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Towards the synthesis of aminodibenzo[*b*,*e*][1,4]dioxin derivatives via cationic ruthenium complexes

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Abstract

Double nucleophilic aromatic substitution reactions between *N*-substituted (η^6-1,2-dichlorobenzene)RuCp$^+$ salts and substituted 1,2-benzenediols have been carried out under mild conditions to prepare *N*-substituted (η^6-dibenzo[*b*,*e*][1,4]dioxin)ruthenium(II) complexes. The dibenzodioxin ligands were subsequently liberated by photolysis, with radiation from a sunlamp or from a medium pressure Hg lamp (300 nm).

Keywords: Ruthenium; Dibenzodioxin ligands; Crystal structure; Aminoarenes

1. Introduction

Earlier we synthesised functionalized dibenzo[*b*,*e*]-[1,4]dioxins under mild conditions by double aromatic nucleophilic substitution reactions between (η^6-1,2-dichlorobenzene)(η^5-2,4-cyclopentadien-1-yl)iron(1 +) salts and substituted 1,2-benzenediols [1]. The dibenzodioxin ligands were liberated routinely from the initially formed heterocyclic (cyclopentadienyl)iron complexes by irradiation with ultraviolet light. Since ruthenium(1 +) η^6 complexes of functionalized arenes are prepared readily under milder conditions [2], and are generally more stable (albeit less reactive) than their iron analogues, we have investigated their use for the preparation of functionalized dibenzo[*b*,*e*][1,4]dioxins. Our interest in the synthesis of the latter compounds was stimulated by the potent in vitro cytotoxicity and significant in vivo antitumour activity of *N*-[2-(dimethylamino)ethyl]dibenzo[*b*,*e*][1,4]dioxin-1-carboxamide (**1**) [3]. Of particular interest in the present study were attempts to prepare dibenzo[*b*,*e*][1,4]dioxins containing a nitrogen substituent.

2. Results and discussion

(η^6-Haloarene)(η^5-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphates used as starting materials in the present study were prepared as described previously [4] by thermally-promoted ligand exchange between the haloarenes **2–10** and tris(acetonitrile)(η^5-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphate(1 −) (**11**) [5–7]. Haloarene complexes **12–20** prepared in this manner are listed in Table 1. Substituted (η^5-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphates were then prepared from the chloroarene complexes **12** and **13** by stirring with selected nucleophiles to give salts **21–26** (Table 2). Complex **21** was prepared by reaction of sodium methoxide with **12, 17, 18**, or **19**, which, as expected [8,9], reacted in that order. Attempts to displace selectively one of the chlorine atoms of a trichloro complex, e.g. **15**, by using one molar equivalent of sodium methoxide afforded only mixtures of cationic products. Attempts to effect disubstitution of **13** with butylamine as the nucleophile (cf. Ref. [10]) afforded only the monosubstituted product **23**, even after refluxing for 70 h, reflecting the lower reactivity of a ruthenium complex towards S_NAr relative to the corresponding iron complex [1]. No coupling product was observed when **13** was treated with 1,2-benzenediamine,

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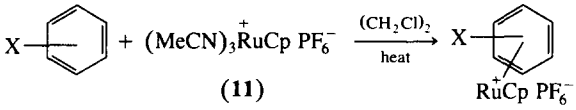
but when either **12** or **13** was treated with sodium benzimidazolate (cf. Ref. [11]) monosubstituted products **24** and **25** were obtained. Reaction of **12** with morpholine (cf. Ref. [12]) gave a high yield of the complex **26**.

Since a potential route to aminodibenzo[*b*,*e*][1,4]dioxins is by the base-promoted coupling of a cationic complex of a 1,2-dichlorobenzene with a 1,2-benzenediol, the preparation of some nitrogen-substituted (η^6-halobenzene)rutheniumCp$^+$ complexes was investi-

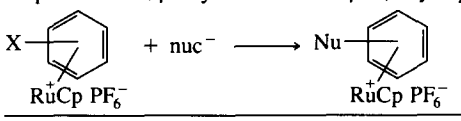
Table 1
Preparation of (η^5-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphates(1 −)



(**11**)

Starting material		Product	Yield (%)	m.p. (dec) (°C)
Chlorobenzene	**2**	**12**	89	282–284
o-Dichlorobenzene	**3**	**13**	75	198–202
p-Dichlorobenzene	**4**	**14**	61	245–248
1,2,3-Trichlorobenzene	**5**	**15**	61	224–227
1,2,4-Trichlorobenzene	**6**	**16**	41	> 310
Bromobenzene	**7**	**17**	84	250–251
Iodobenzene	**8**	**18**	91	242–241
Iodylbenzene	**9**	**19**	44	233–234
1,2-Dichloro-4-iodobenzene	**10**	**20**	46	194–196

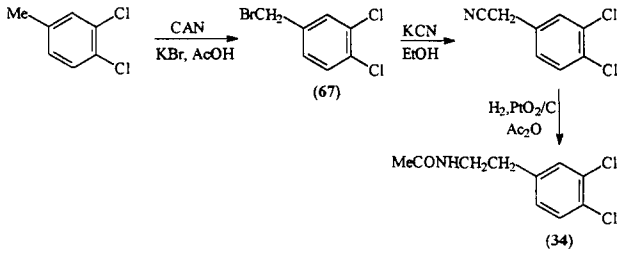
Table 2
Preparation of (η^6-aryl-substituted)(η^5-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphates(1 −)



Starting material	Nucleophile	Product	Yield (%)	m.p. (°C)
12	CH_3O^-	**21**	79	oil
12	N_3^-	**22**	83	155–158
13	$BuNH_2$	**23**	57	oil
12	Na benzimidazolate	**24**	61	198–199
13	Na benzimidazolate (2 mol.)	**25**	30	oil
12	morpholine	**26**	97	158–159

Table 3
Preparation of (η^6-*N*-aryl)(η^5-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphates(1 −) from **11**

Starting material		Product	Yield (%)	m.p. (°C)
Benzenamine	**27**	**47**	86	308–310
2,3-Dichlorobenzenamine	**28**	**48**	62	204–205
3,4-Dichlorobenzemanine	**29**	**49**	46	oil
1,2-Benzenediamine	**30**	**50**	65	oil
4-Chloro-1,2-benzenediamine	**31**	**51**	39	oil
N-(2,3-Dichlorophenyl)acetamide	**32**	**52**	43	199–202
N-(2,3-Dichlorophenyl)-2,2,2-trifluoroacetamide	**33**	**48,53**		oil
N-[2-(3,4-Dichlorphenyl)ethyl]acetamide	**34**	**54**	83	oil
N,*N*-Dimethylbenzenamine	**35**	**55**	74	189–190
N,*N*-Dimethyl-2,3-dichlorobenzenamine	**36**	**56**	68	153–165
N,*N*-Di-2-propenylbenzenamine	**37**	**57**	82	oil
2-Phenyl-1*H*-isoindole-1,3(2*H*)-dione	**38**	**58**	81	234–236
Azobenzene	**39**	**59**	73	175–176
Azoxybenzene	**40**	**60**	92	152–153
4,4′-Dichloroazobenzene	**41**	**61**	41	189–191
4,4′-Dimethoxyazobenzene	**42**	**62**	53	214–215
t-Butyl phenylimino 3-propanoate	**43**	**63**	91	119–120
Di-t-butyl phenylimino 3,3′-dipropanoate	**44**	**64**	71	118–120
t-Butyl(2,3-dichlorophenyl)imino 3-propanoate	**45**	**65**	86	143–144
Di-t-butyl (2,3-dichlorophenyl)imino 3,3′-dipropanoate	**46**	**66**	86	oil

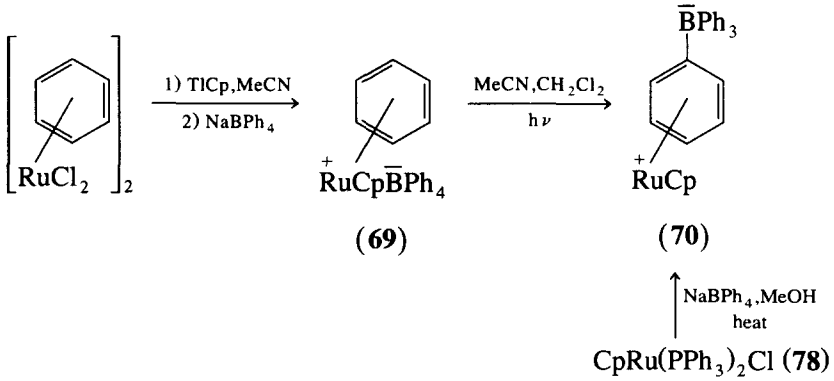


Scheme 1.

gated (Table 3). The primary aromatic amines **27–31** each reacted with **11** to give the corresponding cationic (η^6-aminoarene)ruthenium(II) complex. However, because competing N–H deprotonation (by either carbonate used as the base, or by phenoxide) of these complexes could occur under the conditions used for the intended coupling reactions, generating a neutral (η^5-iminocyclohexadienyl) species unreactive towards displacement of halogen, various complexes in which the nitrogen atom was protected were also prepared. Use of an acetamide as a protecting group, as in **32**, led to a low yield of the desired product **52**, but *N*-(2,3-dichlorophenyl)-2,2,2-trifluoroacetamide (**33**), generated from reaction of 2,3-dichlorobenzenamine with trifluoroacetic anhydride, gave a mixture (3:2) of **48** and the desired trifluoroacetamide complex **53**. The acetamidoethyl derivative **34**, in which the nitrogen group is on the side-chain, was prepared according to Scheme 1; column chromatography was necessary to separate the intermediate **67** from 3,4-dichlorophenylmethyl nitrate (**68**), which was formed in up to 35% yield (cf. Ref. [13]).

Transfer of $RuCp^+$ from complex **11** to the *N,N*-dimethylbenzenamines **35** and **36**, to the *N,N*-di-2-propenylbenzenamines **37** and **71**, to the imines **74** and **75**, to the phthalimides **38** and **77**, to 1-azido-2,3-dichlorobenzene (**76**), and to the silyl-substituted benzenamines **72** and **73** was investigated. Although the 1-aza-2-disilacyclopentanes **72** and **73** appeared to offer significant potential advantages in doubly-protecting the primary amine nitrogen, in the event the ease of cleavage of Si–N bonds by F^- resulted in the recovery of only (η^6-aminoarene)$RuCp^+$ complexes **47** and **48** after reaction of **72** and **73**, respectively, with the hexafluorophosphate salt **11**. In an attempt to avoid this problem by using a counterion which did not contain halogen, (η^6-benzene)(η^5-2,4-cyclopentadien-1-yl) ruthenium(1 +) tetraphenylborate (1 −) (**69**) was prepared (Scheme 2) from bis(η^6-benzene)di-μ-chlorodichloro-diruthenium, thallium(I) cyclopentadienide, and sodium tetraphenylborate. However, attempts to prepare tris(acetonitrile)(η^5-2,4-cyclopentadien-1-yl)ruthenium-(1 +) tetraphenylborate(1 −) by photolysis of **69** afforded only neutral (η^5-2,4-cyclopentadien-1-yl)[(η^6-phenyl)triphenylborato(1 −)]ruthenium(1 +) (**70**), the structure of which was confirmed by independent synthesis from chloro(η^5-2,4-cyclopentadien-1-yl)bis(triphenylphosphine)ruthenium(II) (**78**) and sodium tetraphenylborate [14].

Reaction of the transfer reagent **11** with the N, *N*-dialkylaminoarenes **35** and **36** gave the desired complexes. While *N*-phenylphthalimide (**38**) gave a high yield of the expected complex **58**, no complexation occurred with the 2,3-dichlorophenyl analogue **77**. Similarly, compound **37** reacted as expected with **11**, but the 2,3-dichlorophenyl analogue **71** and 2,3-dichlorophenyl azide (**76**) each gave mixtures containing no cationic complex. *N*-Phenylimines **74** and **75** gave the corresponding (η^6-aminoarene)complexes. Likewise, azobenzene (**39**) (for a recent synthesis of the corresponding iron(1 +) complex see Ref. [15]) and azoxybenzene (**40**) each formed a single cationic complex. In the latter case it was not possible to confirm from NMR measurements which phenyl ring was bound to the cyclopentadienylruthenium(II) moiety, since reported data [16] were incomplete and ambiguity existed over assignment of signals due to quaternary carbons. However, an X-ray crystal structure (Fig. 1) of the η^6 complex **60** showed that, as anticipated, the cyclopentadienylruthenium moiety had complexed to the relatively electron-rich phenylazo ring and not to the azoxy ring. 4,4(-Dichloroazobenzene (**41**), 2,2′,3,3′-tetrachloroazobenzene (**79**), 3,3′,4,4′-tetrachloroazo-benzene (**80**), and 4,4′-dimethoxyazobenzene (**42**) were each prepared by treat-



Scheme 2.

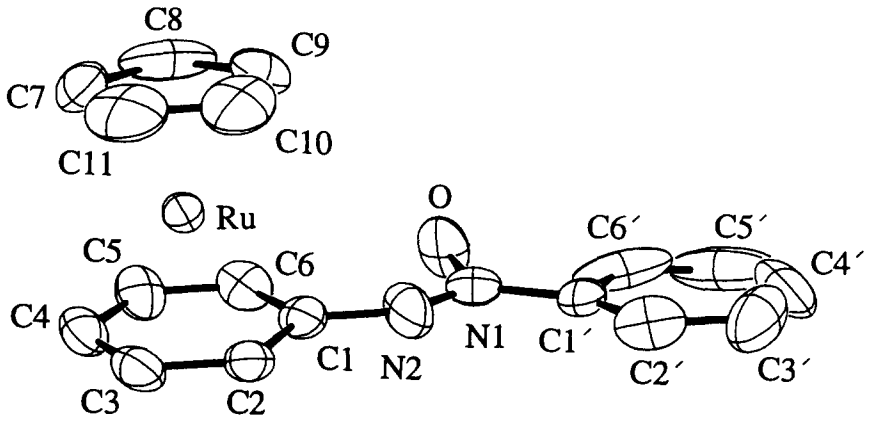


Fig. 1. The molecular geometry and atomic numbering for **60**. Atoms are represented as 35% probability ellipsoids.

ment of the appropriate benzeneamine with barium manganate in refluxing benzene [17], but only **41** and **42** formed an η^6 complex on thermolysis with **11**.

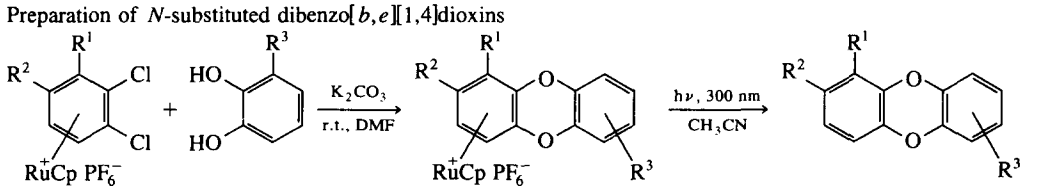
A t-butyl propanoate ester was also considered as an alternative form of protection, the intended strategy being that the t-butyl group(s) could be cleaved after the double S_NAr displacement, loss of CO_2 and ethylene then exposing the primary amine on the heterocycle. Initially, benzenamine was reacted with t-butyl 2-propenoate [18] to give a mixture of t-butyl phenylimino-3,3′-propanoate (**43**) (16%) and di-t-butyl phenylimino-3,3′-dipropanoate (**44**) (25%), which were separated by column chromatography. Each of these esters underwent complexation on thermolysis with **11** in the usual manner. The corresponding 2,3-dichloro analogues **45** and **46** were also prepared, although the mono ester **45** was obtained in only low yield (10%). The diester **46** was prepared in a stepwise manner by deprotonating 2,3-dichlorobenzenamine with sodium hydride/imidazole in THF for a brief period (5 min) and then adding t-butyl 2-propenoate in two portions. Both of the aminoethyl derivatives **45** and **46** reacted with **11** to form a cationic complex, **65** and **66** respectively, in high yield (although **66** was an unstable oil).

Another protecting group for a primary arylamine which has been introduced recently [19] is a tetrahydro-1,3-dialkyl-5-aryl-1,3,5-triazin-2(1-*H*)-one, which blocks both N–H sites and contains neither an electrophilic carbonyl (cf. acetylamino compounds) nor a nucleophilic nitrogen atom. Moreover, 2-iodobenzeneamine masked as a 1,3-dibenzyltriazone has been exploited in a recent synthesis directed towards strychnine [20]. Since the triazone is an *N,N*-dialkylamino derivative (cf. **35**) it should form a $RuCp^+$ complex readily. Relevant to the present study, cleavage of the triazone to expose the amine occurs under mildly acidic conditions [19]. Accordingly, the 1,3-dimethyltriazone **100** was synthesized (27%; cf. Ref. [19]) from benzeneamine, and then treated with **11** to form the η^6 cationic complex **101** (100%). Disappointingly, but not unexpectedly, 2,3-dichlorobenzeneamine did not give the corresponding triazone (**102**).

The final protecting group considered was a triazine. Although the triazine derived from benzeneamine formed the monocationic complex **103** in high yield, it is apparent that this route would ultimately involve sacrifice of two of the three arylamine units incorporated in this heterocycle. Consequently, this approach was not pursued.

Dibenzo[*b*,*e*][1,4]dioxin complexes resulting from

Table 4
Preparation of *N*-substituted dibenzo[*b*,*e*][1,4]dioxins



(Dichlorobenzene)Ru$^+$Cp PF_6^-			1,2-Benzenediol		(η^6-Dibenzodioxin)RuCp$^+$ complex				Dibenzo[*b*,*e*][1,4]dioxin			
	R^1	R^2		R^3	Time (h)	Product	Yield (%)	m.p. (°C)	Time (h)	Product	Yield (%)	m.p. (°C)
13	H	H	**81**	H	23	**83**	55	280–283	23 [a]	**88**	83	114–116
13	H	H	**82**	CO_2Me	23	**84**	65	204–207	3 [b]	**89**	95	85–87
56	NMe_2	H	**81**	H	20	**85**	57	169–170	5 [a]	**90**	19	oil
56	NMe_2	H	**82**	CO_2Me	50	**86**	23	240–242	24 [a]	**91**	42	oil
54	H	CH_2CH_NHCOMe	**81**	H	24	**87**	46	oil	5 [b]	**92**	92	oil

[a] Irradiation with a sunlam, 300 W. [b] Irradiation through quartz with Rayonet photo-reactor (3000 Å).

reaction of some of the above salts with either 1,2-benzenediol (**81**) or with the methoxycarbonyl-substituted 1,2-benzenediol **82** are given in Table 4, together with the decomplexed heterocycles liberated after photolysis, either by irradiation of the $RuCp^+$ salts through quartz at 300 nm (Rayonet) or by using a sunlamp. Compound **91**, which carries a substituent on each aromatic ring, was assigned tentatively as the *anti* isomer, since a nOe effect was not observed between the 1H NMR signals due to the *N,N*-dimethyl group and the methyl ester protons in the precursor complex **86**. Although this orientation is the opposite to that predicted from electronic effects [1], a *syn* relationship would be expected to give rise to a nOe since a computer-generated representation indicated the distance between N–Me and OMe in this isomer to be 0.8–1.0 Å.

For some substituted dibenzodioxins, after the heterocycle is liberated from the $CpRu^+$ moiety it is impossible to distinguish which aromatic ring was complexed originally. Thus, the possibility of introducing a nitrogen substituent into the 1,2-benzenediol partner was investigated. However, no coupling was observed when either 3-nitro-1,2-benzenediol (**93**) or 4-nitro-1,2-benzenediol (**94**) were treated with the (1,2-dichlorobenzene)ruthenium(II) complex **13**. In an attempt to convert the nitro group into a less acidic and thus a less deactivating group reduction of the diacetate of the 3-nitro isomer **93** was attempted, but this afforded a mixture of unstable products. In contrast, catalytic hydrogenation of the diacetate **95** [21] of 4-nitro-1,2-benzenediol followed by acetylation gave 4-*N*-acetylamino-1,2-benzenediol diacetate (**96**) (75%), hydrolysis of which gave 4-acetylamino-1,2-benzenediol (**97**) (91%). Although the melting point (148–153°C) was considerably lower than the literature value (182–184°C) [22] both the IR and NMR data were consistent with the structure **97**. However, attempts to couple the acetylamino diol **97** with complex **13** were unsuccessful.

A further substituted 1,2-benzenediol **98** possessing an acetylaminoethyl side chain was prepared by *N*-acetylation of dopamine hydrochloride with *N*-methoxydiacetamide [23]. Coupling of the amide with the salt (**13**) gave the 2-substituted dibenzo[*b,e*][1,4]dioxin salt **99**, which was demetallated by photolysis to afford the dibenzodioxin **92**, identical with that prepared earlier.

This study has shown that the nitrogen atom in an aminosubstituted 2,3-dichlorobenzene must be dialkylated (e.g. **36**) in order for the derived ruthenium(II) complex to be formed in high yield, and for this salt (e.g. **56**) then to be used successfully in a double S_NAr coupling sequence leading to an aminodibenzo[*b,e*][1,4]dioxin (e.g. **85** or **86**). However, such an *N,N*-dialkylated product would be difficult to convert into the primary amine required for further transformations without also affecting the heterocyclic system.

3. Experimental

For general experimental details see Ref. [4]. Unless otherwise stated all NMR spectra were determined in CD_3COCD_3.

3.1. Standard preparation of (η^5-2,4-cyclopentadien-1-yl)(η^6-halobenzene)ruthenium(1 +) hexafluorophosphates(1 −)

A mixture of tris(acetonitrile)(η^5-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphate(1 −) (**11**) and the halobenzene (molar ratio 1:1.2–3.0) in 1,2-dichloroethane was heated under reflux under N_2 for 14–18 h. The solution was cooled and the solvent removed to leave a brown residue (sometimes triturated with hexanes to remove non-complexed arene), which was purified by column chromatography on alumina. The column was eluted with CH_2Cl_2/hexanes (1:1) to remove unreacted ligand if necessary, and then flushed with CH_2Cl_2 and finally with CH_2Cl_2/EtOH (49:1) to afford the desired product. The cationic complex was usually purified further by isopiestic recrystallization from Me_2CO/Et_2O.

3.2. (η^5-2,4-Cyclopentadien-1-yl)(η^6-halobenzene)ruthenium(1 +) hexafluorophosphates(1 −)

(a) (η^6-Chlorobenzene)(η^5-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphate(1 −) (**12**) was prepared from chlorobenzene (2.1 mmol) as a pale cream powder (89%), m.p. 282–284°C (dec.) (lit. [4] 175–179°C (dec.)) (correct IR and NMR spectra).

(b) (η^5-2,4-Cyclopentadien-1-yl)(η^6-1,2-dichlorobenzene)ruthenium(1 +) hexafluorophosphate(1 −) (**13**) was prepared from 1,2-dichlorobenzene (2.7 mmol) as a brown solid (75%), m.p. 198–202°C (dec.) (lit. [4] 236–238°C (dec.)) (correct ^{1}H NMR spectrum).

(c) (η^5-2,4-Cyclopentadien-1-yl)(η^6-1,4-dichlorobenzene)ruthenium(1 +) hexafluorophosphate(1 −) (**14**) was prepared from 1,4-dichlorobenzene (3.8 mmol) as a brown powder (61%), m.p. 245–248°C (dec.) (lit. [7] 248–250°C (dec.)) (correct ^{1}H NMR spectrum).

(d) (η^5-2,4-Cyclopentadien-1-yl)(η^6-1,2,3-trichlorobenzene)ruthenium(1 +) hexafluorophosphate(1 −) (**15**) was prepared from 1,2,3-trichlorobenzene (0.84 mmol) as brown crystals (61%), 224–227°C (dec.). ν_{max}(film) 1557, 1416, 1398, 1362 (C=C), 835 cm^{-1} (PF). δ(H) 5.78 (s, Cp); 6.56 (t, *J* 5.9 Hz, H(5)); 7.01 (d, *J* 5.9 Hz, H(4, 6)). δ(C) 80.5 (C(1, 3)); 85.9 (C(5)); 87.0 (Cp); 88.4 (C(4, 6)); 106.7 (C(2)).

(e) (η^5-2,4-Cyclopentadien-1-yl)(η^6-1,2,4-trichlorobenzene)ruthenium(1 +) hexafluorophosphate(1 −) (**16**) was prepared from 1,2,4-trichlorobenzene (1.6

mmol) as a brown powder (41%), m.p. > 310°C. ν_{max}(film) 1415 (C=C), 836 (PF), 737 cm^{-1} (C–Cl). δ(H) 5.82 (s, Cp); 6.93 (dd, *J* 6.1, 1.4 Hz, H(5)); 7.13(d, *J* 6.1 Hz, H(6)); 7.57(d, *J* 1.4 Hz, H(3)). δ(C) 87.0 (C(1)); 87.3 (Cp); 87.9 (C(3)); 88.5 (C(5)); 82.3 (C(6)); 105.4 (C(4)); 106.2 (C(2)).

(f) (η^6-Bromobenzene)(η^5-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphate(1 −) (**17**) was prepared (84%) from bromobenzene (0.95 mmol) as cream square crystals, m.p. 250–251°C. Anal. Found: C, 28.5; H, 2.3. $C_{11}H_{10}BrF_6PRu$ Calc.: C, 28.2; H, 2.1%. ν_{max}(film) 1436, 1418, 1403 (C=C), 826 cm^{-1} (PF). δ(H) 5.62 (s, Cp); 6.39 (m, H(3,4,5)); 6.82 (dd, *J* 5.9, 1.2 Hz, H(2,6)). δ(C) 81.1 (C(1)); 83.5 (Cp); 86.4 (C(4)); 87.3 (C(2, 6)); 90.9 (C(3, 5)).

(g) (η^5-2,4-Cyclopentadien-1-yl)(η^6-iodobenzene)-ruthenium(1 +) hexafluorophosphate(1 −) (**18**) was prepared (91%) from iodobenzene (1.8 mmol) as long brown crystals, m.p. 242–244°C. Anal. Found: C, 25.9; H, 2.2. $C_{11}H_{10}F_6IPRu$ Calc.: C, 25.6; H, 1.9%. ν_{max}(film) 1491, 1432, 1418, 1400 (C=C), 842 cm^{-1} (PF). δ(H) 5.56 (s, Cp); 6.28 (dd, *J* 5.9, 5.8 Hz, H (3.5)); 6.38 (t, *J* 5.8 Hz, H(4)); 6.80 (d, *J* 5.9 Hz, H (2.6)). δ(C) 54.4 (C(1)); 83.5 (Cp); 86.1 (C (4)); 87.7 (C(3.5)); 95.4 (C(2.6)).

(h) (η^5-2,4-Cyclopentadien-1-yl)(η^6-iodylbenzene)-ruthenium(1 +) hexafluorophosphate(1 −) (**19**) was prepared (44%) from iodylbenzene (0.65 mmol) as brown needles, m.p. 233–234°C. Anal. Found: C, 26.2; H, 2.3. $C_{11}H_{10}F_6IO_2PRu.0.5(CH_3CH_2)_2O$ Calc.: C, 26.7; H, 2.6%. ν_{max}(film) 1491, 1416 (C=C), 834 cm^{-1} (PF). δ(H) 5.58 (s, Cp); 6.32 (dd, *J* 5.8, 5.6 Hz, H(3, 5)); 6.41 (t, *J* 5.6 Hz, H(4)); 6.82 (d, *J* 5.8 Hz, H(2, 6)). δ(C) 54.5 C(1)); 83.6 (Cp); 86.3 (C(4)); 87.8 (C(3, 5)); 95.5 (C(2, 6)).

(i) (η^5-2,4-Cyclopentadien-1-yl)(η^6-1,2-dichloro-4-iodobenzene)ruthenium(1 +) hexafluorophosphate-(1 −) (**20**) was prepared (46%) from 1,2-dichloro-4-iodobenzene (0.85 mmol) as brown crystals, m.p. 194–196 °C. Anal. Found: C, 22.6; H, 1.4. $C_{11}H_8Cl_2F_6IPRu$ Calc.: C, 22.6; H, 1.4%. ν_{max}(film) 1513, 1415 (C=C), 837 cm^{-1} (PF). δ(H) 5.77 (s, Cp); 6.95 (d, *J* 6.0 Hz, H (5)); 7.02 (d, *J* 6.0 Hz, H (6)); 7.56 (s, H(3)). δ(C) 73.1 (C(4)); 83.9 (C(1)); 85.5 (C(2)); 87.4 (Cp); 89.0 (C(6)); 96.15 (C(5)); 96.2 (C(3)).

3.3. (η^5-2,4-Cyclopentadien-1-yl)(η^6-methoxybenzene)ruthenium(1 +) hexafluorophosphate(1 −) (21)

Sodium methoxide in MeOH (0.3 ml, 10 mg ml^{-1}, 0.056 mmol) was added to a solution of complex **12** (13 mg, 0.031 mmol) in MeOH (2 ml) and the solution was stirred at room temperature for 10 min. Solvent was removed under reduced pressure, the residue was extracted into CH_2Cl_2 (10 ml), and solvent was removed from the filtered extract to afford **21** (10 mg, 79%) as a pale cream solid. δ(H) 3.88 (s, OCH_3); 5.52 (s, Cp); 6.13 (t, *J* 5.5 Hz, H (4)); 6.28 (dd, *J* 6.2, 5.5 Hz, H (3,5)); 6.41 (d, *J* 6.2 Hz, H(2,6)). δ(C) 57.7 (OCH_3); 75.3 (C(2,6)); 80.7 (Cp); 83.9 (C(4)); 85.2 (C(3,5)); 135.5 (C(1)).

3.4. (η^6-Azidobenzene)(η^5-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphate(1 −) (22)

A stirred mixture of complex **12** (45 mg, 0.11 mmol), sodium azide (7 mg, 0.11 mmol) and 18-crown-6 (5 mg, 0.02 mmol) in CH_2Cl_2 (3 ml) was heated under reflux for 21 h. The cooled solution was filtered, and the solvent was removed to leave a mixture (3:22) (^{1}H NMR) (43 mg, 83%) of **12** and **22**. Isopiestic recrystallization from Me_2CO/Et_2O gave the azido complex **22** as orange-brown crystals, m.p. 155–158°C (dec.) Anal. Found: C, 31.1; H, 2.6; N, 9.1. $C_{11}H_{10}F_6N_3$-PRu.0.25Me_2CO Calc.: C, 31.1; H, 2.6; N, 9.4%. ν_{max}(film) 2136 (N_3), 1418 (C=C), 1090 (CN), 836 cm^{-1} (PF). δ(H) 5.63 (s, Cp); 6.24 (t, *J* 5.8 Hz, H(4)); 6.45 (dd, *J* 6.2, 5.8 Hz, H(3,5)); 6.55 (d, *J* 6.2 Hz, H(2,6)). δ(C) 79.4 (C(3,5)); 82.0 (Cp); 85.3 (C(4)); 85.8 (C(2.6)); 114.8 (C(1)).

3.5. [η^6-1-(N-1-Butylamine)-2-chlorobenzene](η^5-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphate(1 −) (23)

A solution of the complex **13** (0.34 g. 0.74 mmol) in THF (25 ml) was treated with butylamine (1 ml, 10.1 mmol) in acetic acid (1.5 ml) and the solution was heated under reflux under N_2 for 70 h. Solvent was removed under reduced pressure, the residue was extracted with CH_2Cl_2, and the extract was worked up to give an oil which was chromatographed on alumina. Elution with CH_2Cl_2/EtOH (49:1) afforded **23** (0.21 g, 57%) as an unstable brown oil. ν_{max}(film) 3462 (NH) 1557, 1455 (C=C), 839 cm^{-1} (PF). δ(H) 0.95 (t, *J* 7.3 Hz, CH_3); 1.39 (m, CH_2CH_3); 1.69 (m, CH_2Et); 3.35 (br t, *J* 5.8 Hz, CH_2N); 5.36 (s, Cp); 5.98 (ddd, *J* 5.5, 5.4, 0.8 Hz, H(4)); 6.04 (ddd, *J* 5.9, 5.4, 0.9 Hz, H(5)); 6.19 (d, *J* 5.9 Hz, H(6)); 6.57 (dd, *J* 5.5, 0.9 Hz, H(3)). δ(C) 14.0 (CH_3); 20.5 (CH_2CH_3); 30.6 (CH_2Et); 43.5 (CH_2N); 66.9 (C(6)); 80.7 (C(4)); 81.5 (Cp); 84.2 (C(5)); 86.2 (C(3)); 89.7 (C(2)); 126.7 (C(1)).

3.6. (η^5-2,4-Cyclopentadien-1-yl)[N-(η^6-phenyl)benzimidazole]ruthenium(1 +) hexafluorophosphate-(1 −) (24)

The complex **12** (96 mg, 0.23 mmol) and sodium benzimidazolate (67 mg, 0.48 mmol) were stirred in CH_3CN (5 ml) under N_2 for 20 h, solvent was removed, and the residue was dissolved in Me_2CO. Ether was added to the solution to give **24** (69 mg, 61%) as a cream powder, m.p. 198–199°C. Anal. Found: C, 42.8;

H, 3.2; N, 5.5. $C_{18}H_{15}F_6N_2PRu$ Calc.: C, 42.8; H, 3.0; N, 5.5%. ν_{max}(film) 1531, 1500, 1469 (C=C), 837 cm^{-1} (PF). δ(H) 5.67 (s, Cp); 6.47 (t, *J* 5.8 Hz, H(4)); 6.65 (dd, *J* 6.2, 5.80 Hz, H(3, 5)); 7.09 (d, *J* 6.2 Hz, H(2, 6)); 7.38 (td, *J* 7.4, 1.4 Hz, H(6′)); 7.46 (td, *J* 7.4, 1.4 Hz, H(5′)); 7.77 (d, *J* 7.4 Hz, H(7′)); 7.87 (d, *J* 7.4 Hz, H(4′)); 8.55 (s, H(2′)). δ(C) 86.7 (Cp) 82.9 (C(3, 5)); 86.5 (C(2, 6)); 86.6 (C(4)); 107.4 (C(1)); 112.0 (C(7′)); 121.6 (C(4′)); 124.4 (C(5′)); 125.3 (C(6′); 133.9 (C(7a′)); 144.1 (C(2′)); 145.6 (C(3a′)).

3.7. [N-(η⁶-2-Chlorophenyl)benzimidazole](η⁵-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphate(1 −) (25)

A mixture of complex **13** (0.54 g, 1.18 mmol) and sodium benzimidazolate (0.38 g, 2.71 mmol) in CH_3CN (15 ml) was stirred under N_2 at room temperature for 24 h. Workup as for **24** gave **25** (0.20 g, 30%) as an unstable brown oil. δ(H) 5.12 (s, Cp); 5.41 (dd, *J* 4.4, 2.5 Hz, H(6)); 5.66 (dd, *J* 4.4, 2.5 Hz, H(4.5)); 6.30 (dd, *J* 4.4, 2.5 H(3)); 7.21 (ddd, *J* 7.7, 7.2, 1.4 Hz, H(5′)); 7.29 (ddd, *J* 7.6, 7.2, 1.4 Hz, H(6′)); 7.51 (d *J* 7.6 Hz, H(7′)); 7.68 (d, *J* 7.7 Hz, H(4′)); 8.32 (s, H(2′)). δ(C) 74.6 (C(5)); 75.3 (C(4)); 78.0 (Cp); 83.55 (C(3)); 85.3 (C(6)); 93.7 (C(1,2)); 113.1 (C(7′)); 120.6 (C(4′)); 122.6 (C(5′)*); 123.4 (C(6′)*); 142.2 (C(7a′)); 146.4 (C(2′)); 153.4 (C(3a′)).

3.8. (η⁵-2,4-Cyclopentadien-1-yl)[N-(η⁶-phenyl)morpholine]ruthenium(1 +) hexafluorophosphate(1 −) (26)

A mixture of complex **12** (57 mg, 0.14 mmol) and morpholine (0.5 ml, 5.72 mmol) in degassed CH_3CN (3 ml) was heated under reflux under N_2 in the dark for 24 h. Solvent was removed and the residue was triturated with Et_2O to remove excess morpholine and then extracted into CH_2Cl_2 to give a solid which was chromatographed on alumina. Elution with CH_2Cl_2/EtOH (49:1) afforded **26** (62 mg, 97%) as a yellow solid, m.p. 158–159°C. Anal. Found: C, 38.2; H, 4.0; N, 2.8. $C_{15}H_{18}F_6NOPRu$ Calc.: C, 38.0; N, 2.9%. ν_{max}(film) 1541, 1451, 1250 (C=C), 1124 (C-O), 832 cm^{-1} (PF). δ(H) 3.12 (m, 4H, CH_2N); 3.79 (m 4H, CH_2O); 5.47 (s, Cp); 6.08 (br s, (H(2′,3′,4′,5′,6′)). δ(C) 47.8 (CH_2N); 66.2 (CH_2O); 70.7 (C(3′,5′)); 79.1 (Cp); 82.7 (C(4′)); 84.5 (C(2′,6′)); 126.3 (C(1′)).

3.9. (η⁶-Benzenamine)(η⁵-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphate(1 −) (47)

A solution of complex **11** (0.23 g, 0.53 mmol) and benzenamine (**27**) (0.1 ml, 1.71 mmol) in $(CH_2Cl)_2$ (30 ml) was heated under reflux under Ar for 17 h. Solvent was removed and the residue was washed with hexanes and extracted with $(CH_2Cl)_2$. The product was chromatographed on alumina to afford **47** (0.18 g, 86%) which crystallized from Me_2CO/Et_2O as purple crystals, m.p. 308–310°C (dec.) Anal. Found: C, 32.9; H, 3.2; N, 3.3. $C_{11}H_{12}F_6NPRu$ Calc.: C, 32.7; H, 3.0; N, 3.5%). ν_{max}(film) 3390 (NH), 1552 (C=C), 841 cm^{-1} (PF). δ(H) 1.18 (s, NH_2); 5.27 (s, Cp); 5.84 (t, *J* 5.1 Hz, H(4)); 6.01 (m, H(2,3,5,6)). δ(C) 71.2 (C(2,6)); 79.9 (Cp); 81.0 (C(4)); 84.6 (C(3,5)); 127.3 (C(1)).

3.10. (η⁵-2,4-Cyclopentadien-1-yl)(η⁶-2,3-dichlorobenzenamine)ruthenium(1 +) hexafluorophosphate(1 −) (48)

A degassed solution of the complex **11** (0.23 g, 0.53 mmol) and 2,3-dichlorobenzenamine (**28**) (0.13 g, 0.83 mmol) in $(CH_2Cl)_2$ (25 ml) was heated under reflux under Ar for 16 h. Workup afforded **48** (0.16g, 62%) which crystallized from Me_2CO/Et_2O as red needles, m.p. 204–205°C (dec.). Anal. Found: C, 28.2; H, 2.5; N, 2.9. $C_{11}H_{10}Cl_2F_6NPRu$ Calc.: C, 27.9; H, 2.1; N, 3.0%). ν_{max}(film) 3384 (NH), 832 cm^{-1} (PF). δ(H) 5.45 (s, Cp); 6.17 (t, J_{obs} 5.9 Hz H(5)); 6.25 (br s, NH_2); 6.28 (d, *J* 6.0 Hz, H(6)); 6.51 (d, *J* 5.5 Hz, H(4)). δ(C) 70.4 (C(6)); 81.1 (C(2,4)); 83.7 (Cp, C(5)); 105.1 (C(3)); 126.7 (C(1)).

3.11. (η⁵-2,4-Cyclopentadien-1-yl)(η⁶-3,4-dichlorobenzenamine)ruthenium(1 +) hexafluorophosphate(1 −) (49)

A solution of the complex **11** (0.11 g, 0.26 mmol) and 3,4-dichlorobenzenamine (**29**) (78 mg, 0.48 mmol) in $(CH_2Cl)_2$ (30 ml) was heated under N_2 for 19.5 h. The solution was chromatographed on alumina, to afford **49** (57 mg, 46%) as an unstable red oil. δ(H) 5.44 (s, Cp); 6.00 (br s, NH_2); 6.06 (dd, *J* 6.3, 1.6 Hz, H(6)); 6.60 (d, *J* 1.6 Hz, H(2)); 6.68 (d, *J* 6.3 Hz, H(5)). δ(C) 69.7 (C(6)); 71.7 (C(2)); 82.4 (C(4)); 83.7 (Cp); 85.4 (C(5)); 129.5 (C(3)); 132.0 (C(1)).

3.12. (η⁶-1,2-Benzenediamine)(η⁵-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphate(1 −) (50)

A solution of complex **11** (0.11 g, 0.26 mmol) and 1,2-benzenediamine (**30**) (88 mg, 0.82 mmol) in $(CH_2Cl)_2$ (15 ml) was heated under reflux under N_2 for 14 h. Workup afforded **50** (72 mg, 65%) as an unstable red oil. δ(H) 5.08 (s, Cp); 5.61 (dd, *J* 4.3, 2.4 Hz, H(3,6)); 6.06 (dd, *J* 4.3, 2.4 Hz, H(4,5)). δ(C) 78.0 (C(3,6)); 79.1 (C(4,5)); 79.3 (Cp); 111.2 (C(1,2)).

3.13. (η⁶-4-Chloro-1,2-benzenediamine)(η⁵-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphate(1 −) (51)

A solution of the complex **11** (0.19 g, 0.45 mmol) and 4-chloro-1,2-benzenediamine (**31**) (0.13 g, 0.91 mmol) in $(CH_2Cl)_2$ (15 ml) was heated under reflux

under N_2 for 16.5 h. Workup afforded **51** (79 mg, 39%) as an unstable dark red oil. ν_{max}(film) 3389 (NH), 2925 (CH), 1526, 1473, 1414 (C=C), 838 cm^{-1} (PF). δ(H) 5.17 (s, Cp); 6.03 (d, *J* 5.8 Hz, H(5)); 6.15 (d, *J* 5.8 Hz, H(6)); 6.50 (br s, H(2)). δ(C) 71.9 (C(3)); 74.4 (C(6)); 80.4 (C(5)); 81.3 (Cp); 98.9 (C(4)); 110.9 (C(1)*); 111.0 (C(2)*).

3.14. (η^5-2,4-Cyclopentadien-1-yl)[N-(η^6-2,3-dichlorophenyl)acetamide]ruthenium(1 +) hexafluorophosphate(1 −) (52)

Complex **11** (0.32 g, 0.75 mmol) was added in portions over 6 h to a refluxing solution of *N*-(2,3-dichlorophenyl)acetamide (**32**) [27] (0.19 g, 0.93 mmol) in refluxing $(CH_2Cl)_2$ (40 ml). The solution was heated under reflux for 14 h and worked up to give a solid which was chromatographed on alumina to afford **52** (0.16 g, 43%) as a pale brown solid, m.p. 199–202°C. Anal. Found: C, 30.6; H, 2.5; N, 2.6. $C_{13}H_{12}Cl_2F_6NPRu$ Calc.: C, 30.3; H, 2.3; N, 2.7%. ν_{max}(KBr) 3397 (br NH), 1723 (CO), 1560 (NH), 845 cm^{-1} (PF). δ(H) 2.22 (s, CH_3); 5.60 (s, Cp); 6.45 (dd, *J* 6.1, 5.8 Hz, H(5)); 6.84 (d, *J* 5.8 Hz, H(6)); 7.25 (d, *J* 6.1 Hz, H(4)). δ(C) 24.2 (CH_3); 81.5 (C(6)); 84.7 (C(4)); 85.3 (Cp); 86.4 (C(5)); 99.8 (C(2)); 105.9 (C(3)); 108.6 (C(1)); 171.1 (CO).

3.15. N-(2,3-Dichlorophenyl)-2,2,2-trifluoroacetamide (33)

Trifluoroacetic anhydride (7.0 ml, 49.6 mmol) was added slowly to 2,3-dichlorobenzenamine (3.86 g, 23.8 mmol) and the mixture was stirred for 20 min. Solvent was removed under reduced pressure and the residue was dissolved in CH_2Cl_2 (50 ml). The solution was washed with water (50 ml), and brine (50 ml) and then dried, and the solvent was removed to afford **33** (4.14 g, 67%) as pale brown crystals, m.p. 49–50°C. Anal. Found: C, 37.4; H, 1.8; N, 5.4. $C_8H_4Cl_2F_3NO$ Calc.: C, 37.2; H, 1.6; N, 5.4%. ν_{max}(KBr) 3300 (NH), 1711 (CO), 1587, 1542 (C=C), 1338, 1158 (C–F), 1277 (CN), 737 cm^{-1} (C–Cl). δ(H) ($CDCl_3$) 7.30 (t, *J* 8.2 Hz, H(5)); 7.36 (dd, *J* 8.2, 1.5 Hz, H(4)); 8.28 (dd, *J* 8.2, 1.6 Hz, H(6)); 8.49 (br s, NH). δ(C) 115.5 (q, *J* 288.8 Hz, CF_3); 119.8 (C(6)); 122.5 (C(2)); 127.4 (C(4)); 128.1 (C(5)); 133.4 (C(3)*); 133.6 (C(1)*); 154.2 (q, *J* 38 Hz, CO). *m/z* 257/259/261 (30/18/3, M^+); 238/240/242 (2/1/< 1, M–F); 222/224 (100/33. M–Cl); 188/190/192 (8/5/2, $M-CF_3$); 160/162/164 (20/15/4, $M-COCF_3$).

3.16. (η^5-2,4-Cyclopentadien-1-yl)[N-(η^6-2,3-dichlorophenyl)-2,2,2-trifluoroacetamido]ruthenium(1 +) hexafluorophosphate(1 −) (53)

A solution of the acetamide **33** (0.22 g, 0.75 mmol) and the complex **11** (0.24 g, 0.55 mmol) in degassed CH_2Cl_2 (30 ml) was heated under reflux under Ar for 16.25 h. Workup gave an oil which was chromatographed on alumina. Elution with hexanes/CH_2Cl_2 (4:1) afforded a mixture (72 mg) of 2,3-dichlorobenzenamine (**28**) and the acetamide **33**. Elution with CH_2Cl_2/EtOH (49:1) gave a mixture (3:2, ^{1}H NMR) (61 mg) of **48** and **53**. For **53**; ν_{max}(film) 3095 (NH), 1694 (CO), 1538 (C=C), 1335 (C–F), 1270 (C–N), 842 cm^{-1} (PF). δ(H) 5.34 (s, Cp); 6.06 (t, J_{obs} 5.9 Hz, H(5)); 6.46 (dd, *J* 5.6, 0.6 Hz, H(6)); 6.73 (dd, *J* 6.1, 0.6 Hz, H(4)). δ(C) 79.5 (C(6)); 82.9 (Cp); 85.4 (C(4)); 88.2 (C(5)). No quaternary carbon signals were observed.

3.17. 1-(Bromomethyl)-3,4-dichlorobenzene (67)

A solution of 1,2-dichloro-4-methylbenzene (2.5 g, 15.5 mmol), cerium(III) ammonium nitrate (18.1 g, 33.0 mmol) and potassium bromide (1.92 g, 16.0 mmol) in acetic acid (60 ml) was heated at 80–90°C for 1.5 h. Workup and chromatography on silica gel with hexanes as eluent afforded starting material (0.11 g, 4%), and **67** (2.13 g, 57%) as a colourless liquid. ν_{max}(neat) 1469, 1396 (C=C), 1224, 1133, 1034 (C–H), 706, 688 (C–Cl), 656 cm^{-1} (C–Br). δ(H) ($CDCl_3$, 60 MHz) 4.26 (s, CH_2); 7.01 (d, *J* 6.0 Hz, (H(5)); 7.10 (s, H(2)); 7.15 (d, *J* 6.0 Hz, H(6)).

Elution of the column with Et_2O gave 3,4-dichlorophenylmethyl nitrate (**68**) (1.13 g, 35%) as a white solid, m.p. 135–140°C. δ(H) ($CDCl_3$) (s, CH_2); 7.45 (dd, *J* 8.2, 2.0 Hz, H(6)); 8.01 (d, *J* 8.2 Hz, H(5)); 8.20 (d, *J* 2.0 Hz, H(2)). δ(C) 72.8 (CH_2); 127.3 (C(1)); 128.0 (C(2)); 130.9 (C(4)); 131.2 (C(5)*); 131.3 (C(6)*); 133.1 (C(3)). *m/z* 221/223/225 (34/24/17, M^+); 175/177/179 (42/19/5, $M-NO_2$); 159/161/163 (37/24/5, $M-ONO_2$); 145/147/249 (68/56/18, $M-CH_2ONO_2$); 111 (100, $M-CH_2ONO_2$,Cl).

3.18. 3,4-Dichlorobenzenacetonitrile

A solution of 1-(bromomethyl)-3,4-dichlorobenzene (**67**) (0.47 g, 1.99 mmol) in EtOH (25 ml) was treated with a solution of KCN (0.20 g, 1.60 mmol) in water (3 ml) and the mixture was heated at ca. 60°C under reflux for 4 h. Workup and chromatography on silica gel using hexanes/Et_2O (19:1) as eluent, afforded 3,4-dichlorobenzenacetonitrile (0.17 g, 79%) as a yellow oil. ν_{max}(film) 2258 (C–N), 1472 (C=C), 1133, 1035 (C–H), 811 cm^{-1} (C–Cl). δ(H) ($CDCl_3$) 3.73 (s, CH_2); 7.19 (dd, *J* 8.3, 2.1 Hz, H(6)); 7.44 (d, *J* 2.1 Hz, H(2)); 7.46 (d *J* 8.3 Hz, H(5)). δ(C) 22.8 (CH_2); (C(1)); 127.2 (C(6)); 128.7 (CN); 129.9 (C(5)); 131.0 (C(2)); 132.5 (C(4)); 133.3 (C(3)).

3.19. N-[2-(3,4-Dichlorophenyl)ethyl]acetamide (34)

A solution of 3,4-dichlorobenzenacetonitrile (0.35 g, 1.85 mmol) in acetic anhydride (10 ml) and platinum(IV) oxide (28 mg) was hydrogenated at 40 psi for 5 h. The catalyst was filtered off and the solution was made alkaline with dilute sodium hydroxide. Workup gave **34** (0.38 g, 89%) as pale yellow crystals, m.p. 46–49°C. δ(H) ($CDCl_3$) 1.95 (s, CH_3); 2.78 (t, J_{obs} 7.0 Hz, CH_2); 3.46 (ddd, J_{obs} 7.1, 6.9, 6.2 Hz, CH_2N); 5.70 (br s, NH); 7.03 (dd, J 8.2, 2.0 Hz, H(6)); 7.28 (d, J 2.0 Hz, H(2)); 7.37 (d, J 8.2 Hz, H(5)). δ(C) 23.2 (CH_3); 34.7 (CH_2); 40.3 (CH_2N); 128.1 (C(6)); 128.3 (C(4)); 130.4 (C(3)); 130.5 (C(2)*); 130.6 (C(5)*); 132.4 (C(1)); 170.3 (CO).

3.20. (η⁵-2,4-Cyclopentadien-1-yl)[N-2-(η⁶-3,4-dichlorophenyl)ethyl)acetamido]ruthenium(1 +) hexafluorophosphate(1 −) (54)

A solution of complex **11** (0.68 g, 1.56 mmol) and *N*-[2-(3,4-dichlorophenyl)ethyl]acetamide (**34**) (0.38 g, 1.63 mmol) in degassed $(CH_2Cl)_2$ (40 ml) was heated under Ar for 16 h. Workup and chromatography on alumina, with hexanes/CH_2Cl_2 (4:1) as eluant, removed **34**. Elution with CH_2Cl_2/EtOH (99:1) gave **54** (0.71 g, 83%) as a brown oil. Anal. Found: C, 33.0; H, 3.1. $C_{15}H_{16}Cl_2F_6NOPRu$ Calc.: C, 33.2; H, 3.0%. ν_{max}(film) 3432, 3296 (N–H), 1652 (CO), 1538, 1471, 1418 (C=C), 1295 (C–N), 842 cm^{-1} (PF). δ(H) 1.85 (s, CH_3); 2.80 (t, J 7.0 Hz, CH_2); 3.48 (t, J_{obs} 6.5 Hz, CH_2N); 5.70 (s, Cp); 6.45 (d, J 6.0 Hz, H(6)); 6.96 (d, J 6.0 Hz, H(5)); 7.06 (s, H(2)); 7.38 (br s, NH). δ(C) 23.1 (CH_3); 34.4 (CH_2); 40.7 (CH_2N); 85.7 (Cp); 87.7 (C(6)); 88.0 (C(5)); 89.5 (C(2)); 105.7 (C(1)); 106.1 (C(3)*); 106.6 (C(4)*); 171.0 (CO).

3.21. (η⁶-Benzene)(η⁵-2,4-cyclopentadien-1-yl)ruthenium(1 +) tetraphenylborate(1 −) (69)

A stirred degassed solution of bis(η⁶-benzene)di-μ-chlorodichlorodiruthenium (1.96 g, 3.92 mmol) in CH_3CN (70 ml) was treated with thallium(I) cyclopentadienide (1.99 g, 7.39 mmol) and the solution was stirred in the dark under N_2 for 5 h. The solution was filtered, water (50 ml) was added, and the solution was refiltered. A solution of sodium tetraphenylborate (4.38 g, 12.8 mmol) in water (50 ml) was added and the mixture stirred for 30 min. The solvent was reduced to ca. 10 ml and the powder was filtered off, washed with water, and dried in vacuo to afford **69** (4.16 g, 100%) which crystallized from CH_3CN/Et_2O as brown crystals, m.p. 277–278°C. Anal. Found: C, 74.5; H, 5.8. $C_{35}H_{31}BRu$ Calc.: C, 74.6; H, 5.5%. ν_{max}(solution) 1632, 1444, 1375 (C=C), 736, 709 cm^{-1} (aromatics). δ(H) ($(CD_3)_2SO$) 5.44 (s, Cp); 6.20 (s, C_6H_6); 6.80 (tt, J 7.0, 2.2 Hz, 4H H(4)); 6.94 (dd, J 7.4, 7.0 Hz, 8H, H(3,5)); 7.19 (m, 8H, H(2,6)). δ(C) 79.9 (Cp); 85.7 (C_6H_6); (121.4 (C(4)); 125.2 (C(2,6)); 135.4 (C(3,5)); 163.3 (q, J 49 Hz, C(1)).

3.22. (η⁵-2,4-Cyclopentadien-1-yl)[(η⁶-phenyl)triphenylborato(1 −)]ruthenium (70)

Chloro(η⁵-2,4-cyclopentadien-1-yl)bis(triphenylphosphine)ruthenium(II) (**78**) [26] (0.23 g, 0.31 mmol) and sodium tetraphenylborate (0.23 g, 0.67 mmol) were heated under reflux in MeOH (60 ml), under Ar for 16 h. The cooled solution was filtered, and the filtrate was then reduced to ca. 40 ml and set aside at ca. 5°C for 24 h. The precipitate was filtered off, washed with hexanes, and dried to afford **70** (35 mg, 23%) as a fawn powder, m.p. 285–286°C. δ(H) ($CDCl_3$) 4.76 (s, Cp); 5.63 (m, H(2,4,6)); 6.23 (m, H(3,5)); 7.19 (m, 15H, BPh_3). δ(C) 78.3 (Cp); 83.7 (C(3,5)); 92.1 (C(2,6)); 104.0 (C(4)); 123.4 (C(4′)); 126.3 (C(2′,6′)); 135.6 (C(3′,5′)); the quaternary carbon signals were not detected. m/z 485 (8, M^+); 409 (100, M–Ph); 331 (53, M–2Ph); 244 (12, M–BPh_3); 167 (21, RuCp).

3.23. (1-Phenyl-2,2,5,5-tetramethyl)-1-aza-2,5-disilacyclopentane (72)

A stirred solution of resublimed (×2) zinc(II) iodide (0.63 g, 1.99 mmol), 1,1′-(1,2-ethanediyl)bis[*N*,*N*,1,1-tetramethylsilanamine [25] (1.27 g, 5.47 mmol), and benzenamine (0.5 ml, 5.44 mmol) was heated to 135–140°C for 5 h under a stream of Ar. The mixture was distilled to afford **72** (0.77 g, 60%) as a colourless liquid, b.p. 85–90°C. ν_{max}(neat) 1621, 1576, 1499, 1485 (C=C), 1254, 881 (Si–C), 752, 698 cm^{-1} (aromatics). δ(H) ($CDCl_3$) 0.20 (s, 12H, $SiCH_3$); 0.85 (s, 4H, $SiCH_2$); 6.90 (m, H(3,4,5)); 7.19 (dd, J 8.0, 1.9 Hz, H(2,6)). δ(C) −0.12 ($SiCH_3$); 8.4 ($SiCH_2$); 120.1 (C(4)); 123.5 (C(2,6)); 128.9 (C(3,5)); 147.4 (C(1)). m/z 235 (36, M^+); 220 (100, M^+–CH_3); 200 (3, M–$2CH_3$); 145 (9, $(CH_3)_2SiCH_2CH_2Si(CH_3)_2$).

Attempted complexation of **72** by treatment with **11** for 8 h afforded only **47** (77%).

3.24. [1-(2,3-Dichlorophenyl)-2,2,5,5-tetramethyl]-1-aza-2,5-disilacyclopentane (73)

A stirred solution of resublimed zinc(II) iodide (0.13 g, 0.41 mmol), 1,1′-(1,2-ethanediyl)bis[*N*,*N*,1,1-tetramethylsilanamine] (0.33 g, 0.71 mmol), and 2,3-dichlorobenzenamine (0.10 g, 0.64 mmol) was heated at ca. 140°C for 5.25 h, under Ar. The solution was distilled to afford **73** (50 mg, 26%), b.p. 110–115°C, 2 mmHg, as white crystals. Anal. Found: C, 47.7; H, 6.3; N, 4.5. $C_{12}H_{19}Cl_2NSi_2$ Calc.: C, 47.4; H, 6.3; N, 4.6%). ν_{max}(film) 1573, 1446 (C=C), 1249, 846 (Si–C), 784,

714 cm^{-1} (aromatics). δ(H) ($CDCl_3$) 0.07 (s, 12H, Si CH_3); 0.92 (s, 4H, Si CH_2); 6.84 (dd, *J* 7.9, 1.6 Hz, H(6)); 7.06, dd (*J* 8.0, 7.9 Hz, H(5)); 7.21 (dd, *J* 8.0, 1.6 Hz, H(4)). δ(C) −0.02 ($SiCH_3$); 8.3 ($SiCH_2$); 125.8 (C(2,6)); 126.6 (C(4)); 129.8 (C(5)); 133.4 (C(3)); 145.2 (C(1)). *m/z* 303/305/307 (24/20/6, M^+); 288/290/292 (100/76/19, M–CH_3); 252 (16).

Attempted complexation of the disilacyclopentane **73** by reaction with **11** for 7.5 h gave **48** (76%).

3.25. (η⁵-2,4-Cyclopentadien-1-yl)(η⁶-N,N-dimethylbenzenamine)ruthenium(1 +) hexafluorophosphate-(1 −) (55)

A solution of complex **11** (0.22 g, 0.50 mmol) and *N,N*-dimethylbenzenamine (**35**) (66 mg, 0.55 mmol) in $(CH_2Cl)_2$ (30 ml) was heated under reflux under Ar for 17.5 h. Workup and column chromatography afforded **55** (0.16 g, 74%) which crystallized from Me_2CO/Et_2O as brown crystals, m.p. 189–190°C. Anal. Found: C, 36.0; H, 3.8; N, 3.2. $C_{13}H_{16}F_6NPRu$ Calc.: C, 36.1; H, 3.7; N, 3.2%. ν_{max}(film) 1560 (C=C), 1362 (CN), 837 cm^{-1} (PF). δ(H) 2.91 (s, 6H, CH_3); 5.37 (s, Cp); 5.95 (m, H(2,3,4,5,6)). δ(C) 40.0 (CH_3); 68.8 (C(2,6)); 78.7 (Cp); 81.3 (C(4)); 85.2 (C(3,5)); 129.7 (C(1)).

3.26. (η⁵-2,4-Cyclopentadien-1-yl)(η⁶-N,N-dimethyl-2,3-dichlorobenzenamine)ruthenium(1 +) hexafluorophosphate(1 −) (56)

A solution of complex **11** (0.39 g, 0.90 mmol) and *N,N*-dimethyl-2,3-dichlorobenzenamine (**36**) [27] (0.26 g, 1.38 mmol) in $(CH_2Cl)_2$ (30 ml) was heated under reflux under Ar for 16 h. Workup afforded **56** (0.31 g, 68%) which crystallized from Me_2CO/Et_2O as fawn microcrystals, m.p. 163–165°C. Anal. Found: C, 31.0; H, 2.8; N, 2.9. $C_{13}H_{14}Cl_2NPRu$ Calc.: C, 31.1; H, 2.8; N, 2.8%). δ(H) 3.03 (s, 6H, CH_3); 5.64 (s, Cp); 6.30 (t, *J* 6.0 Hz, H(5)); 6.45 (d, *J* 6.0 Hz, H(6)); 6.73 (d, J_{obs} 5.7 Hz, H(4)). δ(C) 44.6 (CH_3); 79.8 (C(4)); 8.12 (C(2)); 83.5 (Cp); 83.8 (C(6)); 84.6 (C(5)); 87.0 (C(3)); 127.2 (C(1)).

3.27. (η⁵-2,4-Cyclopentadien-1-yl)(η⁶-N,N-di-2-propenylbenzenamine)ruthenium(1 +) hexafluorophosphate(1 −) (57)

A solution of the complex **11** (0.20 g, 0.46 mmol) and *N,N*-di-2-propenylbenzenamine (**37**) [28] (0.34 g, 1.97 mmol) in base-filtered, degassed $(CH_2Cl)_2$ (25 ml) was heated under reflux under N_2 for 15 h. Workup gave **57** (0.18 g, 82%) as an unstable brown oil. ν_{max}(film) 1555 (C=C), 841 cm^{-1} (PF). δ(H) 4.00 (d, *J* 5.2 Hz, 4H, CH_2N); 5.30 (s, Cp); 6.00 (m, 11H, H(2,3,4,5,6, $CH_2=$, CH)). δ(C) 53.3 (CH_2N); 68.9 (C(2,6)); 79.5 (Cp); 80.9 (C(4)); 84.3 (C(3,5)); 117.4 (C(1)); 118.0 ($CH_2=$); 132.6 (CH).

3.28. 2,3-Dichloro-N,N-di-2-propenylbenzenamine (71)

Butyllithium (1.5 ml, 1.2 mol l^{-1} in hexanes, 1.8 mmol) was added dropwise over 5 min to a solution of 2,3-dichlorobenzenamine (**28**) (0.28 g, 1.74 mmol) in Et_2O (4 ml) under Ar, the solution was stirred for 5 min, and then allyl bromide (0.15 ml, 1.77 mmol) was added dropwise. The solution was stirred for 5 h at room temperature, butyllithium (1.5 ml, 1.2 mol l^{-1}, 1.8 mmol) was then added dropwise, followed by allyl bromide (0.15 ml, 1.77 mmol) and the mixture was stirred for 18 h. The solution was hydrolyzed with water (10 ml), and the product was extracted into ether. Workup gave an oil which on vacuum distillation afforded **71** (0.24 g, 58%) as a clear liquid, b.p. 130–135°C, 0.6 mmHg (Kugelrohr). Anal. Found: C, 60.2; H, 5.8; N, 5.6. $C_{12}H_{13}Cl_2N$ Calc.: C, 59.5; H, 5.4; N, 5.8%. ν_{max}(neat) 1643 (C=C), 1588, 1503, 1455 (aryl C=C), 1322 (CN), 993, 923, 763, 702 cm^{-1} (aromatics). δ(H) ($CDCl_3$) 3.70 (dt, *J* 6.1, 1.2 Hz, 4H, NCH_2); 5.17 (m, 4H, $CH_2=$); 5.79 (ddt, *J* 17.2, 10.1, 6.1 Hz, 2H, CH); 6.93 (dd, *J* 7.3, 2.4 Hz, H(6)); 7.07 (dd, *J* 7.9, 7.3 Hz, H(5)); 7.11 (dd, *J* 7.9, 2.4 Hz, H(4)). δ(C) 54.8 (CH_2); 117.8 ($=CH_2$); 121.5 (C(6)); 124.4 (C(4); 126.6 (C(5)); 128.4 (C(2)); 133.9 (C(3)); 134.4 (CH); 149.6 (C(1)). *m/z* 241/243/245 (2/15/3, M^+); 214/216/218 (38/21/2, M–CH_2CH); 206/208 (39/4, M–Cl); 172/174/176 (23/20/6, M–C_5H_9).

Attempted complexation of the propenylbenzenamine **71** by thermolysis with **11** gave a complicated mixture.

3.29. N-(Phenylmethylene)benzenamine (74)

Benzenamine (1.85 ml, 20 mmol) was added with stirring to benzaldehyde (1.95 ml, 19 mmol) and the mixture was allowed to stand for 15 min. The precipitate was dissolved in hot EtOH (4 ml) and then crystallized by cooling the solution with scratching. Further purification by vacuum distillation gave **74** (3.32 g, 97%) as a pale cream solid, m.p. 51.5–52°C, 0.6 mmHg (Kugelrohr). ν_{max}(film) 1623 (CN), 1591, 1578 (C=C), 758 cm^{-1} (aromatics). δ(H) ($CDCl_3$) 7.22 (m, H(2,4,6)); 7.42 (m, H(3,3',4',5,5')); 7.89 (dd, *J* 6.6, 3.0 Hz, H(2',6')); 8.43 (s, CH = N). δ(C) 120.8 (C(2,6)); 125.9 (C(4)); 128.7 (C(2',6')*); 128.7 (C(3',5')*); 129.0 (C(3,5)*); 131.3 (C(4')); 136.2 (C(1')); 152.0 (C(1)); 160.3 (CH = N).

Attempted complexation of **74** by treatment with **11** gave **47** (28%).

3.30. N-(3,4-Dichlorophenyl)-2,2,2-trifluoroacetimidoyl chloride (75)

Triethylamine (0.3 ml, 4.16 mmol), CCl_4 (7 ml), and trifluoroacetic acid (0.3 ml) were added sequentially to ice-cold triphenylphosphine (2.86 g, 10.9 mmol). The mixture was stirred for 10 min, and then 3,4-dichloro-

benzenamine (0.67 g, 4.14 mmol) was added. The mixture was heated under reflux for 3 h, solvent was removed, and the residue extracted with hexanes. Removal of solvent from the filtered solution and vacuum distillation (Kugelrohr) of the oil gave **75** (0.15 g, 13%) as a colourless liquid, b.p. 80–85°C, 0.5 mmHg. ν_{max}(neat) 1707, 1687 (C=C), 1287, 1165 (CF), 747 cm^{-1} (C–Cl). δ(H) ($CDCl_3$) 6.87 (dd, *J* 8.6, 2.4 Hz, H(6)); 7.24 (d, *J* 2.4 Hz, (H(2)); 7.52 (d, *J* 8.6 Hz, H(5)). δ(C) 116.6 (q, *J* 278 Hz, CF_3); 120.1 (C(6)); 122.7 (C(2)); 131.0 (C(5)); 131.4 (C(4)); 133.4 (C(3)); 134.1 (q, *J* 44 Hz, CN); 142.5 (C(1)).

Attempted complexation of **75** by reaction with **11** gave **48**.

3.31. (η⁵-2,4-Cyclopentadien-1-yl)[(1',2',3',4',5',6'-η)-2-phenyl-1H-isoindole-1,3(2H)-dione]ruthenium(1 +) hexafluorophosphate(1 −) (58)

A solution of complex **11** (0.48 g, 1.10 mmol) and 2-phenyl-1*H*-isoindole-1,3(2*H*)-dione (**38**) [29] (0.26 g, 1.17 mmol) in degassed $(CH_2Cl)_2$ (40 ml) was heated under N_2 for 15.5 h. Workup and crystallization from Me_2CO/Et_2O gave **58** (0.47 g, 81%) as pale cream crystals, m.p. 234–236°C. Anal. Found: C, 42.8; H, 2.8; N, 2.6. $C_{19}H_{14}F_6NO_2PRu$ Calc.: C, 42.7; H, 2.6; N, 2.6%. ν_{max}(solution) 1741, 1715 (CO), 1380, 1360, 1270 (C=C), 846 cm^{-1} (PF). δ(H) 5.61 (s, Cp); 6.39 (t, *J* 5.7 Hz, H(4')); 6.56 (t, J_{obs} 6.0 Hz, H(3',5')); 6.77 (d, *J* 6.1 Hz, H(2',6')); 8.00 (d, *J* 1.9 Hz, H(4,5,6,7)). δ(C) 82.5 (Cp); 84.9 (C(2',6')); 85.9 (C(4')); 86.1 (C(3',5')); 86.9 (C(1')); 124.6 (C(4,7)); 132.2 (C(3a,7a)); 136.1 (C(5,6)); 166.9 (CO).

3.32. 2-(2,3-Dichlorophenyl)-1H-isoindole-1,3(2H)-dione (77)

A solution of 2,3-dichlorobenzenamine (0.98 g, 6.08 mmol) and phthalic anhydride (1.04 g, 7.03 mmol) in acetic acid (10 ml) was heated under reflux for 1 h. Crystals were filtered from the cooled solution and recrystallized from EtOH to afford **77** (0.74 g, 42%) as white crystals, m.p. 191–192.5°C. ν_{max}(film) 1776, 1718 (CO), 1460, 1383 (C=C), 721 cm^{-1} (aromatics). δ(H) ($CDCl_3$) 7.29 (dd, *J* 7.9, 1.9 Hz, H(6')); 7.38 (t, *J* 7.9 Hz, H(5')); 7.59 (dd, *J* 7.9, 1.9 Hz, H(4')) 7.81 (dd, *J* 5.5, 3.1 Hz, H(5,6)); 7.96 (dd, *J* 5.5, 3.1 Hz, H(4,7)). δ(C) 124.0 (C(4,7)); 127.6 (C(6')); 128.9 (C(4')); 131.4 (C(2',5')); 131.7 (C(3')); 134.2 (C(1')); 134.6 (C(3a,5,6,7a)); 166.2 (CO).

Attempted complexation of **77** by reaction with **11** gave a mixture containing no cationic species.

3.33. (η⁶-2,4-Azobenzene)(η⁵-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphate(1 −) (59)

A solution of complex **11** (0.13 g, 0.30 mmol) and azobenzene (**39**) (92 mg, 0.51 mmol) in base-filtered, degassed $(CH_2Cl)_2$ (15 ml) was heated under reflux under N_2 for 15.5 h. Workup gave **59** (0.11 g, 73%) which crystallized from Me_2CO/Et_2O as orange needles, m.p. 175–176°C. Anal. Found: C, 41.5; H, 3.3; N, 5.6. $C_{17}H_{15}F_6N_2PRu$ Calc.: C, 41.4; H, 3.0; N, 5.7%. ν_{max}(film) 1505, 1487, 1441 (C=C), 835 cm^{-1} (PF). δ(H) 5.59 (s, Cp); 6.50, (t, *J* 5.7 Hz, H(4)); 6.63 (dd, *J* 6.1, 5.7 Hz, H (3,5)); 7.04 (d, *J* 6.1 Hz, H(2,6)); 7.66 (m, H(3',4',5')); 7.95 (dd, *J* 7.8, 1.9 Hz, H(2',6')). δ(C) 82.5 (Cp); 82.7 (C(3,5)); 87.0 (C(2,6)); 87.8 (C(4)); 117.1 (C(1)); 124.3 (C(3',5')); 130.4 (C(2',6')); 134.2 (C(4')); 152.7 (C(1')).

3.34. (η⁵-2,4-Cyclopentadien-1-yl)(η⁶-phenyl-NNO-azoxybenzene)ruthenium(1 +) hexafluorophosphate-(1 −) (60)

A solution of complex **11** (0.26 g, 0.60 mmol) and azoxybenzene (**40**) (0.27 g, 1.34 mmol) in degassed $(CH_2Cl)_2$ (25 ml) was heated under reflux under N_2 for 15 h. Workup and column chromatography gave **60** (0.28 g, 92%), which crystallized from Me_2CO/Et_2O as yellow crystals, m.p. 152–153°C. Anal. Found: C, 40.1; H, 2.9; N, 5.4. $C_{17}H_{15}F_6N_2OPRu$ Calc.: C, 40.1; H, 2.9; N, 5.5%. ν_{max}(film) 1480 (NO), 1452, 1417 (C=C), 837 cm^{-1} (PF). δ(H) 5.57 (s, Cp); 6.39 (t, *J* Hz, H(4)); 6.50 (dd, *J* 6.0, 5.7 Hz, H(3,5)); 6.50 (d, *J* 6.0 Hz, H(2,6)); 7.64 (dd, J_{obs} 8.0, 6.9 Hz, H(3',5')); 7.77 (tt, *J* 7.2, 1.3 Hz, H(4')); 8.27 (d, *J* 7.3 Hz, H(2',6')). δ(C) 82.0 (Cp); 84.1 (C(2,6)); 86.5 (C(3,5)); 86.8 (C(4)); 110.2 (C(1)); 123.3 (C(2',6')); 130.1 (C(3',5')); 134.1 (C(4')); 148.1 (C(1')).

3.35. [η⁶-(4-Chlorophenyl)(4'-chlorophenyl)azobenzene](η⁵-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphate(1 −) (61)

Complex **11** (0.27 g, 0.62 mmol) was added (50 mg h^{-1}) to a refluxing solution of 4,4'-dichloroazobenzene (**41**) [30] (0.16 g, 0.63 mmol) in $(CH_2Cl)_2$ (30 ml) under N_2 and the mixture was heated under reflux for 3 h. Workup and chromatography on alumina afforded **61** (0.14 g, 41%), which crystallized from Me_2CO/Et_2O as black crystals, m.p. 189–191°C. Anal. Found: C, 36.6; H, 2.6; N, 4.8. $C_{17}H_{13}Cl_2F_6N_2PRu$ Calc.: C, 36.3; H, 2.3; N, 5.0%. ν_{max}(film) 1495, 1439, 1417 (C=C), 837 cm^{-1} (PF). δ(H) 5.71 (s, Cp); 7.10 (dd, *J* 6.5, 1.3 Hz, H(3,5)); 7.18 (dd, *J* 6.5, 1.4 Hz, H(2,6)); 7.68 (dd, *J* 8.8, 2.0 Hz, H(3',5')); 7.99 (dd, *J* 8.8, 2.0 Hz, (H(2',6')). δ(C) 82.6 (C(2,6)); 84.7 (Cp); 88.6 (C(3,5)); 107.4 (C(4)); 116.4 (C(1)); 126.0 (C(2',6')); 130.7 (C(3',5')); 139.9 (C(4')); 151.3 (C(1')).

3.36. (η⁵-2,4-Cyclopentadien-1-yl)[η⁶-(4-methoxyphenyl)(4'-methoxyphenyl)azobenzene]ruthenium(1 +) hexafluorophosphate(1 −) (62)

Complex **11** (0.16 g, 0.37 mmol) was added (50 mg h^{-1}) over 3 h to a refluxing solution of 4,4'-di-

methoxyazobenzene (**42**) [31] (82 mg, 0.34 mmol) in $(CH_2Cl)_2$ (20 ml) under N_2 and the mixture was heated under reflux for 3.5 h. Workup and chromatography on alumina, with elution by CH_2Cl_2/hexanes (1:1) and then CH_2Cl_2, afforded **62** (0.10 g, 53%) which crystallized from Me_2CO/Et_2O as yellow crystals, m.p. 214–215°C. Anal. Found: C, 41.3; H, 3.7; N, 4.9. $C_{19}H_{19}F_6N_2O_2PRu$ Calc.: C, 41.2; H, 3.4; N, 5.1%. ν_{max}(film) 1503, 1450, 1416 (C=C), 1258 (C–O), 834 cm^{-1} (PF). δ(H) 3.95 (s, OCH_3); 3.96 (s, OCH_3); 5.57 (s, Cp); 6.66 (d, *J* 6.7 Hz, H(3,5)); 6.95 (d, *J* 6.7 Hz, H(2,6)); 7.16 (d, *J* 9.1 Hz H(3′,5′)); 7.93 (d, *J* 9.1 Hz, H(2′,6′)). δ(C) 56.4 (OCH_3); 58.1 (OCH_3); 75.1 (C(3,5)); 80.9 (C(2,6)); 81.9 (Cp); 115.6 (C(3′,5′)); 126.7 (C(2′,6′)); no signals due to quaternary carbons were detected.

3.37. *t-Butyl phenylimino-3-propanoate (43) and di-t-butyl phenylimino-3,3′-dipropanoate (44)*

A solution of benzenamine (4.2 ml, 46 mmol), t-butyl 2-propenoate (20 ml, 37 mmol) and copper(I) chloride (0.84 g, 8.5 mmol) in acetic acid (6.5 ml, 0.11 mol) was heated under reflux under N_2 for 24 h. The cooled solution was filtered, the filtrate was extracted with Et_2O and the extract was worked up to give a liquid. Column chromatography on silica gel, with hexanes/Et_2O (19:1) as eluant, gave **44** (4.0 g, 25%) as a yellow liquid. ν_{max}(neat) 1731 (CO), 1600, 1504 (C=C), 1368 (C–O), 747, 694 cm^{-1} (aryl H). δ(H) ($CDCl_3$) 1.44 (s, 18H, $C(CH_3)_3$); 2.50 (dd, *J* 7.5, 7.1 Hz, 4H, CH_2CO_2); 3.61 (dd, *J* 7.5, 7.1 Hz, 4H, NCH_2) 6.7 (m, H(2,4,6)); 7.23 (m, H(3,5)). δ(C) 20.1 ($C(CH_3)_3$); 33.6 (CH_2CO_2); 46.8 (NCH_2); 80.6 (($C(CH_3)_3$); 112.4 (C(2,6)); 116.6 (C(4)); 129.4 (C(3,5)); 146.9 (C(1)); 171.4 (CO); and **43** (1.66 g, 16%) as a yellow liquid. ν_{max}(neat) 3417 (NH), 1732 (CO), 1588, 1557, 1505 (C=C), 846, 763, 703 cm^{-1} (aromatics). δ(H) ($CDCl_3$) 1.44 (s, $C(CH_3)_3$); 2.49 (t, *J* 6.4 Hz, CH_2CO_2); 3.37 (t, *J* 6.4 Hz, NCH_2); 6.59 (dd, J_{obs} 8.6, 1.0 Hz H(2.6)); 7.69 (tt, *J* 7.4, 1.0 Hz, H(4)); 7.15 (dd, *J* 7.4, x 7.4 Hz, H(3,5)). δ(C) 28.0 ($C(CH_3)_3$); 35.0 (CH_2CO_2); 39.5 (NCH_2); 80.6 ($C(CH_3)_3$); 112.9 (C(2,6)); 117.4 (C(4)); 129.1 (C(3,5)); 147.7 (C(1)); 171.6(CO).

3.38. *[t-Butyl (η^6-phenyl)imino-3-propanoate](η^5-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphate(1 −) (63)*

A solution of complex **11** (0.10 g, 0.26 mmol) and t-butyl phenylimino-3-propanoate (**43**) (62 mg, 0.28 mmol) in $(CH_2Cl)_2$ (25 ml) was heated under reflux under N_2 for 15 h. Workup gave **63** (0.12 g, 91%) which after dissolution-reprecipitation with Me_2CO/Et_2O afforded pale brown crystals, m.p. 119–120°C. Anal. Found: C, 40.8; H, 4.8; N, 2.5. $C_{18}H_{24}F_6NO_2PRu$ Calc.: C, 40.6; H, 4.5; N, 2.6%. δ(H) 1.44 (s, $C(CH_3)_3$); 2.58 (t, *J* 6.4 Hz, CH_2CO_2); 3.41 (td, *J* 6.3, 6.2 Hz NCH_2); 5.33 (s, Cp); 5.93, (m, H(2,4,6)); 6.05 (m, H(3,5)). δ(C) 26.8 ($C(CH_3)_3$); 34.3 (CH_2CO_2); 39.5 (NCH_2); 69.3 (C(3,5)); 73.2 ($C(CH_3)_3$); 79.6 (Cp); 81.3 (C(4)); 84.4 (C(2,6)); 127.1 (C(1)); 171.2 (CO).

3.39. *(η^5-2,4-Cyclopentadien-1-yl[di-t-butyl(η^6-phenyl)imino-3,3′-dipropanoate]ruthenium(1 +) hexafluorophosphate(1 −) (64)*

A solution of complex **11** (52 mg 0.119 mmol) and di-t-butyl phenylimino-3,3′-dipropanoate (**44**) (50 mg, 0.14 mmol) in $(CH_2Cl)_2$ (15 ml) was heated under reflux N_2 for 16 h. Workup afforded **64** (56 mg, 71%) which after dissolution-reprecipitation with CH_2Cl_2/Et_2O gave pale brown crystals, m.p. 118–120°C. Anal. Found: C, 45.5; H, 5.8; N, 1.9. $C_{25}H_{36}F_6NO_4PRu$ Calc.: C, 45.5: H, 5.5: N, 2.1%) ν_{max}(film) 1713 (CO), 1555, 1470, 1415, 1371 (C=C), 1153 (C–O), 823 cm^{-1} (PF). δ(H) 1.45 (s, 18H, $C(CH_3)_3$); 2.65 (t, *J* 6.9 Hz, 4H, CH_2CO_2); 3.69 (t, *J* 6.9 Hz, 4H, NCH_2); 5.36 (s, Cp); 5.97 (m, H(2,4,6)); 6.10 (m, H(3,5)). δ(C) 28.2 ($C(CH_3)_3$); 32.8 (CH_2CO_2); 47.1 (NCH_2); 68.6 (C(3,5)): 79.8 (Cp); 81.2 (C(4)); 81.4 ($C(CH_3)_3$); 84.1 (C(2,6)); 127.1 (C(1)); 171.2 (CO).

3.40. *t-Butyl (2,3-dichlorophenyl)imino-3-propanoate (45)*

A mixture of 2,3-dichlorobenzenamine (3.01 g, 18.5 mmol), t-butyl 2-propenoate (13.5 ml, 92.3 mmol) and copper(I) chloride (0.55 g, 5.5 mmol) in acetic acid (10 ml) was heated under reflux under N_2 for 24 h. The cooled solution was filtered, the filtrate was extracted with ether, and the ether layer was worked up to give an oil which was chromatographed on silica gel. Elution with hexanes gave 2,3-dichlorobenzenamine (0.16 g), followed by **45** (0.54 g, 10%) which on vacuum distillation was obtained as a pale yellow liquid, b.p. (Kugelrohr) 215–220°C, 2 mmHg. δ(H) ($CDCl_3$) 1.46 (s, CMe_3); 2.55 (t, *J* 6.4 Hz, CH_2CO_2); 3.45 (td, *J* 6.3, 6.2 Hz, NCH_2); 4.84 (br s, NH); 6.56 (dd, *J* 8.2, 1.3 Hz, H(6)); 6.79 (dd, *J* 8.0, 1.3 Hz, H(4)); 7.07 (dd, *J* 8.2, 8.0 Hz, H(5)). δ(C) 28.1 ($C(CH_3)_3$); 35.0 (CH_2CO_2); 39.5 (NCH_2); 81.2 (CMe_3); 108.9 (C(6)); 117.4 (C(2)); 118.0 (C(4)); 127.7 (C(5)); 132.9 (C(3)); 145.1 (C(1)); 171.1 (CO).

3.41. *[t-Butyl (η^6-2,3-dichlorophenyl)imino-3-propanoate](η^5-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphate(1 −) (65)*

A solution of complex **11** (0.11 g, 0.26 mmol) and t-butyl (2,3-dichlorophenyl)imino-3-propanoate (**45**) (75

mg, 0.26 mmol) in $(CH_2Cl)_2$ (15 ml) was heated under N_2 for 14 h. Workup afforded **65** (0.13 g, 86%) which on dissolution-reprecipitation with Me_2CO/Et_2O gave grey crystals, m.p. 143–144°C. Anal. Found: C, 36.0; H, 3.4; N, 2.1. $C_{18}H_{22}Cl_2F_6NO_2PRu$ Calc.: C, 35.9; H, 3.7; N, 2.3%. ν_{max}(film) 3389 (NH), 1722 (CO), 1557, 1430 (C=C), 1158 (C–O), 838 cm^{-1} (PF). δ(H) 1.46 (s, CMe_3); 2.70 (t, *J* 6.5 Hz, CH_2CO_2); 3.60 (m, NCH_2); 5.45 (s, Cp); 6.07 (br s, NH); 6.21 (m, H(5,6)); 6.54 (d, *J* 5.0 Hz, H(4)). δ(C) 28.2 ($C(CH_3)_3$); 33.9 (CH_2CO_2); 40.0 (NCH_2); 66.6 (C(6)); 81.5 ($C(CH_3)_3$); 82.6 (C(4)); 83.2 (C(5)); 83.6 (Cp); 91.0 (C(2)); 105.0 (C(3)); 126.0 (C(1)); 171.3 (CO).

3.42. Di-t-butyl (2,3-dichlorophenyl)imino-3,3'-dipropanoate (46)

2,3-Dichlorobenzenamine (0.52 g, 3.23 mmol) in THF (5 ml) was added to a cooled (0°C) solution of sodium hydride (0.38 g, 7.94 mmol) and imidazole (47 mg, 0.69 mmol) in THF (5 ml) and the mixture was stirred for 5 min. t-Butyl 2-propenoate (1 ml, 6.84 mmol) was added, the solution warmed to room temperature, and stirred for 3 h. Workup gave mainly t-butyl (2,3-dichlorophenyl)imino-3-propanoate (**45**) (^{1}H NMR) as a yellow oil which was dissolved in THF (5 ml) and added to a cold solution of sodium hydride (0.29 g, 6.08 mmol) and imidazole (34 mg, 0.5 mmol) in THF (5 ml). The solution was stirred at room temperature for 5 min, t-butyl 2-propenoate (0.6 ml, 4.10 mmol) was added, and the mixture was stirred for 3 h. Workup gave an oil which was chromatographed on silica gel, with hexanes/CH_2Cl_2 (49:1) as eluant, to give the monoester **45** (0.31 g, 33%), and then with hexanes/CH_2Cl_2 (4:1) to give the diester **46** (0.21 g, 16%) as a pale yellow oil. ν_{max}(neat) 1728 (CO), 1589, 1504, 1455, 1367 (C=C), 1151 (C–O), 845, 762 cm^{-1} (aromatics). δ(H) ($CDCl_3$) 1.45 (s, CMe_3); 1.46 (s, CMe_3); 1.89 (m, CH_2CO_2); 2.32 (m, CH_2CO_2); 3.34 (m, 4H, NCH_2); 6.54 (dd, *J* 8.2, 1.3 Hz, H(6)); 6.78 (dd, *J* 8.0, 1.3 Hz, H(4)); 7.05 (dd, *J* 8.2, 8.0 Hz, H(5)). δ(C) 25.3 (CH_2CO_2); 28.1 ($C(CH_3)_3$); 30.4 (CH_2CO_2); 45.0 (NCH_2); 45.5 (NCH_2); 80.6 ($C(CH_3)_3$); 81.5 (CMe_3); 108.8 (C(6)); 117.2 (C(2)); 117.9 (C(4)); 127.7 (C(5)); 132.9 (C(3)); 145.0 (C(1)); 172.1 (CO)); 173.3 (CO). *m/z* 417/419/421 (16/10/1, M^+); 361/363/365 (9/5/1, $M-CH_2C(CH_3)_2$); 288/290/292 (28/21/3, $M-CH_2CH_2CO_2^tBu$); 174/176/178 (100/65/12, $C_6H_3Cl_2NCH_3$).

In one preparation, elution of the column with CH_2Cl_2/hexanes (1:1) gave *N*-(2,3-dichlorophenyl)-3-[(2,3-dichlorophenyl)amino]propanamide (ca. 1%) which crystallized from CH_2Cl_2/hexanes as a white solid, m.p. 123–124°C. Anal. Found: C, 47.8; H, 3.2; N, 7.5. $C_{15}H_{12}Cl_4N_2O$ Calc.: C, 47.6; H, 3.9; N, 7.4%. ν_{max}(film) 3408 (NH), 1699 (CO), 1586, 1505, 1456, 1404 (C=C), 762 cm^{-1} (aromatics). δ(H) ($CDCl_3$) 2.78 (t, *J* 6.1 Hz, CH_2CO); 3.64 (q, *J* 6.1 Hz, NCH_2); 4.89 (br t, J_{obs} 5.7 Hz, $NHCH_2$); 6.64 (dd, *J* 8.2, 1.3 Hz H(6')); 6.87 (dd, *J* 8.0, 1.3 Hz, H(4')); 7.09 (dd, *J* 8.2, 8.0 Hz, H(5')); 7.23 (m, H(4,5)); 7.99 (br s, NHCO); 8.27 (m, H(6)). δ(C) 36.7 (CH_2CO); 39.7 (NCH_2); 109.1 (C(6')); 117.9 (C(2')); 118.7 (C(4')); 119.8 (C(6)); 120.9 (C(2)); 125.5 (C(4)); 127.7 (C(5,5')); 132.7 (C(3)*); 133.1 (C(3')*); 135.8 (C(1)); 144.8 (C(1')); 169.4 (CO). *m/z* 376/378/380/382 (30/38/15/5, M^+); 174/176/178 (100/62/14, $C_6H_3Cl_2NHCH_2$); 161/163/165 (52/33/1, $C_6H_3Cl_2NHCH_2$).

3.43. (η^5-2,4-Cyclopentadien-1-yl)[di-t-butyl (η^6-2,3-dichlorophenyl)imino-3,3'-dipropanoate] ruthenium(1 +) hexafluorophosphate(1 −) (66)

A solution of complex **11** (0.18 g, 0.41 mmol) and di-t-butyl (2,3-dichlorophenyl)imino-3,3'-dipropanoate (**46**) (0.18 g, 0.42 mmol) in $(CH_2Cl)_2$ (15 ml) was heated under reflux N_2 for 15 h. Workup afforded **66** (0.25 g, 86%) as an unstable brown oil. ν_{max}(film) 1723 (CO), 1557, 1368, 1251 (C=C), 1154 (C–O, 839 cm^{-1} (PF). δ(H) 1.43 (s, 18H, CMe_3); 1.89 (m, CH_2CO_2); 2.36 (m, CH_2CO_2); 3.54 (m, 4H, NCH_2); 5.43 (s, Cp); 6.24 (m, H(5,6)); 7.56 (d, *J* 4.9 Hz, H(4)). δ(C) 25.9 (CH_2CO_2); 28.2 ($C(CH_3)_3$); 30.9 (CH_2CO_2); 44.4 (NCH_2); 45.6 (NCH_2); 80.5 (CMe_3); 80.6 (CMe_3); 82.8 (C(6)); 83.2 (C(4)); 83.6 (C(2,5)); 83.8 (Cp); 105.1 (C(3)); 126.3 (C(1)); 172.6 (CO); 173.5 (CO). *m/z* 582/584/586/588 (42/100/98/45, M^+); 526/528/530/532 (9/20/18/10, $M-CH_2C(CH_3)_2$); 470/472/474/476 (32/52/50/30, $M-2CH_2C(CH_3)_2$).

Attempted coupling of the complex **66** with 1,2-benzenediol and potassium carbonate in THF for 23 h was unsuccessful.

3.44. [(η^5-2,4-Cyclopentadien-1-yl)tetrahydro-1,3-dimethyl-(η^6-5-phenyl-)1,3,5-triazin-2(1H)-one]ruthenium(1 +) hexafluorophosphate (101)

A solution of **11** (156 mg, 0.36 mmol) and tetrahydro-1,3-dimethyl-5-phenyl-1,3,5-triazin-1(*1H*)-one (**100**) [19] (74 mg, 0.36 mmol) in $(CH_2Cl)_2$ (10 ml) was heated under reflux for 16 h. Chromatography on alumina gave **101** (134 mg, 100%) as a brown solid. Anal. Found: $M^{+\cdot}$ 372.0648. $C_{16}H_{20}N_3O^{102}Ru$ Calc.: 372.0650. ν_{max}(film) 1644 (urea, CO), 838 cm^{-1} (PF). δ(H) 2.94, s, CH_3; 4.91, s, CH_2; 5.32, Cp; 6.09, t, *J* 5.2 Hz, H(4'); 6.19, t, *J* 5.2 Hz, H(3',5'); 6.33, d, *J* 6.2 Hz, H(2',6'). δ(C) 32., (CH_3); 64.5 (CH_2); 74.0 (C(2',6')); 80.9 Cp; 83.3 (C(4'); 85.2 (C(3',5')); 122.3 (C(1')); 157.7 (CO). *m/z* 372 (M^+).

*3.45. [Hexahydro-1,3,5-bis(phenyl)(η^6-phenyl)-1,3,5-triazine]ruthenium(1 +) hexafluorophosphate(1 −) (**103**)*

Complex **11** (8 mg) and hexahydro-1,3,5-triphenyl-1,3,5-triazine (5.4 mg 0.017 mmol) were refluxed in degassed $(CH_2Cl)_2$ for 21 h. Workup afforded **103** (8.2 mg, 100%) as a brown residue. ν_{max}(film) 3399 (NH), 839 cm^{-1} (PF). δ(H) 3.88 s, CH_2; 5.30, s, Cp; 6.19, m, 6H, (H(2′, 3′,4′, 5′,6′)); 7.61,m, 10H, (H(2″,3″,4″,5″,6″)).

*3.46. 1-Azido-2,3-dichlorobenzene (**76**)*

A solution of sodium nitrite (1.30 g, 18 mmol) in water (5 ml) was added dropwise over 5 min to a cooled solution of 2,3-dichlorobenzenamine (2.88 g, 17 mmol) in concentrated hydrochloric acid (4 ml) and water (7 ml) and the mixture was stirred with cooling in an ice-bath for 1 h and filtered. A solution of sodium azide (1.10 g, 17 mmol) in water (5 ml) was added to the cooled filtrate and the mixture was stirred for 1 h. The solid was filtered off and crystallized from EtOH to afford **76** (1.25 g, 37%) as white needles, m.p. 59–61°C. ν_{max}(film) 2118 (N_3), 1574, 1449, 1428 (C=C), 769, 697 cm^{-1} (aromatics). δ(H) ($CDCl_3$) 7.04 (dd, *J* 6.2, 3.3 Hz, H(6)); 7.21 (m, H(4,5)). δ(C) 117.5 (C(6)); 123.7 (C(2)); 126.2 (C(4)); 127.5 (C(5)); 134.5 (C(3)); 139.1 (C(1)).

Attempted complexation of **76** by thermolysis with **11** gave a complicated mixture.

*3.47. (η^5-2,4-Cyclopentadien-1-yl)[(1,2,3,4,4a,10a-η)-dibenzo[b,e][1,4]dioxin]ruthenium(1 +) hexafluorophosphate(1 −) (**83**)*

A mixture of the complex **13** (94 mg, 0.20 mmol), 1,2-benzenediol (81) (49 mg, 0.45 mmol) and potassium carbonate (99 mg, 0.20 mmol) in THF (20 ml) was heated under reflux under N_2 for 23 h. The cooled solution was acidified with hydrochloric acid (6 mol l^{-1}), and stirred with an aqueous solution of ammonium(1 +) hexafluorophosphate(1 −) (66 mg, 0.41 mmoln for 20 min. Solvents were removed under reduced pressure and the residue was triturated with Et_2O, and then extracted with CH_2Cl_2 to afford **83** (89 mg, 55%) as a grey powder, m.p. 280–283°C (dec.). ν_{max}(film) 1490, 1466 (C=C), 1288 (C–O), 830 cm^{-1} (PF). δ(H) 5.51 (s, Cp) 6.16 (dd, *J* 4.2, 2.3 Hz, H(2,3)); 6.54 (dd, *J* 4.2, 2.3 Hz, H(1,4)); 7.03 (dd, *J* 6.1, 3.6 Hz, H(7,8)); 7.17 (dd, *J* 6.1, 3.6 Hz, H(6,9)). δ(C) 76.4 (C(1,4)); 82.2 (Cp); 83.7 (C(2,3)); 118.4 (C(6,9)); 119.6 (C(4a,10a)); 127.1 (C(7,8)); 140.0 (C(5a,9a)).

*3.48. (η^5-2,4-Cyclopentadien-1-yl)[methyl 5a,6,7,8,9a-η)dibenzo[b,e][1,4]dioxin-1-carboxylate]ruthenium-(1 +) hexafluorophosphate(1 −) (**84**)*

A mixture of complex **13** (0.28 g, 0.60 mmol), methyl-2,3-dihydroxybenzoate (**82**) [32] (0.13 g, 0.76 mmol), and potassium carbonate (0.12 g, 1.04 mmol) was heated under reflux in THF (30 ml) for 23 h. The solution was acidified with aqueous hydrochloric acid, an aqueous solution of ammonium(1 +) hexafluorophosphate(1 −) (0.21 g, 1.30 mmol) in water (5 ml) was added, and the mixture stirred for 15 min. Solvents were removed to leave a solid which was extracted into CH_2Cl_2 and precipitated with Et_2O to afford **84** (0.22 g, 65%) as a pale grey powder, m.p. 204–207°C. Anal. Found: C, 41.3; H, 2.6. $C_{19}H_{15}F_6O_4PRu$ Calc.: C, 41.2; H, 2.7%. ν_{max}(KBr) 1717 (CO), 1286 (C–O), 836 cm^{-1} (PF). δ(H) 3.91 (s, CH_3); 5.56 (s, Cp); 6.22 (d, *J* 4.2 Hz, H(7)*); 6.23 (d, *J* 4.2 Hz, H(8)*); 6.64 (dd, *J* 4.2, 2.3 Hz, H(6)); 6.66 (dd, *J* 4.2, 2.3 Hz, H(9)); 7.28 (d, *J* 5.2 Hz, H(2,4)); 7.62 (t, *J* 5.2 Hz, H(3)). δ(C) 52.8 (CH_3); 76.5 (C(9)*); 76.7 (C(6)*); 82.4 (Cp); 83.9 (C(7)#); 83.9 (C(8)#); 119.1 (C(5a)+); 119.5 (C(9a)+); 121.8 (C(1)); 122.0 (C(4)); 126.3 (C(3)); 128.6 (C(2)); 139.7 (C(4a)); 140.8 (C(10a)); 164 (CO).

*3.49. (η^5-2,4-Cyclopentadien-1-yl)[1,2,3,4,4a,10a-η)-1-N,N-dimethylaminodibenzo[b,e][1,4]dioxin]ruthenium-(1 +) hexafluorophosphate(1 −) (**85**)*

A mixture of the complex **56** (0.21 g, 0.43 mmol), 1,2-benzenediol (73 mg, 0.66 mmol), and potassium carbonate (0.14 g, 0.99 mmol) was heated under reflux in THF (15 ml) under Ar for 20 h. The cooled solution was acidified with hydrochloric acid (6 mol l^{-1}), a solution of ammonium(1 +) hexafluorophosphate(1 −) (0.11 g, 0.66 mmol) in water (1 ml) was added, and the solution was stirred for 15 min. Workup as above gave **85** (0.13 g, 57%) which crystallized from CH_2Cl_2 as a pale grey crystalline solid, m.p. 169–170°C. Anal. Found: C, 42.0; H, 3.5; N, 2.4. $C_{19}H_{18}F_6NO_2PRu$ Calc.: C, 42.4; H, 3.4; N, 2.6%. ν_{max}(film) 1537, 1486, 1434 (C=C), 1276, 1105 (C–O), 838 cm^{-1} (PF). δ(H) 2.99 (s, 6H, Me); 5.41 (s, Cp); 5.94 (t, *J* 5.9 Hz, H(3)); 6.07 (d, *J* 5.9 Hz, H(2)); 6.25 (d, J_{obs}5.4 Hz, H(4)); 7.05 (m, H(9)); 7.20 (m, H(6,7,8)). δ(C) 43.7 (CH_3); 72.5 (C(4)); 75.6 (C(2)); 80.0 (Cp); 80.1 (C(3)); 115.7 (C(4a,10a)); 117.7 (C(6)#); 118.1 (C(9)#); 126.7 (C(1)); 126.8 (C(7)*); 127.0 (C(6)*); 140.4 (C(9a)+); 140.5 (C(5a)+).

*3.50. (η^5-2,4-Cyclopentadien-1-yl)[methyl (5a,6,7,8,9,9a-η)-6-N,N-dimethylaminodibenzo[b,e][1,4]dioxin-1-carboxylate]ruthenium(1 +) hexafluorophosphate(1 −) (**86**)*

A mixture of complex **56** (96 mg, 0.19 mmol), methyl 2,3-dihydroxybenzoate (**82**) (58 mg, 0.35 mmol),

and potassium carbonate (95 mg, 0.69 mmol) was heated under reflux in THF (15 ml) under N_2 for 50 h. The cooled solution was acidified with hydrochloric acid (6 mol l^{-1}) and stirred with an aqueous solution of ammonium(1 +) hexafluorophosphate(1 −) (35 mg, 0.21 mmol) for 15 min. The mixture was worked up to give a black powder, which was chromatographed on alumina. Elution with CH_2Cl_2/EtOH (49:1) afforded a mixture (7:13) (42 mg) of the complexes **56** and **86**, which were separated by isopiestic recrystallisation with Me_2CO/Et_2O to yield **86** (26 mg, 23%) as green needles, m.p. 240–242°C. Anal. Found: C, 42.5; H, 3.4; N, 2.0. $C_{21}H_{20}F_6NO_4PRu$ Calc.: C, 42.3; H, 3.4; N, 2.3%. ν_{max}(film) 1715 (CO), 1541, 1458, 1436 (C=C), 1283 (C–O), 837 cm^{-1} (PF). δ(H) 3.09 (s, NMe_2); 3.91 (s, CO_2CH_3); 5.50 (s, Cp); 6.03 (t, *J* 5.5 Hz, H(8)); 6.13 (d, J_{obs} 5.8 Hz, H(7)); 6.32 (d, *J* 5.5 Hz, H(9)); 7.29 (m, H(3,4)); 7.65 (dd, *J* 6.4, 3.2 Hz, H(2)). δ(C) 42.8 ($N(CH_3)_2$); 52.9 (CO_2CH_3); 52.9 (CO_2CH_3); 67.9 (C(9)); 74.3 (C(7)); 80.2 (C(8)); 80.4 (Cp); 118.8 (C(5a)*); 119.4 (C(9a)*); 121.9 (C(4)); 122.1 (C(1)); 126.2 (C(3,6)); 128.4 (C(2)); 140.2 (C(4a)#); 140.9 (C(10a)#); 164.7 (CO).

3.51. Dibenzo[b,e][1,4]dioxin (88)

A solution of complex **83** (0.16 g, 0.31 mmol) in CH_3CN (50 ml) was degassed with a stream of N_2 for 10 min, and irradiated with a sunlamp (Wotan, Ultra Vitalux, 300 W) for 23 h. Solvent was removed and the residue was extracted into Et_2O to afford **88** (48 mg, 83%) as white crystals, m.p. 114–116°C (lit. [33] 119°C). ν_{max}(film) 1590, 1496, 1465 (C=C), 1289 (C–O), 743 cm^{-1} (aromatics). Correct ^{1}H NMR [34], ^{13}C NMR [34], and mass [35] spectra.

3.52. Methyl dibenzo[b,e][1,4]dioxin-1-carboxylate (89)

A solution of complex **84** (87 mg, 0.16 mmol) in degassed CH_3CN (40 ml) was irradiated through quartz for 3 h using a Rayonet photo reactor with a medium pressure (3000 Å) mercury lamp. Solvent was removed under reduced pressure to leave an oil which was triturated with ether to afford **89** (36 mg, 95%) as white crystals, m.p. 85–87°C (lit.[36] 92–94°C). ν_{max}(film) 1732 (CO), 1596 (C=C), 1292 (C–O), 843, 808, 750 cm^{-1} (aromatics). Correct ^{1}H NMR [37], ^{13}C NMR [1], and mass [1] spectra.

Workup of the residue and ^{1}H NMR examination showed the presence of complex **11**. Repetition of the reaction but with radiation from a sunlamp for 18 h afforded **89** (67%).

3.53. 1-N,N-Dimethylaminodibenzo[b,e][1,4]dioxin (90)

A degassed solution of complex **85** (67 mg, 0.13 mmol) in CH_3CN (30 ml) was photolysed with a sunlamp under N_2 for 5 h. Workup gave **90** (5.4 mg, 19%) as a colourless oil. ν_{max}(film) 1496, 1466 (C=C), 1280 (C–O), 838, 748 cm^{-1} (aromatics). δ(H) ($CDCl_3$) 2.87 (s, Me_2); 6.55 (dd, *J* 8.1, 1.6 Hz, H(6)); 6.62 (dd, *J* 8.3, 1.6 Hz H(9)); 6.88 (m, H(4,7,8)); 6.97 (dd, *J* 4.7, 4.1 Hz, H(3)); 7.13 (d, *J* 4.7 Hz H(2)).

3.54. Methyl 6-N,N-dimethylaminodibenzo[b,e][1,4]dioxin-1-carboxylate (91)

A degassed solution of complex **86** (30 mg, 0.05 mmol) in CH_3CN (50 ml) was photolysed under N_2 for 24 h by use of a sunlamp. Workup gave **91** (6 mg, 42%) as a colourless oil. ν_{max}(film) 1723 (CO), 1464 (C=C), 1268 (C–O), 749, 710 cm^{-1} (aromatics). δ(H) ($CDCl_3$) 2.89 (s, NMe_2) 3.92 (s, CO_2CH_3)); 6.45 (dd, *J* 8.0, 1.4 Hz, H(7)); 6.57 (dd, *J* 8.2, 1.4 Hz, H(9)); 6.82 (dd, *J* 8.2, 8.0 Hz, H(8)); 6.89 (dd, *J* 7.6, 8.0 Hz, H(3)); 6.97 (dd, *J* 8.0, 2.1 Hz, H(4)); 7.44 (dd, *J* 7.6, 2.1 Hz, H(2)). δ(C) ($CDCl_3$) 43.2 (NMe_2); 52.2 (CO_2CH_3); 109.2 (C(9)); 113.4 (C(4)); 120.0 (C(1)); 120.1 (C(3)); 122.8 (C(7)); 123.6 (C(2)); 125.9 (C(8)); 142.3 (C(4a,5a,9a,10a)); 165.3 (C(6)); 189.5 (CO). *m/z* 285 (100, M^+); 270 (35, M^+-CH_3).

3.55. (η^5-2,4-Cyclopentadien-1-yl)[1,2,3,4,4a,10a-η)-2-(2-acetylaminoethyl)dibenzo[b,e][1,4]dioxin]ruthenium(1 +) hexafluorophosphate(1 −) (87)

A mixture of the alumina-chromatographed (CH_2Cl_2) complex **54** (0.54 g, 0.34 mmol), 1,2-benzenediol (0.11 g, 1.0 mmol), and potassium carbonate (90 mg, 0.64 mmol) in THF (25 ml) was heated under reflux under Ar for 24 h. The cooled solution was acidified with hydrochloric acid (6 mol l^{-1}), a solution of ammonium(1 +) hexafluorophosphate(1 −) (56 mg, 0.34 mmol) in water (0.5 ml) was added, and the mixture was stirred for 15 min. Workup and column chromatography on alumina using CH_2Cl_2/EtOH (19:1) as eluent gave **87** (89 mg, 46%) as a brown oil. ν_{max} 3390 (NH), 1694 (CO), 1556, 1535, 1520 (C=C); 1288 (C–N), 760 cm^{-1} (PF). δ(H) 1.89 (s, (CH_3); 3.44 (m, CH_2); 3.79 (m, CH_ACH_BN); 3.89 (m, CH_ACH_BN); 5.54 (s, Cp); 6.31 (d, *J* 5.7 Hz, H(4)*); 6.56 (d, *J* 5.7 Hz, H(3)*); 6.78 (s, H(1)); 7.05 (m, H(6,9)); 7.17 (m, H(7,8)). δ(C) 23.0 (CH_3); 33.8 (CH_2); 40.4 (CH_2N); 75.8 (C(4)); 77.6 (C(3)); 78.4 (C(2)); 82.5 (Cp); 84.7 (C(1)); 118.1 (C(6)*); 118.2 (C(9)*); 118.8 (C(4a)#); 119.1 (C(10a)#); 127.0 (C(7,8)); 134.6 (C(5a)); 140.0 (C(9a)); 170.6 (CO).

3.56. 2-(2-Acetylaminoethyl)dibenzo[b,e][1,4]dioxin (92)

A degassed solution of complex **87** (40 mg, 0.069 mmol) in CH_3CN (35 ml) was photolysed at 3000 Å for 5 h. Workup afforded **92** (17 mg, 92%) as a yellow oil.

ν_{max}(film) 3362 (NH), 2958, 2928 (CH), 1723 (CO), 1654, 1540, 1471, 1378 (C=C), 1289 cm^{-1} (C–O). δ(H) ($CDCl_3$) 2.01 (s, CH_3); 2.72 (t, *J* 7.0 Hz, CH_2); 3.45 (m, CH_2NH); 5.57 (br s, NH); 7.01 (d, *J* 8.2 Hz, H(4)); 7.29 (br s, H(1)); 7.42 (m, H(3,7,8)); 7.43 (d, *J* 8.1 Hz, H(6,9)).

*3.57. 3-Nitro-1,2-benzenediol (**93**) and 4-nitro-1,2-benzenediol (**94**)*

Fuming nitric acid (2.5 ml) was added dropwise to a stirred cooled (0°C) solution of 1,2-benzenediol (0.53 g, 59 mmol) in Et_2O (150 ml) and the solution was warmed to room temperature and stirred for 22 h. Workup and column chromatography on silica gel, with hexanes/Et_2O (1:1) as eluant, gave a solid, which was triturated with chloroform to afford the 3-nitro isomer **93** (4.4 g, 48%) as a red-brown powder, m.p. 83–84°C (lit. [38] 84°C). ν_{max}(film) 3478 (OH), 1620 (C=C), 1546, 1367 (NO_2), 1238 (C–O), 842 (CN), 799, 738 cm^{-1} (aromatics). δ(H) ($CDCl_3$) 5.94 (br s, 3-OH); 6.91 (dd, *J* 8.6, 8.0 Hz, H(5)); 7.24 (dd, *J* 8.0, 1.5 Hz, H(4)); 7.65 (dd, *J* 8.6, 1.5 Hz, H(6)); 10.62 (br s, 2-OH). δ(C) ($CDCl_3$) 115.8 (C(6)); 119.7 (C(4)); 121.7 (C(5)); 142.8 (C(2)); 145.5 (C(1,3)).

The residue was triturated with Et_2O to give 4-nitro-1,2-benzenediol (**94**) (1.67 g, 18%) as a yellow powder, m.p. 160–162°C (lit. [35] 176°C). ν_{max}(film) 3288 (OH), 1592, 1505, 1337 (NO_2), 1286 (C–O), 874 (CN), 791, 747 cm^{-1} (aromatics). δ(H) 6.99 ($CDCl_3$) (d, *J* 9.5 Hz, H(6)); 7.70 (m, H(3,5)); 9.09 (br s, 1,2-OH). δ(C) 113.3 (C(3)); 115.6 (C(5)); 117.6 (C(6)); 141.6 (C(4)); 145.9 (C(2)); 152.8 (C(1)).

3.58. 3-Nitro-1,2-benzenediol diacetate

A solution of 3-nitro-1,2-benzenediol (**93**) (0.79 g, 5.12 mmol) in acetic anhydride (8 ml) and sulfuric acid (0.5 ml) was stirred for 1 h, ice (ca. 10 g) was added and the resulting precipitate worked up to afford 3-nitro-1,2-benzenediol diacetate (0.85 g, 69%), which crystallized from EtOH as white crystals, m.p. 70–70.5°C (lit. [39] 67–68°C). ν_{max}(film) 1778 (CO), 1537, 1358 (NO_2), 1198 (C–O), 821, 804, 739 cm^{-1} (aromatics). δ(H) ($CDCl_3$) 2.32 (s, CH_3); 2.36 (s, CH_3); 7.39 (t, *J* 8.2 Hz, H(5)); 7.49 (dd, *J* 8.2, 1.8 Hz, H(4)); 7.97 (dd, *J* 8.2, 1.8 Hz, H(6)). δ(C) ($CDCl_3$) 20.3 (CH_3); 20.4 (CH_3); 122.7 (C(4)); 126.0 (C(6)); 128.9 (C(5)); 136.9 (C(3)); 142.8 (C(2)); 144.2 (C(1)); 167.2 (CO); 167.7 (CO).

Attempts to form 3-amino-1,2-benzenediol diacetate by hydrogenation of the nitrodiacetate were unsuccessful.

*3.59. 4-N-Acetylamino-1,2-benzenediol diacetate (**96**)*

A mixture of 4-nitro-1,2-benzenediol diacetate (**95**) [36] (0.88 g, 3.66 mmol) and 10% palladium–carbon (100 mg) in ethanol (20 ml) was kept under hydrogen at 40 psi for 2.5 h. The solution was filtered, the residue rinsed with ethyl acetate, and the solvent was removed from the filtrate to leave an oil, which was dissolved in acetic anhydride (4 ml) and stirred for 21 h. Workup gave **96** (0.65 g, 75%) as a pale brown powder, m.p. 143–144°C. ν_{max}(film) 1771 (CO), 1684 (CO), 1505, 1372, 1209, 1189 cm^{-1} (C=C). δ(H) ($CDCl_3$) 2.06 (s, CH_3); 2.08 (s, CH_3); 2.27 (s, $NHCOCH_3$); 6.99 (d, *J* 8.8 Hz, H(6)); 7.09 (dd, *J* 8.8, 2.3 Hz, H(5)); 7.57 (d, *J* 2.3 Hz, H(2)); 8.00 (br s, NH). δ(C) 20.6 (CH_3); 24.1 ($NHCOCH_3$); 114.9 (C(2)); 117.6 (C(6)); 123.2 (C(5)); 136.6 (C(1)); 137.8 (C(4)); 141.8 (C(3)); 168.6 (CO); 169.0 (CO); 176.0 (NHCO). *m/z* 251 (10, M^+); 209 (37, M–CH_2CO); 167 (100 M–CH_2CO); 125 (98, M–3CH_2CO).

*3.60. 4-N-Acetylamino-1,2-benzenediol (**97**)*

Sodium hydrogencarbonate (0.47 g, 5.61 mmol) in water (4 ml) was added to a solution of 4-*N*-acetylamino-1,2-benzenediol diacetate (**96**) (0.65 g, 2.57 mmol) in methanol (10 ml) and the mixture was stirred under N_2 for 2 h, acidified with hydrochloric acid (6 mol l^{-1}), and concentrated to leave a solid. This was extracted into ethyl acetate, to afford **97** (0.39 g, 91%) as a brown crystalline solid, m.p. 148–153°C (lit. [40] 182–184°C). ν_{max}(film) 3288 (br OH), 1651 (CO), 1631, 1566, 1520, 1434, 1372 (C=C), 1282, 1246 cm^{-1} (C–O). δ(H) ($CDCl_3$) 2.08 (s, CH_3); 6.71 (d, *J* 8.5 Hz, H(6)); 6.79 (dd, *J* 8.5, 2.0 Hz, H(5)); 7.45 (d, *J* 2.0 Hz, H(2)); 7.99 (br s, OH) 9.02 (br s, OH). δ(C) 24.0 (CH_3); 108.6 (C(2)); 111.6 (C(6)); 115.7 (C(5)); 132.8 (C(1)); 142.1 (C(4)); 145.7 (C(3)); 169.0 (CO).

Attempts to prepare [(5a,6,7,8,9,9a-η)-2-acetylaminodibenzo[*b*,*e*][1,4]dioxin](η^5-2,4-cyclopentadien-1-yl)ruthenium(1 +) hexafluorophosphate(1 −) from the complex **13** and **97** were unsuccessful.

3.61. N-[2-(3,4-Dihydroxybenzene)ethyl]acetamide

A mixture of 4-(2-aminoethyl)-1,2-benzenediol hydrochloride (0.45 g, 2.37 mmol), *N*-methoxydiacetamide [20] (0.62 g, 4.71 mmol), and sodium acetate (0.24 g, 2.88 mmol) in DMF (7 ml) was stirred at room temperature for 4.5 h. Water (25 ml) was added to the mixture, which was extracted with ethyl acetate to afford *N*-[2-(3,4-dihydroxybenzene)ethyl]acetamide (0.14 g, 31%), which was dissolved in the minimum amount of MeOH with gentle heating and precipitated as a cream solid by the addition of Et_2O. It was used immediately. ν_{max}(film) 3289 (br OH), 1656 (CO), 1557, 1434, 1371 (C=C), 1288 cm^{-1} (C–O). The product was too insoluble ($CDCl_3$) to obtain adequate NMR data.

3.62. [(5a,6,7,8,9,9a-η)-2-(2-Acetylaminoethyl)dibenzo[b,e][1,4]dioxin](η^5-2,4-cyclopentadien-1-yl)ruthenium-(1 +) hexafluorophosphate(1 −) (99)

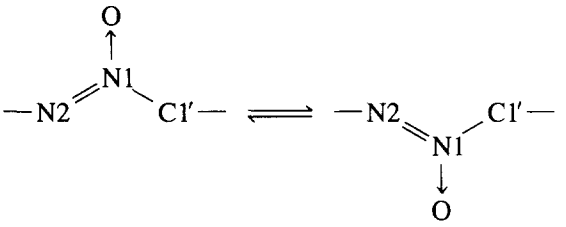
A mixture of complex **13** (0.43 g, 0.94 mmol), *N*-[2-(3,4-dihydroxybenzene)ethyl]acetamide (0.13 g, 0.79 mmol), and potassium carbonate (0.24 g, 3.92 mmol) in DMF (10 ml) was stirred at room temperature, under N_2 for 15 h. The solution was acidified with hydrochloric acid (6 mol l^{-1}) and then stirred with aqueous ammonium(1 +) hexafluorophosphate(1 −) (0.15 g, 0.94 mmol) for 15 min. The volume was reduced to ca. 5 ml, and the product was extracted into CH_2Cl_2 to give an oil which was chromatographed on alumina. Elution with CH_2Cl_2/EtOH (9:1) afforded **99** (64 mg, 15%) as a dark brown solid. ν_{max}(film) 3123 (NH), 1654 (CO), 1492, 1417 (C=C), 1296 (C–O), 838 cm^{-1} (PF). δ(H) 1.82 (s, CH_3); 2.74 (br t, CH_2); 3.39 (m, CH_2NH); 5.50 (s, Cp); 6.17 (m, H(7,8)); 6.56 (m, H(6,9)); 6.94 (d, *J* 1.8 Hz, H(1)); 6.96 (d, *J* 8.3 Hz, H(4)); 7.02 (dd, *J* 8.3, 1.8 Hz, H(3)); 7.10 (br s, NH). δ(C) 22.9 (CH_3); 35.7 (CH_2); 40.8 (CH_2NH); 76.6 (C(6,9)); 82.1 (Cp); 83.7 (C(7)*); 83.7 (C(8)*); 117.7 (C(1)#); 118.2 (C(4)#); 119.7 (C(9a)); 119.9 (C(5a)); 127.3 (C(3)); 138.5 (C(4a)); 139.5 (C(2)); 139.9 (C(10a)); 170.0 (CO).

3.63. 2-(2-Acetylaminoethyl)dibenzo[b,e][1,4]dioxin (92)

A degassed solution of the complex **99** (38 mg, 0.067 mmol) in CH_3CN (20 ml) was photolysed using a 3000 Å lamp in a Rayonet photo-reactor, under N_2 for 3 h. Workup gave **92** (8 mg, 46%) as a pale brown oil (correct IR and NMR data).

Table 5
Crystal data and intensity collection parameters for **60**

Empirical formula	$C_{17}H_{15}F_6N_2OPRu$
Formula weight	509.35
Temperature	295(1) K
Wavelength	0.71070 Å (graphite monochromator)
Crystal system	Triclinic
Space group	$P\bar{1}$
a	8.572(3) Å
b	10.719(1) Å
c	11.207(4) Å
α	81.41(2)°
β	68.82(2)°
γ	70.43(2)°
Volume	904.2(4) Å^3
Z	2
μ	1.01 mm^{-1}
Density (calculated)	1.87 Mg m^{-3}
Reflections collected	4215
Unique reflections	4019 (R_{int} = 0.012)
Observed data	4154 $I > 3\sigma(I)$
Final *R* indices	R_1 = 0.0464, wR_2 = 0.0523



Scheme 3.

4. X-ray crystal structure for 60

Crystals of diffraction quality for complex **60** were prepared by vapour diffusion. The data were corrected for distortion based on psi scan measurements. Unit cell and intensity data were recorded at room temperature on a Nonius CAD-4 diffractometer. The space group $P\bar{1}$ was assumed from intensity statistics and verified by subsequent structure solution. Pertinent crystal data are given in Table 5. The structure was solved by conventional Patterson and electron density maps, and refined using full-matrix least-squares on *F* using SHELX-76 [41]. Hydrogen atoms were included in calculated positions with isotropic temperature factors tied to one of two common variables. Other atoms were assigned anisotropic thermal parameters. The azoxy group was

Table 6
Atomic coordinates for **60**

Atom	*x*	*y*	*z*	U_{iso}
Ru	0.04083(5)	0.23116(4)	0.17810(4)	0.0480(2)
P	0.2304(2)	0.64968(15)	0.20894(16)	0.0667(8)
F1	0.0574(6)	0.7201(7)	0.1821(6)	0.165(6)
F2	0.3314(8)	0.7112(6)	0.0817(6)	0.138(4)
F3	0.4037(8)	0.5780(7)	0.2380(99)	0.177(6)
F4	0.2629(11)	0.5261(6)	0.1402(7)	0.173(6)
F5	0.1206(9)	0.5893(6)	0.3368(6)	0.137(4)
F6	0.1892(11)	0.7735(6)	0.2861(6)	0.168(5)
O1A	−0.1403(12)	0.0018(8)	0.4691(9)	0.090(5)
O1B	−0.3247(16)	0.0385(9)	0.2223(9)	0.103(6)
N1A	−0.2276(9)	0.0038(9)	0.3991(7)	0.048(4)
N1B	−0.2915(11)	0.0064(10)	0.3250(8)	0.058(5)
N2	−0.2486(10)	0.0802(8)	0.3435(11)	0.126(6)
C1	−0.2069(6)	0.1963(5)	0.3075(5)	0.059(2)
C2	−0.1343(7)	0.2463(5)	0.3797(5)	0.061(2)
C3	−0.0950(8)	0.3661(6)	0.3411(6)	0.073(3)
C4	−0.1215(7)	0.4371(5)	0.2312(7)	0.071(3)
C5	−0.1953(8)	0.3895(5)	0.1614(7)	0.077(3)
C6	−0.2372(7)	0.2709(6)	0.1982(6)	0.075(3)
C7	0.2868(11)	0.2370(8)	0.0327(12)	0.095(5)
C8	0.2083(13)	0.1581(14)	−0.0082(7)	0.113(7)
C9	0.2061(11)	0.0502(7)	0.0781(10)	0.091(5)
C10	0.2716(10)	0.0616(10)	0.1639(10)	0.091(5)
C11	0.3231(9)	0.1743(13)	0.1347(12)	0.115(7)
C1′	0.3079(7)	−0.1124(5)	0.4039(5)	0.058(3)
C2′	−0.2677(9)	−0.1881(8)	0.5033(7)	0.090(4)
C3′	−0.3167(13)	−0.2989(10)	0.5395(10)	0.107(6)
C4′	−0.4036(17)	−0.3291(10)	0.474(2)	0.146(11)
C5′	−0.4434(16)	−0.261(2)	0.3880(17)	0.182(14)
C6′	−0.3991(10)	−0.1495(15)	0.3437(7)	0.117(7)

Table 7
Interatomic distances for **60**

Atom–atom	Distance (Å)	Atom–atom	Distance (Å)
C1–Ru	2.213(5)	C1′–N1A	1.598(11)
C2–Ru	2.209(5)	N2–N1B	1.050(11)
C3–Ru	2.216(6)	C1′–N1B	1.455(12)
C4–Ru	2.214(6)	C1–N2	1.372(9)
C5–Ru	2.211(6)	C2–C1	1.430(8)
C6–Ru	2.208(5)	C6–C1	1.416(9)
C7–Ru	2.163(7)	C3–C2	1.403(8)
C8–Ru	2.146(8)	C4–C3	1.398(10)
C9–Ru	2.165(7)	C5–C4	1.403(9)
C10–Ru	2.166(7)	C6–C5	1.399(9)
C11–Ru	2.171(7)	C8–C7	1.449(16)
F1–P	1.537(5)	C11–C7	1.320(15)
F2–P	1.558(5)	C9–C8	1.392(15)
F3–P	1.554(6)	C10–C9	1.315(14)
F4–P	1.525(5)	C11–C10	1.376(15)
F5–P	1.586(6)	C2′–C1′	1.356(10)
F6–P	1.563(5)	C6′–C1′	1.377(14)
N1A–O1A	1.259(11)	C3′–C2′	1.349(14)
N1B–O1B	1.256(12)	C4′–C3′	1.35(2)
N2–O1B	1.867(15)	C5′–C4′	1.20(2)
N1B–N1A	1.141(12)	C6′–C5′	1.35(2)
N2–N1A	0.960(12)		

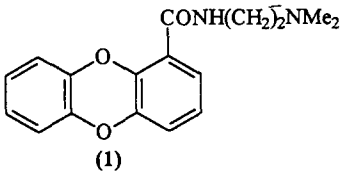
found to be disordered randomly between two orientations (Scheme 3), and N1 and O were each refined as two separate half-atoms.

The final R factor was 0.0464 for 4154 observed reflections [$I > 3\sigma(I)$]. Atomic positions are listed in Table 6. Tables of calculated hydrogen positions and anisotropic thermal parameters and full lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

5. Description of the crystal structure

The complex **60** is monomeric, with the geometry shown in Fig. 1. Only one of the two possible N1–O positions is shown. Important bond distances and angles are listed in Table 7. The average Ru–C(cyclopentadiene) and Ru–C(aryl) distances are 2.162(4) and 2.212(1) Å, respectively.

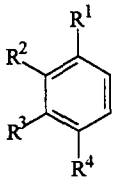
6. Appendix A



(1)

$(MeCN)_3\overset{+}{R}uCp\ PF_6^-$

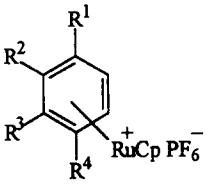
(11)



(2: R^1 = Cl, $R^2 = R^3 = R^4$ = H
3: $R^1 = R^2$ = Cl, $R^3 = R^4$ = H
4: $R^1 = R^4$ = Cl, $R^2 = R^3$ = H
5: $R^1 = R^2 = R^3$ = Cl, R^4 = H
6: $R^1 = R^2 = R^4$ = Cl, R^3 = H
7: R^1 = Br, $R^2 = R^3 = R^4$ = H
8: R^1 = I, $R^2 = R^3 = R^4$ = H
9: $R^1 = IO_2$, $R^2 = R^3 = R^4$ = H
10: $R^1 = R^2$ = Cl, R^3 = H, R^4 = I
27: $R^1 = NH_2$, $R^2 = R^3 = R^4$ = H
28: $R^1 = NH_2$, $R^2 = R^3$ = Cl, R^4 = H
29: $R^1 = NH_2$, $R^3 = R^4$ = Cl, R^4 = H
30: $R^1 = R^2 = NH_2$, $R^3 = R^4$ = H
31: $R^1 = R^2 = NH_2$, R^3 = H, R^4 = Cl
32: R^1 = NHCOMe, $R^2 = R^3$ = Cl, R^4 = H
33: R^1 = $NHCOCF_3$, $R^2 = R^3$ = Cl, R^4 = H
34: $R^1 = R^2$ = Cl, R^3 = H, $R^4 = CH_2CH_2NHCOMe$

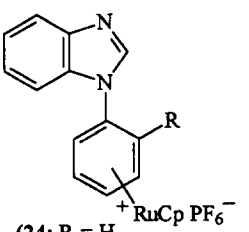
35: $R^1 = NMe_2$, $R^2 = R^3 = R^4$ = H
36: $R^1 = NMe_2$, $R^2 = R^3$ = Cl, R^4 = H
37: $R^1 = N(CH_2CH{=}CH_2)_2$, $R^2 = R^3 = R^4$ = H
43: $R^1 = NHCH_2CH_2CO_2Bu^t$, $R^2 = R^3 = R^4$ = H
44: $R^1 = N(CH_2CH_2CO_2Bu^t)_2$, $R^2 = R^3 = R^4$ = H
45: $R^1 = NHCH_2CH_2CO_2Bu^t$, $R^2 = R^3$ = Cl, R^4 = H
46: $R^1 = N(CH_2CH_2CO_2Bu^t)_2$, $R^2 = R^3$ = Cl, R^4 = H
71: $R^1 = N(CH_2CH{=}CH_2)_2$, $R^2 = R^3$ = Cl, R^4 = H
75: $R^1 = R^2$ = Cl, R^3 = H, R^4 = N = C (Cl) CF_3
76: $R^1 = N_3$, $R^2 = R^3$ = Cl, R^4 = H
81: $R^1 = R^2$ = OH, $R^3 = R^4$ = H
82: $R^1 = R^2$ = OH, $R^3 = CO_2Me$, R^4 = H
93: $R^1 = R^2$ = OH, $R^3 = NO_2$, R^4 = H
94: $R^1 = R^2$ = OH, R^3 = H, $R^4 = NO_2$
95: $R^1 = R^2$ = OCOMe, R^3 =H, $R^4 = NO_2$
96: $R^1 = R^2$ = OCOMe, R^3 = H, R^4 = NHCOMe
97: $R^1 = R^2$ = OH, R^3 = H, R^4 = NHCOMe
98: $R^1 = R^2$= OH, R^3 = H, $R^4 = (CH_2)_2NHCOMe$

7. Appendix B

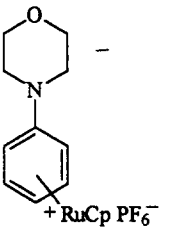


12: R^1 = Cl, $R^2 = R^3 = R^4$ = H
13: $R^1 = R^2$ = Cl, $R^3 = R^4$ = H
14: $R^1 = R^4$ = Cl, $R^2 = R^3$ = H
15: $R^1 = R^2 = R^3$ = Cl, R^4 = H
16: $R^1 = R^2 = R^4$ = Cl, R^3 = H
17: R^1 = Br, $R^2 = R^3 = R^4$ = H
18: R^1 = I, $R^2 = R^3 = R^4$ = H
19: $R^1 = IO_2$, $R^2 = R^3 = R^4$ = H
20: $R^1 = R^2$ = Cl, R^3 = H, R^4 = I
21: R^1 = OMe, $R^2 = R^3 = R^4$ = H
22: $R^1 = N_3$, $R^2 = R^3 = R^4$ = H
23: R^1 = NHBu, R^2 = Cl, $R^3 = R^4$ = H
47: $R^1 = NH_2$, $R^2 = R^3 = R^4$ = H
48: $R^1 = NH_2$, $R^2 = R^3$ = Cl, R^4 = H
49: $R^1 = NH_2$, $R^3 = R^4$ = Cl, R^2 = H
50: $R^1 = R^2 = NH_2$, $R^3 = R^4$ = H
51: $R^1 = R^2 = NH_2$, R^3 = H, R^4 = Cl
52: $R^1 = NHCOCH_3$, $R^2 = R^3$ =Cl, R^4 = H
53: $R^1 = NHCOCF_3$, $R^2 = R^3$ =Cl, R^4 = H
54: R^1=R^2=Cl,R^3=H,R^4=$CH_2CH_2NHCOMe$
55: $R^1 = NMe_2$, $R^2 = R^3 = R^4$ = H
56: $R^1 = NMe_2$, $R^2 = R^3$ = Cl, R^4 = H
57: $R^1 = N(CH_2CH{=}CH_2)_2$, $R^2 = R^3 = R^4$ =H
63: $R^1 = NHCH_2CH_2CO_2Bu^t$, $R^2 = R^3 = R^4$ = H
64: $R^1 = N(CH_2CH_2CO_2Bu^t)_2$, $R^2 = R^3$ =R^4 =H
65: $R^1 = NHCH_2CH_2CO_2Bu^t$, $R^2 = R^3 = R^4$ = H
66: $R^1 = N(CH_2CH_2CO_2Bu^t)_2$, $R^2 = R^3 = R^4$ = H)

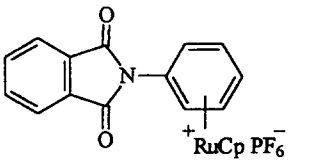
8. Appendix C



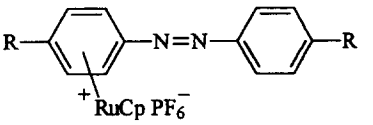
(24: R = H
25:R = Cl)



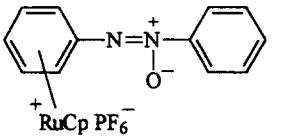
(26)



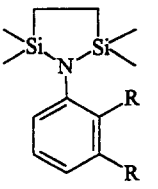
(58)



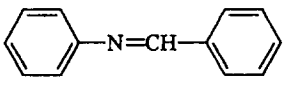
(59: R = H
61: R = Cl
62: R = OMe)



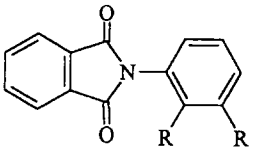
(60)



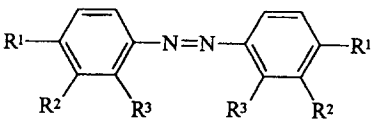
(72: R = H
73: R = Cl)



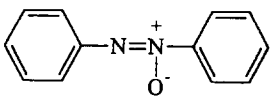
(74)



(38: R = H
77: R = Cl)

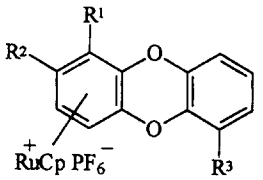


(39: $R^1 = R^2 = R^3 = H$
41: $R^1 = Cl$, $R^2 = R^3 = H$
42: $R^1 = OMe$, $R^2 = R^3 = H$
79: $R^1 = H$, $R^2 = R^3 = Cl$
80: $R^1 = R^2 = Cl$, $R^3 = H$)

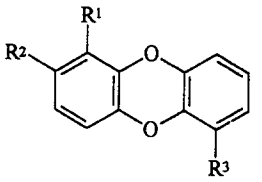


(40)

$RuCp(PPh_3)_2Cl$
(78)



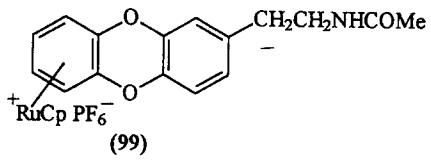
(83: $R^1 = R^2 = R^3 = H$
84: $R^1 = R^2 = H$, $R^3 = CO_2Me$
85: $R^1 = NMe_2$, $R^2 = R^3 = H$
86: $R^1 = NMe_2$, $R^2 = H$, $R^3 = CO_2Me$
87: $R^1 = R^3 = H$, $R^2 = CH_2CH_2NHCOMe$)



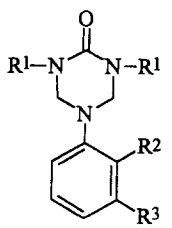
88: $R^1 = R^2 = R^3 = H$
89: $R^1 = R^2 = H$, $R^3 = CO_2Me$
90: $R^1 = NMe_2$, $R^2 = R^3 = H$
91: $R^1 = NMe_2$, $R^2 = H$, $R^3 = CO_2Me$
92: $R^1 = R^3 = H$, $R^2 = CH_2CH_2NHCOMe$)

9. Appendix D

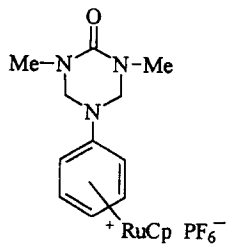
10. Appendix E



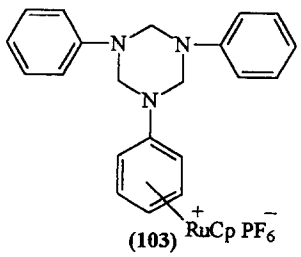
(99)



(100: $R^1 = Me$; $R^2 = R^3 = H$
102: $R^1 = Me$; $R^2 = R^3 = Cl$)



(101)



(103)

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