ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 606 (2000) 188–196

Journal of Organometallic Chemistry

Chiral sandwich compounds of ruthenium(II) and (IV): X-ray crystal structure of $[Ru\{\eta^5\text{-}C_5H_4(neomenthyl)\}_2I]I_3$

Devendra D. Pathak [a], Alan T. Hutton [b], Julie Hyde [a], Angela Walkden [a], Colin White [a,*]

[a] *Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK*
[b] *Department of Chemistry, University of Cape Town, Rondebosch 7701, South Africa*

Received 20 April 2000; received in revised form 2 June 2000

Abstract

The chiral ruthenocenes Ru(Cpnm)Cp′ (where Cpnm = neomenthylcyclopentadienyl and Cp′ = Cpnm or C_5Me_5) have been synthesised and oxidised by halogens to the corresponding ruthenium(IV) salts $[Ru(Cpnm)Cp'X]X_n$ (where X = Br or I; Cp′ = Cpnm, $n = 3$; Cp′ = C_5Me_5, $n = 1$). These ruthenium(IV) compounds all have, to varying degrees, a tendency to revert back to the ruthenocene(II) compounds (X, Br > I; Cp′, Cpnm > C_5Me_5). Thus, for $[Ru(Cpnm)_2Br]Br_3$ this conversion is complete within two days whereas $[Ru(Cpnm)_2I]I_3$ is stable enough for the X-ray structure to have been determined. The electrochemistry and preliminary catalytic studies are reported.

Keywords: Chiral; Ruthenocene; X-ray crystallography; Electrochemistry

1. Introduction

The original definition of a metallocene has nowadays been expanded to include compounds of the type $[M\{(\eta^5\text{-}Cp')_2L_x]^{n+}$ (where Cp′ is any type of cyclopentadienyl, indenyl, tetrahydroindenyl, etc. and $x = 0$–3). The publication of several texts devoted to metallocenes signifies an upsurge of interest in this class of compounds [1]. Chiral metallocenes in particular have attracted considerable attention because of their spectacular success in applications such as stereospecific polymerisation [2] and stereoselective organic transformations [3]. However, this interest has focused primarily on organolanthanides, and those of Group 4 and 5 although compounds of Group 6 such as $Mo(\eta^5\text{-}C_5H_5)_2X_2$ (where X = H or halide) have also been investigated [4]. Further, although the structural framework of ferrocene has been greatly exploited [5], very little attention has been paid to other metallocenes of Group 8. In recent years we have synthesised a number of chiral cyclopentadienyl ruthenium complexes [6] and therefore it was logical for us to extend this to ruthenocene derivatives to explore their potential in asymmetric catalysis.

2. Results and discussion

2.1. Synthesis of chiral ruthenocenes

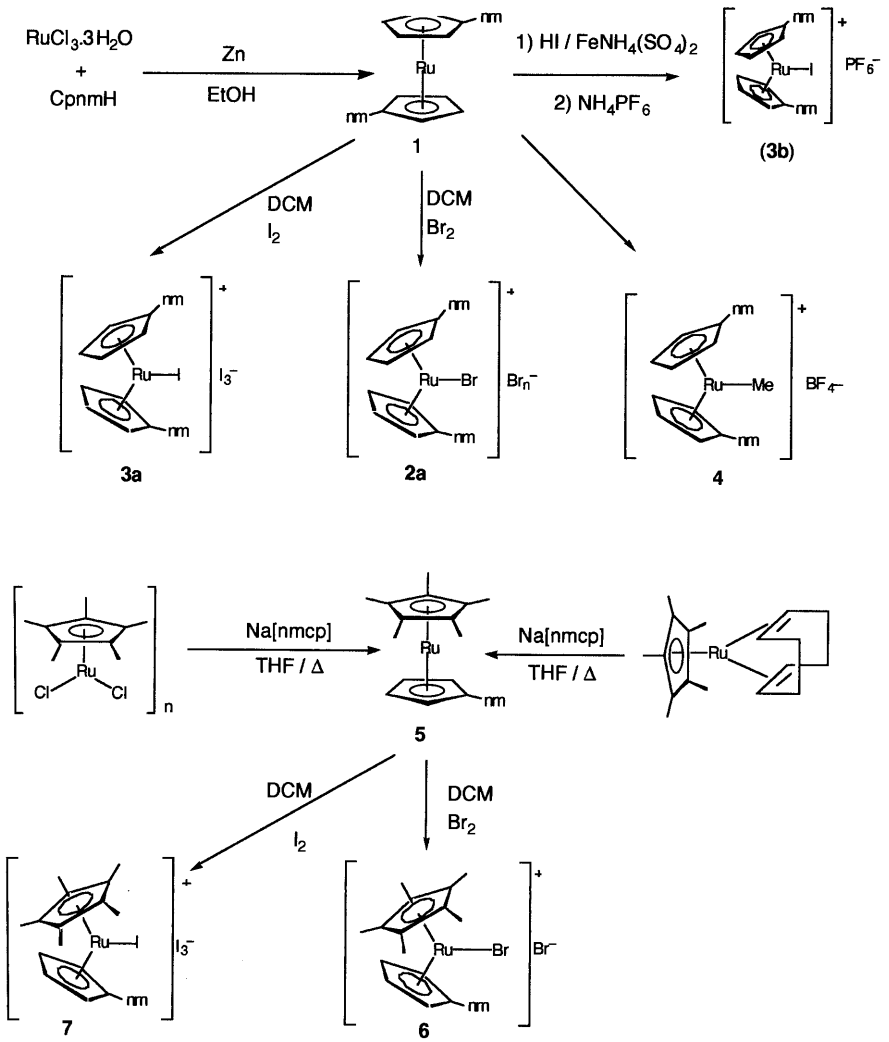
The reactions studied are outlined in Scheme 1. The parent chiral ruthenocene $Ru(\eta^5\text{-}Cpnm)_2$ (**1**) was readily synthesised by the reaction of ruthenium trichloride with neomenthylcyclopentadiene in the presence of zinc; this is analogous to the method reported for the synthesis of ruthenocene [7]. Compound **1** was isolated as brown oil that resisted all attempts to crystallise it. It was characterised by elemental analysis, mass spectroscopy and ^{1}H- and ^{13}C-NMR spectroscopy. A significant feature of the ^{1}H-NMR spectrum was the presence of four cyclopentadienyl signals in the region δ 4.35–4.20; similarly, the ^{13}C-NMR spectrum showed five inequivalent cyclopentadienyl carbons in the region δ 97.4–68.3. Both spectra are consistent with the formation of the desired chiral ruthenocene.

* Corresponding author. Tel.: +44-114-2229310; fax: +44-114-2738673.
E-mail address: colin.white@sheffield.ac.uk (C. White).

0022-328X/00/$ - see front matter
PII: S0022-328X(00)00358-2

Treatment of the parent ruthenocene (**1**) with bromine gave a green oil; this green oil was only stable at room temperature for a limited period reverting completely back to the parent ruthenocene (**1**) within two days. Although satisfactory elemental analysis of the green oil could not be obtained both mass spectroscopy and NMR spectroscopy are consistent with this being $[Ru(Cpnm)_2Br]Br_n$ (**2a**) where n is probably 3 as in the analogous cyclopentadienyl complex [8]. In particular, the ^{1}H- and ^{13}C-NMR spectra showed a significant shift downfield, relative to the initial ruthenium(II) compound **1**, in the cyclopentadienyl signals i.e. δ_H to 6.36–6.00 and δ_C to 118.1–85.6; we found that such a deshielding of the cyclopentadienyl protons to be a characteristic feature on going from ruthenocene(II) to haloruthenocene(IV). The instability of **2a** mirrors that of the achiral analogue $[RuCp_2Br]Br_3$ [8]. In contrast, similar treatment of **1** with iodine yielded a stable green oil that with care could be crystallised to give a very dark green or black solid which correctly analysed for $[Ru(Cpnm)_2I]I_3$ (**3a**). The compound was structurally characterised by X-ray crystallography and the structure is discussed below. The compound **3a** is air-stable and for an ionic ruthenium(IV) complex it is surprisingly soluble in relatively non-polar solvents such as diethyl ether although we have often noted that such high solubility is a feature of neomenthylcyclopentadienyl complexes. Again, the cyclopentadienyl signals in the ^{1}H- and ^{13}C-NMR spectra of **3a** showed a significant shift downfield, relative to the initial ruthenium(II) compound **1**.

Taube et al reported the preparation of the haloruthenium complexes $[RuX(Cp)_2]PF_6$ (where X = Br or I) by the oxidation of an ethereal solution of ruthenocene using Fe(III) in aqueous HX followed by treatment with NH_4PF_6 which caused the products to precipitate from solution [9]. In the hope that it would produce well-defined solids as opposed to the oils we had isolated above, we treated the chiral ruthenocene **1** in an analogous manner. Treatment of **1** with $FeNH_4(SO_4)_2$ in aqueous HBr, followed by treatment of the aqueous layer with NH_4PF_6 did not produce a



Scheme 1.

precipitate. Analysis of the organic layer using ^{1}H-NMR spectroscopy showed unreacted ruthenocene **1** and no evidence of the formation of [RuBr-(Cpnm)$_2$]PF$_6$. A similar reaction in HI again failed to produce a solid precipitate but the ^{1}H spectrum of the product isolated from the organic layer confirmed the presence of [RuI(Cpnm)$_2$]$^+$.

It is known that ruthenocenes are reversibly protonated by strong acids [10,11] and we were curious to see if they could also be methylated by reaction with Me$^+$. Therefore **1** was reacted with Me$_3$OBF$_4$ in diethyl ether to give, after work up an unstable brown oil **4** which on standing quickly reverted to the ruthenium(II) compound **1**. However, the initial ^{1}H- and ^{13}C-NMR spectra of **4** suggested that this was indeed [RuMe(Cpnm)$_2$][BF$_4$]. Thus, the spectra of **4** showed the characteristic downfield shifts in the cyclopentadienyl resonances that we associate with the formation of a ruthenium(IV) compound Section 4. Unfortunately, because the neomenthyl signals obscure the region where a methyl signal might be expected, direct evidence for a methyl group could not be obtained and so the exact nature of **4** must remain speculative.

We [12] and others [13] have demonstrated the stabilising effect of the strongly electron-donating peralkylcyclopentadienyl ligands upon ruthenium(IV) compounds. Frustrated by the instability of the above ruthenium(IV) compounds, we therefore turned our attention to the synthesis of ruthenocene compounds containing a stabilising C$_5$Me$_5$ ligand together with a chiral neomenthylcyclopentadienyl ligand. Our initial synthesis involved the reaction of sodium neomenthylcyclopentadienide with RuCl(COD)(η^5-C$_5$Me$_5$) and was based on the work of Singleton et al [11] who prepared a number of mixed achiral ruthenocenes. This method did indeed yield the desired Ru(η^5-C$_5$Me$_5$)(Cpnm) (**5**), however, we subsequently found that this compound could be prepared in a higher yield and more conveniently by the reaction of sodium neomenthylcyclopentadienide with [RuCl$_2$(η^5-C$_5$Me$_5$)]$_n$. The product was isolated as an air-stable yellow oil.

Reaction of the ruthenocene **5** with bromine gave [RuBr(η^5-C$_5$Me$_5$)(Cpnm)]Br (**6**) isolated as a green solid. Compared to the ruthenium(II) starting complex **5**, the ^{1}H-NMR spectrum (CDCl$_3$) of **6** showed a shift downfield in the cyclopentadienyl signals of nmcp from δ 4.35–4.20 to δ 5.92–5.61 and a shift in the Cp* signal from δ 1.8 to 2.23, consistent with the formation of the desired haloruthenocene(IV) species. We note that for the corresponding [RuBr(η^5-C$_5$Me$_5$)$_2$]Br, the Cp* signal shows a shift of 0.32 p.p.m. downfield relative to [Ru(η^5-C$_5$Me$_5$)$_2$] [11].

Unlike the bromoruthenocene [RuBr(Cpnm)$_2$]Br$_n$ which was unstable in the solid state, [RuBr(η^5-C$_5$Me$_5$)(Cpnm)]Br was found to be stable demonstrating the ability of the pentamethylcyclopentadienyl ligand to stabilise the electron-deficient ruthenium centre. Despite this it was noted that in CDCl$_3$ at room temperature both [RuBr(η^5-C$_5$Me$_5$)(Cpnm)]Br and the related [RuBr(η^5-C$_5$Me$_5$)$_2$]Br slowly underwent reductive elimination to give, respectively, the corresponding ruthenium(II) compounds **5** and Ru(η^5-C$_5$Me$_5$)$_2$; although [RuBr(η^5-C$_5$Me$_5$)$_2$]Br was the more stable, this reductive elimination was complete in 12 days.

The corresponding iodoruthenocene(IV) complex [RuI(η^5-C$_5$Me$_5$)(Cpnm)]I$_3$ (**7**) was isolated as a stable purple solid from the reaction of Ru(η^5-C$_5$Me$_5$)(Cpnm) with iodine. The ^{1}H spectrum of **7** compared to that of the parent complex **5** showed a characteristic shift downfield in the four cyclopentadienyl signals of Cpnm to δ 6.07–5.29 and a shift in the Cp* signal to δ 2.43.

2.2. Exploring the catalytic potential

Titanocenes of the type TiCp$_2$X$_2$ are well known Lewis acids and Bosnich and co-workers have isolated active species of the type [Ti(η^5-C$_5$Me$_5$)$_2$(OH$_2$)$_2$]$^{2+}$, as well as chiral analogues [14]. Although the 18-electron complex [RuI(Cpnm)$_2$]$^+$ is not a Lewis acid, one would anticipate that if one could generate analogous solvent species of the type [Ru(solv)(Cpnm)$_2$]$^{2+}$, then these too would act as chiral Lewis acids. With this in mind we reacted [RuI(Cpnm)$_2$]I$_3$ with two equivalents of silver tetrafluoroborate in dichloromethane containing acetonitrile. We were unable to obtain any evidence for the formation of the desired [Ru(NCMe)(Cpnm)$_2$] [BF$_4$]$_2$ and the ^{1}H-NMR spectrum of the product was consistent with reduction to Ru(Cpnm)$_2$ having taken place.

We have recently reported that the iodide ligand of the complex [RuI(dppe)Cpnm] can be alkylated by CF$_3$SO$_3$R (R = Me or Et) and that the resultant alkyl iodide complex [Ru(IR)(dppe)Cpnm]$^+$CF$_3$SO$_3^-$ can be used as an enantioselective alkylating agent [15]. Mindful of the fact that alkyl halide complexes of Ir(III) such as [IrH$_2$(IMe)$_2$(PPh$_3$)$_2$]SbF$_6$ have been isolated [16], we wondered if the corresponding ruthenium(IV) complexes could be synthesised. With this in mind we treated [RuI(η^5-C$_5$Me$_5$)(Cpnm)]I$_3$ dissolved in CD$_2$Cl$_2$ under nitrogen with 2.2 equivalents of methyl triflate and monitored the ^{1}H-NMR spectrum of the reaction mixture in the hope of obtaining evidence for the formation of [Ru(IMe)(η^5-C$_5$Me$_5$)(Cpnm)]$^{2+}$. In CD$_2$Cl$_2$, free iodomethane has a chemical shift of δ 2.16 and it is typical for halocarbon resonances to shift downfield upon coordination [17], for example, the MeI complexes [Ru(IMe)(CO)$_2$(η^5-C$_5$H$_5$)]PF$_6$, [Ru(IMe)(CO)(PPh$_3$)(η^5-C$_5$H$_5$)]PF$_6$ and [Ru(IMe)(CO)$_2$(η^5-C$_5$Me$_5$)]PF$_6$ show a change in shift relative to methyl iodide [$\Delta\delta$(MeI)] of +0.52, +0.23 and +0.45 p.p.m., respectively. Unfortunately, in our case even after five days there were no new signals downfield of δ 2.16 indicative of a coordinated

Table 1
Redox potentials for selected Ru^{II} and Ru^{IV} sandwich complexes [a]

Compound	Solvent	E_{pa} (V)	E_{pc} (V)
$[Ru(Cpnm)_2]$ (**1**)	CH_2Cl_2	+0.91	
[Ru(Cpnm)(Cp*)] (**5**)	CH_2Cl_2	+0.60	
$[Ru(Cp^*)_2]$	CH_2Cl_2	+0.31	
$[Ru(Cpnm)_2I]I_3$ (**3a**)	CH_3CN	+0.34	+0.09
[RuBr(Cpnm)(Cp*)]Br (**6**)	CH_3CN	+0.21 [b], +1.33	−0.52

[a] Referenced to Ag/Ag^+ (see Section 4 for corresponding ferrocene/ferrocenium E values); E_{pa}, anodic peak potential; E_{pc}, cathodic peak potential.

[b] Disappears on scanning anodically from 0.0 V or at scan rate of 20 mV s^{-1}.

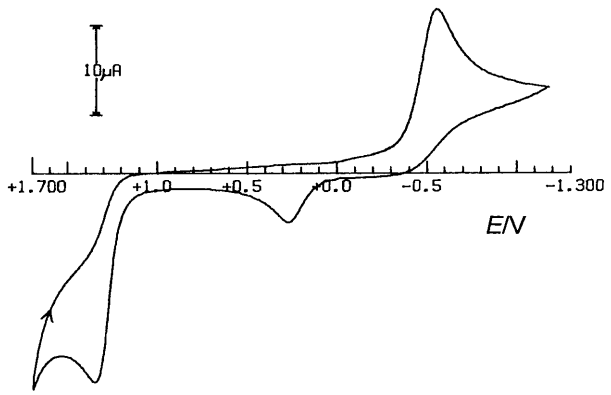


Fig. 1. Cyclic voltammogram of [RuBr(Cpnm)(Cp*)]Br (**6**) in CH_3CN at a scan rate of 100 mV s^{-1}. The potential scale is referenced to Ag/Ag^+ (see Section 4). The scan started at +1.70 V.

iodomethane. It would therefore appear that since the iodomethane is a weak electron donor it is unable to stabilise the electron deficient ruthenium(IV) centre bearing a +2 charge.

2.3. Electrochemical studies

We have investigated the electrochemical behaviour of several of these complexes and our results are summarized in Table 1. The cyclic voltammetry of $[Ru(Cpnm)_2]$ (**1**) and [Ru(Cpnm)(Cp*)] (**5**) in dichloromethane (containing 0.1 M $[^nBu_4N][PF_6]$) at a platinum disk electrode shows that both compounds, like the parent $[Ru(Cp)_2]$ [18], undergo an irreversible, single-step two-electron oxidation. The number of electrons involved in the oxidation was estimated from the current response of the sample compared with that of an equimolar concentration of $[Ru(Cp^*)_2]$, in which a reversible one-electron redox process has been well established [19]. As might be expected from the electron donating ability of the Cp* ligand, we find that $[Ru(Cpnm)_2]$ (**1**) is oxidised at higher potential (is harder to oxidize) than [Ru(Cpnm)(Cp*)] (**5**), and both are oxidized at higher potential than $[Ru(Cp^*)_2]$. It has been proposed [20] that in the latter compound, which displays reversible one-electron redox behaviour, the steric congestion provided by the two Cp* ligands mitigates against any nucleophilic attack or dimerization which might give rise to the irreversible redox behaviour observed in other ruthenocene derivatives at a platinum electrode [18]. Clearly our own compounds **1** and **5** are not sterically crowded enough to fall into this category and behave more like the parent, unsubstituted $[Ru(Cp)_2]$.

Two of the ruthenium(IV) salts were examined at a platinum electrode in acetonitrile solution (0.1 M in $[^nBu_4N][ClO_4]$). The I_3^- salt of $[Ru(Cpnm)_2I]^+$ (**3a**) offered only broad, ill-resolved peaks, indicating that some reduction and a possibly related oxidation was occurring (see Table 1), but the voltammograms were not amenable to further interpretation. The Cp*-containing complex [RuBr(Cpnm)(Cp*)]Br (**6**), on the other hand, showed a well-formed irreversible reduction peak at −0.52 V (see Fig. 1). On switching the scan direction a smaller anodic peak near +0.21 V indicated oxidation of the product of some chemical reaction (possibly elimination of bromide) following the initial reduction of the sample. This anodic peak is not observed if the scan is run anodically from 0.0 V, i.e. if initial reduction of the sample does not occur. In addition, this peak disappears when the voltammogram is run at a slower scan rate (20 mV s^{-1}), indicating that the species being oxidized is a transient one. This complex also shows an oxidation peak at relatively high potential (+1.33 V) which does not derive from the product(s) of the reduction (the peak remains unaltered when the scan is run anodically from 0.0 V); the origin of this peak is not known at present. The data do confirm, however, that the Ru^{IV} complex containing two Cpnm groups (**3a**) undergoes reduction more readily than that containing both Cpnm and Cp* groups (**6**), as might be expected from the presence of the electron-rich Cp* group; this corroborates the observations already made in studying the synthesis and reactions of these complexes.

2.4. Crystal structure of compound *3a*

The structure and atom numbering of iodobis(neomenthylcyclopentadienyl)ruthenium triiodide can be seen in Fig. 2, with selected bond lengths and bond angles in Table 2. The ruthenium is bonded in a classical pentahapto manner to two cyclopentadienyl rings, with $C–C_{av}$ for ring one 1.412(19) Å and ring two 1.421(19) Å, which is comparable to that in other cyclopentadienylruthenium(IV) compounds [8,21]. It can be seen that one of the C–C bond distances in each cyclopentadienyl ligand, opposite to the carbon carrying the neomenthyl group, is noticeably shorter than the rest of the C–C bonds; we have observed this previously in other neomenthylcyclopentadienyl com-

pounds [22]. The cyclopentadienyl rings are virtually planar (RMS deviation for ring one of 0.006 Å and that of ring two 0.008 Å) with Cent–Ru distances of 1.872 and 1.857 Å, respectively. The average Ru–C bond lengths, Ru–C_{av} 2.220(11) and 2.228(10) Å for rings one and two, whereas that in ruthenocene is 2.186 ± 0.02 Å [23]. One might have expected a decrease in the metal–carbon distance on going from Ru(II) to Ru(IV) but presumably steric interaction between the ring carbons and the iodine prevent any such shortening. Alternatively, it has been proposed that the greater distance found in the ruthenium(IV) ruthenocenes is due to the removal of bonding e_{2g} electrons on going from Ru(II) to Ru(IV) [21]. The Ru–C bond lengths are also comparable to those found in other cationic ruthenium(IV) structures such as $[Ru(Cp)_2I]^+$ [8] and $[Ru(C_5Me_5)_2Br]^+$[24]. Although the cyclopentadienyl rings are not parallel, they can be regarded as being in an eclipsed conformation as found for similar ruthenocenes [8,24].

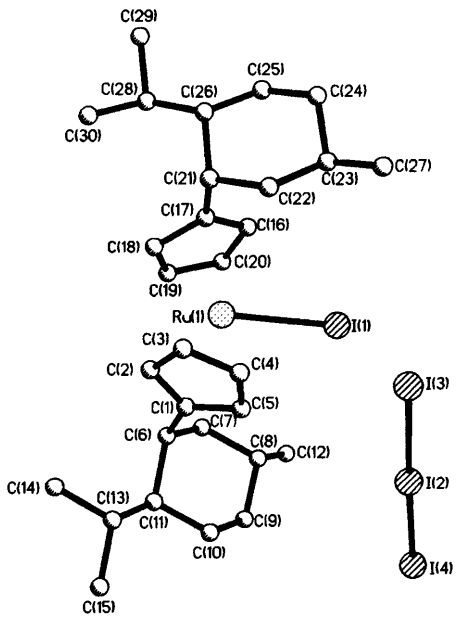


Fig. 2. The molecular structure of **3a** showing the atomic numbering scheme.

Table 2
Selected bond lengths (Å) and angles (°) for compound **3a**

Ru–I	2.732(2)		
I(2)–I(3)	3.005(3)	I(2)–I(4)	2.825(3)
Ru–C(1)	2.268(9)	Ru–C(16)	2.266(9)
Ru–C(2)	2.164(11)	Ru–C(17)	2.272(12)
Ru–C(3)	2.203(12)	Ru–C(18)	2.207(12)
Ru–C(4)	2.212(12)	Ru–C(19)	2.188(11)
Ru–C(5)	2.254(12)	Ru–C(20)	2.207(12)
C(1)–C(2)	1.424(19)	C(16)–C(17)	1.427(18)
C(2)–C(3)	1.439(21)	C(17)–C(18)	1.436(16)
C(3)–C(4)	1.350(21)	C(18)–C(19)	1.436(22)
C(4)–C(5)	1.437(22)	C(19)–C(20)	1.366(17)
C(5)–C(1)	1.408(15)	C(20)–C(16)	1.440(20)
Ru–Cent (ring 1)	1.872	Ru–Cent (ring 2)	1.857
I(3)–I(2)–I(4)	177.8(1)	Cent(1)–Ru–Cent(2)	149.2
Cent(1)–Ru–I(1)	106.2	Cent(2)–Ru–I(1)	104.5

The cyclopentadienyl rings are positioned axially on the neomenthyl groups which are arranged as far apart as possible on either side of the molecule, with the isopropyl groups being as far apart as possible from the metal centre. The neomenthyl groups are in the expected chair conformation with equatorial alkyl substituents. Both of the neomenthyl groups adopt a regular rather than a twisted chair, as can be seen by the RMS deviation of the four atom plane of neomenthyl group one 0.006 Å (C8 and C11 deviate by -0.676 and 0.673 Å, respectively), and of neomenthyl group two 0.017 Å (C23 and C26 deviate by 0.588 and -0.633 Å, respectively). The configuration at the chiral centres of the neomenthyl ligands can be assigned as being '*S*' for C6 and C21, '*R*' for C8 and C23 and '*S*' for C11 and C26 in accordance with previously reported structures [23]. Atom C6 of the neomenthyl group attached the cyclopentadienyl ring was found to deviate from the plane of the ring by 0.057 Å in a direction towards the ruthenium, whereas C21 of the other neomenthyl group deviates by 0.059 Å in a direction away from the metal centre.

The Ru–I and the two Ru–Cent vectors are co-planar, their mutual angles totalling to 359.5°. The dihedral angle between the two cyclopentadienyl rings is 35.3° and can be compared with the analogous $[Ru(Cp)_2I]^+$ where the angle is 32.2° [8]. This indicates that the rings are arranged symmetrically in such a way that they are tilted so that the iodine points out symmetrically from an 'open cup' type of arrangement figure (Fig. 2). The bond distance for the Ru–I of 2.732 (2) Å which is exactly the same as that in $[Ru(Cp)_2I]^+$ of 2.732 Å [8].

Finally the triiodide anion is expected to be linear but there is a slight deviation from linearity I3–I2–I4 = 177.8(1)°, this could be due to the packing arrangement for the ions within the lattice. The average bond distance for the triiodide is 2.915 Å, comparable to the 2.925 ± 0.003 Å reported for the analogous $[Ru(Cp)_2I]I_3$.

3. Conclusions

Although these chiral ruthenocenes can be readily prepared and also oxidised by halogens to the corresponding ruthenium(IV) compounds, the ruthenium(IV) compounds all have, to varying degrees, a tendency to revert back to the ruthenocene(II) compounds (X, $Br > I$; Cp′, $Cpnm > C_5Me_5$); similarly, $[RuMe(Cpnm)_2][BF_4]$ proved unstable. It is pertinent to note that prior to this study only two types of

ruthenocene(IV) species containing a ligand other than a halogen attached to the ruthenium centre have been reported [25] i.e. $[Ru\{SC(NH_2)_2\}(\eta^5\text{-}C_5R_5)_2][PF_6]_2$ and $[RuH(\eta^5\text{-}C_5R_5)_2]^+$ (R = H or Me) and these too persisted only for a few days, decomposing in the solid state even under a nitrogen atmosphere. Thus, we conclude that applications of chiral ruthenocenes, in particular ruthenium(IV) compounds, in enantioselective synthesis will be extremely limited by the instability of these compounds.

4. Experimental

Neomenthylcyclopentadiene [26], $RuCl(COD)(\eta^5\text{-}C_5Me_5)$ [27], $[RuCl_2(\eta^5\text{-}C_5Me_5)]_n$, $[Ru(\eta^5\text{-}C_5Me_5)_2]$ [28] and $[RuBr(\eta^5\text{-}C_5Me_5)_2]Br$ [11] were prepared by literature methods.

4.1. Ru(Cpnm)$_2$ (1)

A mixture of ruthenium trichloride (1.08 g, 4.13 mmol), zinc dust (1.0 g, 15.3 mmol) and neomenthylcyclopentadiene (2.6 g, 12.78 mmol) was heated under reflux in ethanol (30 ml) for 24 h. On cooling, the solvent was removed in vacuo and the residue extracted into diethyl ether (3 × 50 ml). The solution was filtered through a plug of Celite to remove zinc dust and the solvent concentrated to give $Ru(Cpnm)_2$ as a brown oil (2.52 g, 89%). Anal. Found: C, 71.5; H, 9.2. Calc. for $C_{30}H_{46}Ru$: C, 71.0; H, 9.1%. δ_H ($CDCl_3$) 4.35 (2 H, m, C_5H_4), 4.27 (2 H, m, C_5H_4), 4.24 (2 H, m, C_5H_4), 4.19 (2 H, m, C_5H_4), 2.38 (2 H, br s, neomenthyl), 1.66–0.53 (36 H, m, neomenthyl) including 0.68–0.64 (12 H, overlapping doublets, *J* (HH) 7 Hz, neomenthyl CH_3), 0.53 (6 H, d, *J* (HH) 6 Hz, neomenthyl CH_3); δ_C ($CDCl_3$): 97.4 (2 C, s, ipso C of C_5H_4), 74.9 (2 C, s, C_5H_4), 72.9 (2 C, s, C_5H_4), 70.1 (2 C, s, C_5H_4), 68.3 (2 C, s, C_5H_4), 47.6, 36.2, 29.9, 27.6 (8 C, s, neomenthyl CH), 46.5, 36.3, 24.8 (6 C, s, neomenthyl CH_2) and 23.0, 21.9, 21.4 (6 C, s, neomenthyl CH_3); *m*/*z* 508 [M^+], a much smaller peak was observed at *m*/*e* = 1013, consistent with the formation of the dimeric complex, $[Ru(C_5H_3nm)_2]_2$.

4.2. [RuBr(Cpnm)$_2$]Br$_3$ (2a)

A solution of bromine (0.5 g, 3.13 mmol) in dichloromethane (20 ml) was added dropwise to a stirred solution of $Ru(Cpnm)_2$ (0.5 g, 0.99 mmol) in dichloromethane (100 ml) at r.t. and the resultant solution stirred for 36 h. The solvent was removed in vacuo and the residue extracted into diethyl ether (3 × 25 ml). The solution was filtered through a column of Celite and the solvent removed under reduced pressure to give $[RuBr(Cpnm)_2]Br_3$ as a green oil (0.7 g, 86%). δ_H ($CDCl_3$) 6.36 (4 H, br s, C_5H_4), 6.12 (2 H, br s, C_5H_4), 6.00 (2 H, br s, C_5H_4), 3.19 (2 H, br s, neomenthyl), 1.90–0.82 (36 H, m, neomenthyl); δ_C ($CDCl_3$) 118.1 (2 C, s, ipso C of C_5H_4), 106.6 (2 C, s, C_5H_4), 96.2 (2 C, s, C_5H_4), 87.6 (2 C, s, C_5H_4), 85.6 (2 C, s, C_5H_4), 48.2, 35.3, 29.8, 27.8 (8 C, s, neomenthyl CH), 42.8, 35.0, 24.4 (6 C, s, neomenthyl CH_2), 22.9, 22.2, 20.9 (6 C, s, neomenthyl CH_3).

4.3. [RuI(Cpnm)$_2$]I$_3$ (3a)

To a solution of $[Ru(Cpnm)_2]$ (3.81 g, 7.5 mmol) in dichloromethane (100 ml) at r.t., a solution of iodine (0.5 g, 3.13 mmol) in dichloromethane (20 ml) was added dropwise and the mixture stirred for 24 h. The solvent was removed in vacuo and the residue extracted into diethyl ether (3 × 25 ml). The solution was filtered through a column of Celite and concentrated. Excess iodine was extracted into small volumes of carbon tetrachloride and the residue was thoroughly dried to give the product as dark green oil. Repeated fractional crystallization of the crude product from $CHCl_3$-*n*-hexane afforded black air-stable long needles of the desired product: yield 5.23 g (69%). M.p. 136°C. (Anal. Found: C, 35.8; H, 4.7; I, 48.6. Calc. for $C_{30}H_{46}I_4Ru$: C, 35.5; H, 4.6; I, 50.0%). δ_H ($CDCl_3$) 6.51 (2 H, br s, C_5H_4), 6.44 (2 H, br s, C_5H_4), 6.10 (2 H, br s, C_5H_4), 5.79 (2 H, br s, C_5H_4), 3.14 (2 H, br s, neomenthyl), 1.83–0.72 (36 H, m, neomenthyl). δ_C ($CDCl_3$) 114.2 (2 C, s, ipso C of Cp), 99.3 (2 C, s, C_5H_4), 94.6 (2 C, s, C_5H_4), 86.8 (2 C, s, C_5H_4), 84.4 (2 C, s, C_5H_4), 47.8, 35.8, 29.9, 27.9 (8 C, s, neomenthyl CH), 44.2, 34.8, 24.4 (6 C, s, neomenthyl CH_2) 22.9, 22.7, 20.9 (6 C, s, neomenthyl CH_3); FABMS *m*/*z* 508 [M − I].

4.4. Attempted preparation of [RuBr(Cpnm)$_2$]PF$_6$ (2b)

A solution of $FeNH_4(SO_4)_2$ (7 g, 26.3 mmol) in HBr (25 ml of 3 M solution) was added dropwise to a stirred solution of $[Ru(Cpnm)_2]$ (1.2 g, 2.4 mmol) in diethyl ether (50 ml) at r.t. The resulting solution was stirred vigorously for 48 h. The organic phase was separated, dried over anhydrous sodium sulphate, filtered and the solvent removed in vacuo. ^{1}H-NMR analysis confirmed the brown oily residue was starting material. The aqueous phase was washed with toluene (2 × 25 ml) followed by diethyl ether (2 × 25 ml). An aqueous solution of NH_4PF_6 (7 g, 26.3 mmol) was added and the solution stored in the freezer overnight to aid precipitation of the PF_6 salt. However no precipitate of the desired complex formed.

4.5. Attempted preparation of [RuI(Cpnm)$_2$]PF$_6$ (3b)

To a stirred solution of $[Ru(Cpnm)_2]$ (0.5 g, 1 mmol) in diethyl ether (15 ml) at r.t., a solution of

$FeNH_4(SO_4)_2$ (1.86 g, 6.9 mmol) in HI (12 ml of 1 M solution) was added dropwise. The resulting solution was stirred vigorously for 48 h. The organic phase was separated, dried over anhydrous sodium sulphate, filtered and the solvent removed in vacuo. ^{1}H-NMR analysis confirmed the green residue to be that of the triiodide salt (0.6 g, 60%). The aqueous phase was washed with toluene (2×25 ml) followed by diethyl ether (2×25 ml). An aqueous solution of NH_4PF_6 (2 g, 6.9 mmol) was added to the aqueous phase and the solution was stored in the freezer overnight to aid precipitation of the PF_6 salt. However no precipitate of the desired complex formed.

4.6. Reaction of [Ru(Cpnm)$_2$] with [Me$_3$O][BF$_4$]

A solution of $[Ru(Cpnm)_2]$ (1.0 g, 1.97 mmol) and Me_3OBF_4 (0.78 g, 5.27 mmol) in diethyl ether (20 ml) was stirred at r.t. for 24 h. The solvent was removed in vacuo, the crude product extracted into dichloromethane (50 ml) and filtered through a plug of Celite. Removal of the solvent in vacuo gave the crude product as a brown oil (0.82 g, 68%). δ_H ($CDCl_3$) 6.03 (4 H, br s, C_5H_4), 5.84 (2 H, br s, C_5H_4), 5.54 (2 H, br s, C_5H_4), 3.01 (2 H, br s, neomenthyl), 1.83–0.77 (36 H, m, neomenthyl); δ_C ($CDCl_3$) 123.0 (2 C, s, ipso C of C_5H_4), 106.4 (2 C, s, C_5H_4), 96.6 (2 C, s, C_5H_4), 86.7 (2 C, s, C_5H_4), 86.5 (2 C, s, C_5H_4), 48.2, 35.1, 29.6, 27.9 (8 C, s, neomenthyl CH), 41.5, 35.0, 24.5 (6 C, s, neomenthyl CH_2), 22.7, 22.0, 20.9 (6 C, s, neomenthyl CH_3).

4.7. [Ru(η^5-C$_5$Me$_5$)(Cpnm)] (**5**)

(i) Sodium hydride (0.14 g, 3 mmol) was washed in hexane (30 ml) and the solvent cannulaed into a separate flask. Tetrahydrofuran (15 ml) was added to the flask containing sodium hydride and neomenthylcyclopentadiene (0.15 g, 0.7 mmol) was added dropwise with stirring. After the addition was complete, stirring was continued for 3 h during which time there was a colour change from colourless to orange. To the resulting solution, RuCl(COD)(η^5-C_5Me_5) (0.2 g, 0.5 mmol) in tetrahydrofuran (10 ml) was added dropwise and stirring was continued at r.t. for a further 16 h. The solvent was removed in vacuo and the product extracted into diethyl ether. Removal of the solvent gave [Ru(η^5-C_5Me_5)(Cpnm)] as a yellow oil (0.22 g, 38%).

(ii) Neomenthylcyclopentadienylsodium was prepared as above by the dropwise addition of neomenthylcyclopentadiene (2.38 g, 11.7 mmol) to a stirred solution of sodium hydride (0.28 g, 11.7 mmol) in tetrahydrofuran (30 ml) at r.t. $[RuCl_2(\eta^5\text{-}C_5Me_5)]_n$ (0.85 g, 2.6 mmol) was added and the resulting solution heated under reflux for 16 h. On cooling, the solvent was removed in vacuo. The crude product was purified by chromatography on silica eluting with petroleum ether to give Ru(η^5-C_5Me_5)(Cpnm) as a yellow band. Removal of the solvent under reduced pressure gave Ru(η^5-C_5Me_5)(Cpnm) as a yellow oil (0.84 g, 69%). (Anal. Found: C, 68.1; H, 8.8; M^+ 440. $C_{25}H_{38}Ru$ requires C, 68.3; H, 8.7) δ_H ($CDCl_3$) 4.22 (1 H, m, C_5H_4), 4.05 (1 H, m, C_5H_4), 3.96 (1 H, m, C_5H_4), 3.88 (1 H, m, C_5H_4), 2.54 (1 H, br s, neomenthyl), 1.90 (15 H, s, C_5Me_5), 1.70–0.65 (18 H, m, neomenthyl) including 0.84 (3 H, d, *J* (HH) 6 Hz, CH_3 of nm), 0.80 (3 H, d, *J* (HH) 6 Hz, CH_3 of nm), 0.65 (3 H, d, *J* (HH) 6 Hz, CH_3 of nm); δ_C ($CDCl_3$) 94.6 (1 C, s, ipso C of C_5H_4), 84.5 (5 C, s, C_5Me_5), 74.9 (1 C, s, C_5H_4), 73.7 (1 C, s, C_5H_4), 72.0 (1 C, s, C_5H_4), 71.3 (1 C, s, C_5H_4), 49.0, 35.5, 29.3, 28.3 (4 C, s, CH of nm), 41.9, 36.1, 24.1 (CH_2 of nm), 23.2, 22.2, 20.7 (CH_3 of nm), 12.1 (5 C, s, C_5Me_5).

4.8. [RuBr(η^5-C$_5$Me$_5$)(Cpnm)]Br (**6**)

A solution of bromine (0.6 g, 3.1 mmol) in petroleum ether (1 ml) was added dropwise with stirring to a solution of [Ru(η^5-C_5Me_5)(Cpnm)] (0.84 g, 3.1 mmol) in petroleum ether (2 ml). An immediate precipitation of an oily green residue was observed. The solution was left to stir for 2 h to ensure the reaction was complete. The solvent was decanted and the crude product recrystallised from dichloromethane–petroleum ether. Filtration gave the product as a green powder that was thoroughly dried in vacuo (0.58 g, 59%). (Anal. Found: C, 49.8; H, 6.4; Br, 28.0. $C_{25}H_{38}Br_2Ru$ requires C, 50.1; H, 6.4; Br, 26.7) δ_H ($CDCl_3$) 5.92 (1 H, br s, C_5H_4), 5.86 (1 H, br s, C_5H_4), 5.76 (1 H, br s, C_5H_4), 5.61 (1 H, br s, C_5H_4), 3.10 (1 H, br s, neomenthyl), 2.23 (15 H, s, C_5Me_5), 1.97–0.77 (18 H, m, neomenthyl); δ_C ($CDCl_3$): 113.3 (1 C, s, ipso C of C_5H_4), 107.8 (5 C, s, C_5Me_5), 107.3 (1 C, s, C_5H_4), 98.6 (1 C, s, C_5H_4), 90.1 (1 C, s, C_5H_4), 88.7 (1 C, s, C_5H_4), 48.0, 34.8, 29.7, 27.9 (4 C, s, neomenthyl CH), 41.9, 35.1, 24.1 (3 C, s, neomenthyl CH_2), 22.8, 22.2, 20.8 (3 C, s, neomenthyl CH_3), 13.4 (5 C, s, C_5Me_5); *m*/*z* 440 [M − Br].

4.9. [RuI(η^5-C$_5$Me$_5$)(Cpnm)]I$_3$ (**7**)

To a solution of [Ru(η^5-C_5Me_5)(Cpnm)] (0.4 g, 0.9 mmol) in petroleum ether (1 ml), a solution of iodine (0.46 g, 3.6 mmol) in the minimum amount of petroleum ether was added dropwise with stirring. An immediate precipitation was observed and the solution was left to stir for 2 h to ensure the reaction was complete. The precipitate was collected by filtration and purified by recrystallisation from dichloromethane–petroleum ether to give [RuI(η^5-C_5Me_5)(Cpnm)]I_3 as a purple powder which was thoroughly dried in vacuo (0.42 g, 49%). (Anal. Found: C, 31.3; H, 4.1; I, 53.5; M^+ 948. $C_{25}H_{38}I_4Ru$ requires C, 31.7; H, 4.0; I, 53.6; δ_H ($CDCl_3$) 6.07 (1 H, br s, C_5H_4), 5.95 (1 H, br s,

C_5H_4), 5.38 (1 H, br s, C_5H_4), 5.29 (1 H, br s, C_5H_4), 3.16 (br s, 1 H, neomenthyl), 1.91–0.79 (18 H, m, neomenthyl) including 0.97 (3 H, d, *J* (HH) 6 Hz, neomenthyl CH_3), 0.82 (3 H, d, *J* (HH) 6 Hz, neomenthyl CH_3), 0.80 (3 H, d, *J* (HH) 6 Hz, neomenthyl CH_3); δ_C ($CDCl_3$) 110.0 (1 C, s, ipso C of C_5H_4), 105.7 (5 C, s, C_5Me_5), 101.0 (1 C, s, C_5H_4), 96.3 (1 C, s, C_5H_4), 88.0 (1 C, s, C_5H_4), 86.0 (1 C, s, C_5H_4), 47.9, 35.4, 29.9, 28.3 (4 C, s, neomenthyl CH), 42.3, 35.0, 24.1 (3 C, s, neomenthyl CH_2), 22.9, 22.4, 20.7 (3 C, s, neomenthyl CH_3), 14.8 (5 C, s, C_5Me_5); *m*/*z* 440 [M − I]

5. Electrochemistry

Cyclic voltammetry was performed at room temperature on a BAS 100B Electrochemical Analyser using a three-electrode system comprising a platinum disk working electrode, a platinum wire auxiliary electrode and a Ag/Ag^+ reference electrode (0.01 M $AgNO_3$ and 0.1 M $[Bu_4N][ClO_4]$ in acetonitrile). The reported *E* values (Table 1) are with reference to this electrode. Measurements made on acetonitrile solutions were 1–2 mM in sample and 0.1 M in $[^nBu_4N][ClO_4]$. Under these conditions the ferrocene/ferrocenium couple, which was used as a reference, had an *E* value of 0.09 V. When dichloromethane was used as a solvent (0.1 M in $[Bu_4N][PF_6]$) the Fc/Fc^+ couple was recorded at $E = 0.22$ V. All solutions were purged with argon and voltammograms were recorded under a blanket of argon. Unless otherwise stated, the scan rate used was always 100 mV s^{-1}.

5.1. X-ray crystallography

A suitable rectangular crystal ($0.192 \times 0.346 \times 0.125$ mm) was grown from dichloromethane–diethyl ether at room temperature. Room temperature X-ray data were collected in the range $6.5 < 2\theta < 45°$ on a two-circle Stoe diffractometer by the omega scan method. The 2490 independent reflections (of 3455 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by Gaussian methods (minimum and maximum transmission coefficients 0.201 and 0.430). The structure was solved by heavy atom Patterson methods and refined by blocked cascade least squares methods. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0428$ ($Rw = 0.0452$, 315 parameters) with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density -0.779 and 0.796 e $Å^{-3}$. A weighting scheme $w^{-1} = \sigma^2(F) + 0.00075(F)^2$ was used in the latter stages of refinement. Complex scattering factors were taken from reference [29] and from the program package SHELXTL [30] as implemented on the Data General DG30 computer.

5.2. Crystal data for complex **3a**

$C_{30}H_{46}I_4Ru$, $M_r = 1015.39$, monoclinic, space group $P2_1$ (C_2^2 No. 4), $a = 14.318(96)$, $b = 10.300(61)$, $c = 13.103(88)$ Å, $\beta = 67.859(42)°$, $V = 1789.2(20)$ $Å^3$, $Z = 2$, $D_{calc} = 1.884$ g cm^{-3}, Mo–K_α radiation ($= 0.71069$ Å), $\mu(Mo–K_\alpha) = 38.6$ cm^{-1}, $F(000) = 964$.

6. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 144231 for compound **3a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

Acknowledgements

We wish to record our sincere thanks to the EPSRC for a research fellowship (to D.D.P.) and a studentship (to A.W.), to Johnson Matthey for the generous loan of ruthenium trichloride (to C.W.) and to the British Council for travel (C.W. and A.T.H.).

References

[1] (a) A. Togni, R.L. Halterman (Eds.), Metallocenes: Synthesis, Reactivity, Applications, Wiley–VCH, New York, vols. 1–2, 1998. (b) N. Long, Metallocenes: An Introduction to Sandwich Complexes, Blackwell, Malden, 1998.

[2] (a) L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, Chem. Rev. 100 (2000) 1253. (b) M.A. Giardello, M.S. Eisen, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 117 (1995) 12114. (c) H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem. Int. Ed. Engl. 34 (1995) 1143. (d) R. Mülhaupt, B. Rieger, Chimia 49 (1995) 486. (e) F. Langhauser, J. Kerth, M. Kersting, P. Kölle, D. Lilge, P. Müller, Angew. Makromol. Chem. 223 (1994) 155. (f) K.B. Sinclair, R.B. Wilson, Chem. Ind. (1994) 857.

[3] (a) X. Verdaguer, U.E.W. Lange, M.T. Reding, S.L. Buchwald, J. Am. Chem. Soc. 118 (1996) 6784. (b) M.A. Giarrdello, V.P. Conticello, L. Brard, M.R. Gagne, T.J. Marks, J. Am. Chem. Soc. 116 (1994) 10241. (c) C.A. Willoughby, S.L. Buchwald, J. Am. Chem. Soc. 116 (1994) 8952. (d) R.L. Halterman, T.M. Ramsey, Z.L. Chen, J. Org. Chem. 59 (1994) 2642. (e) Z. Chen, R.L. Haltermann, J. Am. Chem. Soc. 114 (1992) 2276. (f) V.P. Conticello, L. Brard, M.A. Giarrdello, Y. Tsuji, M. Sabat, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 114 (1992) 2761.

[4] P. Royo, E. Ryan, in: A. Togni, R.L. Halterman (Eds.), Metallocenes: Synthesis, Reactivity, Applications, vol. 1, Wiley–VCH, New York, 1998 chapter 6 and references therein.

[5] A. Togni, T. Hayashi (Eds.), Ferrocenes, Homogeneous Catalysis, Organic Synthesis, Material Science, VCH, Weinheim, 1995.
[6] (a) C. Lindsay, E. Cesarotti, H. Adams, N.A. Bailey, C. White, Organometallics 9 (1990) 2594. (b) D.D. Pathak, H. Adams, N.A. Bailey, P.J. King, C. White, J. Organomet. Chem. 479 (1994) 237. (c) S. Lo Schiavo, C. Renouard, M.C. Simpson, H. Adams, N.A. Bailey, C. White, J. Chem. Soc. Dalton Trans. (1994) 1731. (d) J.A. Ramsden, D.A. Milner, P.D. Hempstead, N.A. Bailey, C. White, J. Chem. Soc. Dalton Trans. (1995) 2101.
[7] (a) P.Pertici, G. Vitulli, L. Porri, J. Chem. Soc. Chem. Commun. (1975) 846. (b) N.A. Vol'kenau, I.N. Bolesova, L.S. Shul'pina, A.N. Kitaigorodskii, D.N. Kravtsov, J. Organomet. Chem. 288 (1985) 341. (c) P. Pertici, G. Vitulli, J. Chem. Soc. Dalton Trans. (1980) 1961.
[8] Y.S. Sohn, A.W. Schlueter, D.N. Hendrickson, H.B. Gray, Inorg. Chem. 13 (1974) 301.
[9] H. Taube, P.T. Smith, K.S. Kwan, A. Bino, S. Cohen, Inorg. Chem. 23 (1984) 1943.
[10] G.Cerichelli,G.Illuminati,G.Ortaggi,A.M.Giuliani,J.Organomet. Chem. 127 (1977) 357.
[11] M.O. Albers, D.C. Liles, D.J. Robinson, A. Shaver, E. Singleton, M.B. Wiege, Organometallics 5 (1986) 2321.
[12] I.W. Nowell, K. Tabatabaian, C. White, J. Chem. Soc. Chem. Commun. (1979) 547.
[13] (a) H. Nagashima, K. Mukai, Y. Shiota, K. Yamaguchi, K. Ara, T. Fukahori, H. Suzuki, M. Akita, Y. Moro-oka, K. Itoh, Organometallics 9 (1990) 799. (b) T. Arliguie, B. Chaudret, F.A. Jalon, A. Otero, J.A. Lopez, F.J. Lahoz, Organometallics 10 (1991) 1888.
[14] (a) T.K. Hollis, N.P. Robinson, B. Bosnich, J. Am. Chem. Soc. 114 (1992) 5464. (b) W. Odenkirk, B. Bosnich, J. Chem. Soc. Chem. Commun. (1995) 1181.
[15] D.D. Pathak, H. Adams, C. White, J. Chem. Soc. Chem. Commun. (1994) 733.
[16] (a) R.H. Crabtree, J.W. Faller, M.F. Mallea, J.M. Quirk, Organometallics 1 (1982) 1361. (b) M.J. Burk, B. Segmuler, R.H. Crabtree, Organometallics 6 (1987) 2241.
[17] R.J. Kulawiec, J.W. Faller, R.H. Crabtree, Organometallics 9 (1990) 745.
[18] (a) T. Kuwana, D.E. Bublitz, G. Hoh, J. Am. Chem. Soc. 82 (1960) 5811.(b)S.P.Gubin,S.A.Smirnova,L.I.Denisovich,A.A.Lubovich, J.Organomet.Chem.30(1971)243.(c)L.I.Denisovich,N.V.Zakurin, A.A. Bezrukova, S.P. Gubin, J. Organomet. Chem. 81 (1974) 207. (d) R.J. Gale, R. Job, Inorg. Chem. 20 (1981) 42.
[19] U. Koelle, A. Salzer, J. Organomet. Chem. 243 (1983) C27.
[20] K. Hashidzume, H. Tobita, H. Ogino, Organometallics 14 (1995) 1187.
[21] W.Watanabe,I.Motoyam2a,M.Shimoi,T.Iwamoto,Inorg.Chem. 33 (1994) 2518.
[22] (a) E. Cesarotti, A. Chiesa, G.F. Ciani, A. Sironi, R. Vefghi, C. White, J. Chem. Soc. Dalton Trans. (1984) 653. (b) E. Cesarotti, M.Angoletta,N.P.C.Walker,M.B.Hursthouse,R.Vefghi,C.White, J. Organomet. Chem. 286 (1985) 343. (c) P.A. Schofield, H. Adams, N.A. Bailey, E. Cesarotti, C. White, J. Organomet. Chem. 412 (1991) 273.
[23] G.L. Hardgrove, D.H. Templeton, Acta Crystallogr. 12 (1959) 28.
[24] S.P. Deraniyagaia, T.D. Westmoreland, Organometallics 14 (1995) 1239.
[25] K. Kirchner, S. Dasgupta, R. Schmid, J. Chem. Res. (1993) 341.
[26] E. Cesarotti, H.B. Kagan, R. Goddard, C. Kruger, J. Organomet. Chem. 162 (1978) 297.
[27] P.J. Fagan, W.S. Mahoney, J. Calabrese, I.D. Williams, Organometallics 9 (1990) 1845.
[28] T.D. Tilley, R.H. Grubbs, J.E. Bercaw, Organometallics 3 (1984) 274.
[29] InternationalTablesforX-rayCrystallography,vol.4,KynochPress, Birmingham, 1974.
[30] G.M. Sheldrick, SHELXTL, An integrated system for solving, refining and displaying crystal structures from diffraction data (Revision 5.1), University of Göttingen, Germany 1985.