 17.3 Hz, $CH_AH_BCO_2$; 4.09 (d, J 17.3 Hz, $CH_AH_BCO_2$); 4.18 (q, J 7.1 Hz, CH_2CH_3); 5.64 (s, C_5H_5); 6.52 (dd, J 6.4, 1.9 Hz, H(4)); 6.69 (d, J 1.9 Hz, H(6)); 6.76 (d, J 6.4 Hz, H(3)). ^{13}C NMR: δ 14.35 (CH_3); 38.6 (CH_2CO_2); 58.3 (OMe); 62.1 (CH_2CH_3); 74.7 (C(4)); 77.2 (C(6)); 83.5 (C(3)); 97.3 (C(2)); 104.4 (C(1)); 134.1 (C(5)); 169.1 (CO). Minor isomer **60**: ^{1}H NMR (CD_3COCD_3): δ 1.21 (t, J 7.1 Hz, CH_3); 3.87 (s, CH_2CO_2); 3.91 (s, OMe); 4.16 (q, J 7.1 Hz, $CH_AH_BCO_2$); 4.17 (q, J 7.1 Hz, $CH_AH_BCO_2$); 5.63 (s, C_5H_5); 6.60 (d, J 6.5 Hz, H(3)); 6.71 (dd, J 6.5, 1.6 Hz, H(4)); 6.86 (d, J 1.6 Hz, H(6)). ^{13}C NMR: δ 14.35 (CH_3); 35.3 (CH_2CO_2); 58.6 (OMe); 61.9 (CH_2CH_3); 71.65 (C(3)); 83.5 (C_5H_5); 85.7 (C(4)); 89.2 (C(6)); 102.4 (C(1)); 122.2 (C(5)); 133.85 (C(2)); 169.4 (CO).

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