Oxidative addition of diferrocenyl dichalcogenides to [{Ru(η^5-C$_5$Me$_5$)-(μ_3-Cl)}$_4$]. Syntheses, crystal structures and some reactivities of [{Ru(η^5-C$_5$Me$_5$)Cl(μ-ER)}$_2$] (E = S, Se or Te; R = ferrocenyl)

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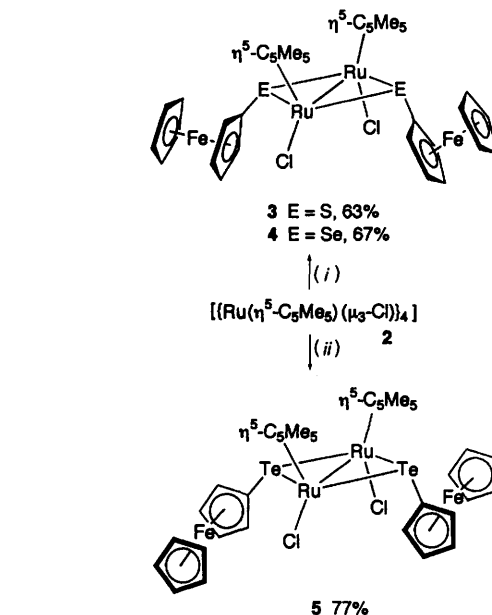
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Reaction of [{Ru(η^5-C$_5$Me$_5$)(μ_3-Cl)}$_4$] with 2 equivalents of REER (E = S, Se or Te; R = ferrocenyl) gave novel ferrocenylchalcogenolate-bridged diruthenium complexes [{Ru(η^5-C$_5$Me$_5$)Cl(μ-ER)}$_2$] in good yields. Reduction of these by sodium amalgam in the presence of buta-1,3-diene afforded [{Ru(η^5-C$_5$Me$_5$)(μ-ER)}$_2$-(μ-s-trans-η^2:$\eta^{2'}$-CH$_2$=CHCH=CH$_2$)], whereas treatment with AgOSO$_2$CF$_3$ produced the co-ordinatively unsaturated complexes [Cl(η^5-C$_5$Me$_5$)Ru(μ-ER)$_2$Ru(η^5-C$_5$Me$_5$)][OSO$_2$CF$_3$]. The structures of five of the complexes have been defined by X-ray crystallography.

Considerable attention has recently been focused on transition-metal complexes with chalcogen ligands as synthetic models of active sites of several metalloenzymes and heterogeneous sulfide catalysts.[1] We have recently found that the chloride ligands in [{Ru(η^5-C$_5$Me$_5$)Cl(μ-Cl)}$_2$] 1[2] can be readily displaced by μ-ER (E = S[3] or Se;[4] R = alkyl or aryl) or μ-RTeTeR[4] units, upon treatment with various thiol, thiolate, selenolate or tellurolate reagents, to form a series of dinuclear (η^5-C$_5$Me$_5$)Ru complexes with ruthenium-(II) and/or -(III) centres.[5-7] Subsequent studies have shown that these diruthenium complexes provide well defined bimetallic reaction sites for unique activation and transformation of organic substrates including alkynes,[8] organic halides[9] and hydrazines.[10] Interestingly these reactions are surprisingly sensitive to the nature of the diruthenium centre, and this has led us to develop a general synthetic methodology for diruthenium complexes possessing bridging chalcogen ligands.

A promising approach to compounds of this class would be oxidative addition of the diorganodichalcogenides to low-valent diruthenium complexes.[11] However, such reactions reported to date usually result in the formation of mixtures of several products, and the desired diruthenium species can only be isolated in low yields. Previously, Killops and Knox[5a] reported that treatment of [{Ru(η^5-C$_5$H$_5$)(CO)$_2$}$_2$] with REER (ER = SMe, SEt, SCH$_2$Ph or SePh), under UV irradiation, gives a mixture of the spectroscopically character-ized complexes [Ru(η^5-C$_5$H$_5$)(CO)$_2$(ER)] and [{Ru(η^5-C$_5$H$_5$)(CO)(μ-ER)}$_2$] in low yields. Schermar and Baddley[6a] observed that thermal reaction of [Ru$_3$(CO)$_{12}$] with PhSeSePh affords [{Ru(CO)$_3$(μ-SePh)}$_2$] (10% yield), the structure of which has recently been crystallographically determined by Cabeza and co-workers.[6b] We have now found that the tetranuclear ruthenium(II) complex [{Ru(η^5-C$_5$Me$_5$)(μ_3-Cl)}$_4$] 2[12] readily reacts with REER (E = S, Se or Te; R = ferrocenyl) at room temperature to form the ferro-cenylchalcogenolate-bridged diruthenium complexes [{Ru-(η^5-C$_5$Me$_5$)Cl(μ-ER)}$_2$] (E = S 3, Se 4 or Te 5)[13] in good yields. Reported herein are the syntheses and crystal structures of these complexes together with their transformation into the s-trans-buta-1,3-diene complexes [{Ru(η^5-C$_5$Me$_5$)(μ-ER)}$_2$(μ-s-trans-η^2:$\eta^{2'}$-CH$_2$=CHCH=CH$_2$)] (E = S 6, Se 7 or Te 8) and the co-ordinatively unsaturated complexes [Cl(η^5-

Scheme 1 (i) REER (E = S or Se; R = ferrocenyl), thf; (ii) RTeTeR, thf

C$_5$Me$_5$)Ru(μ-ER)$_2$Ru(η^5-C$_5$Me$_5$)][OSO$_2$CF$_3$] (E = S 9, Se 10 or Te 11), respectively.

Results and Discussion

A brown suspension of complex 2 in tetrahydrofuran (thf) rapidly turned to a dark green solution which then gradually changed to a dark green suspension on addition of a thf solution of REER (2 equivalents per 2; E = S, Se or Te; R = ferrocenyl) at ambient temperature. Subsequent work-up resulted in isolation of the ferrocenylchalcogenolate-bridged diruthenium complexes [{Ru(η^5-C$_5$Me$_5$)Cl(μ-ER)}$_2$] (E = S 3, Se 4 or Te 5) in typically 63–77% yields (Scheme 1). These were obtained as dark green microcrystalline solids, and have been spectroscopically and crystallographically characterized. It should be noted that these transformations require no thermal activation or photoirradiation which was indispensable
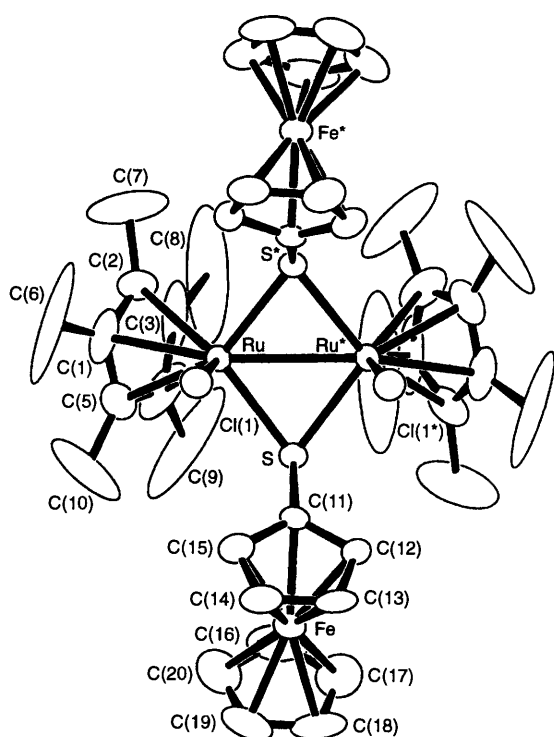
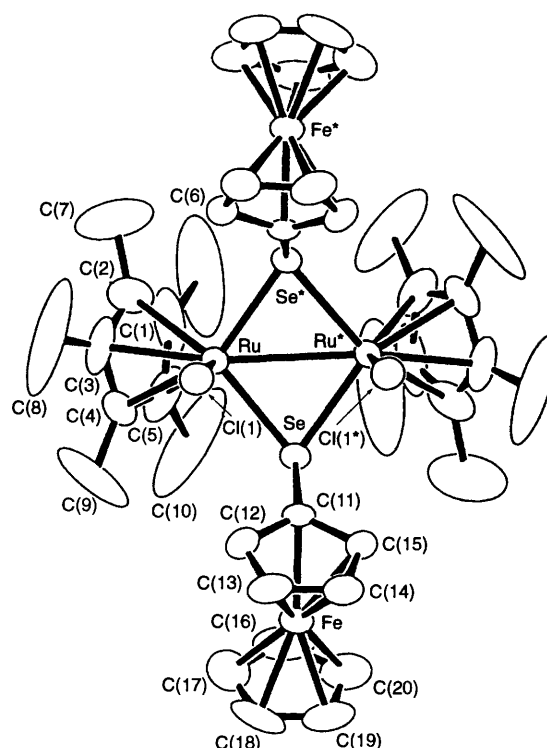**Fig. 1** An ORTEP[14] drawing of complex **3** showing the atomic labelling scheme

Fig. 2 An ORTEP drawing of complex **4** showing the atomic labelling scheme

Table 1 Selected bond distances (Å) and angles (°) for [{Ru(η[5]-C$_5$Me$_5$)Cl(µ-ER)}$_2$] (E = S **3**, Se **4** or Te **5**)

	3	**4**	**5**
Ru–Ru*	2.823(2)	2.9057(8)	3.053(1)
Ru–Cl	2.396(3)	2.398(1)	2.412(2)
Ru–E	2.308(3)	2.4167(6)	2.5884(8)
Ru–E*	2.318(3)	2.4268(7)	2.5868(8)
Ru–C(1)	2.19(1)	2.222(7)	2.242(7)
Ru–C(2)	2.24(1)	2.227(7)	2.256(7)
Ru–C(3)	2.24(2)	2.201(6)	2.255(6)
Ru–C(4)	2.21(2)	2.178(5)	2.193(6)
Ru–C(5)	2.18(1)	2.206(6)	2.235(7)
E–C(11)	1.80(1)	1.928(5)	2.140(7)
Ru*–Ru–Cl	99.92(7)	98.83(3)	99.08(5)
Ru*–Ru–E	52.55(7)	53.30(2)	53.87(2)
Ru*–Ru–E*	52.23(7)	52.98(2)	53.82(2)
Cl–Ru–E	92.7(1)	92.28(4)	91.29(5)
Cl–Ru–E*	91.6(1)	91.23(4)	96.9(2)
E–Ru–E*	104.23(8)	105.81(2)	106.74(3)
Ru–E–Ru*	75.22(8)	73.73(2)	72.31(3)
Ru–E–C(11)	117.2(3)	115.0(1)	120.2(2)
Ru*–E–C(11)	115.6(3)	113.9(1)	114.4(2)

for the previously reported reactions of ruthenium carbonyl complexes with diorganodichalcogenides.[5a,6a,b]

The molecular structure of complex **3** is depicted in Fig. 1, and selected bond distances and angles are listed in Table 1. Fig. 1 clearly shows the dinuclear structure in which the two (η[5]-C$_5$Me$_5$)Ru units are doubly bridged by the µ-SR moieties. The molecule has a crystallographic two-fold axis, such that all the atoms at positions x, y, z have axially related counterparts (labelled with an asterisk) at $-x$, y, $\frac{1}{2} - z$. The two ferrocenyl groups adopt *syn* (axial–axial) configurations, whilst both the two η[5]-C$_5$Me$_5$ and two chloride ligands are *cis* to each other. The intramolecular distance between the ruthenium atoms [2.823(2) Å] corresponds to a Ru–Ru single bond (2.6–2.9 Å).[3,4,8,9] The ^{1}H NMR spectrum of **3** is consistent with this structure, showing the characteristic η[5]-C$_5$Me$_5$ (δ 1.59) and η[5]-

C$_5$H$_5$ (δ 4.26) resonances together with those due to the C$_5$H$_4$S group at δ 4.77 and 3.97 (triplet, 4 H each).

The molecular structure of complex **4** is shown in Fig. 2, and selected bond distances and angles are listed in Table 1. Molecule **4** also has a crystallographic two-fold axis, and the half of it is crystallographically independent. The overall structure (Fig. 2) is similar to that of **3**. Thus, while retaining its shape, the Ru$_2$E$_2$ fragment is simply enlarged to accommodate the bigger Se atoms. This is clearly reflected in both the lengthened Ru–Ru [2.906(1) Å] and Ru–Se bond distances [2.417(1), 2.427(1) Å] compared to those observed for **3** [Ru–Ru 2.823(2); Ru–S 2.308(3), 2.318(3) Å]. The ^{1}H NMR data (see Experimental section) are analogous to those of **3**.

Similar structural features are also observed for complex **5**. However, an ORTEP drawing of this complex (Fig. 3) clearly shows the unambiguous characteristic orientation of the ferrocenyl groups compared with those in **3** and **4**. Selected bond distances and angles are listed in Table 1. The cyclopentadienyl rings of the ferrocenyltellanyl ligands are almost perpendicular to the Ru–Ru* vector, while those of the ferrocenyl-sulfanyl and -selanyl ligands in **3** and **4** are almost parallel to this axis. The diamagnetic nature of **5** suggests the existence of a bonding interaction between the two ruthenium(III) centers, although the Ru–Ru distance of **5** [3.053(1) Å] is longer than those observed for known diruthenium–thiolate and –selenolate compounds (see above).* The ^{1}H NMR spectrum of **5** in C$_6$D$_6$ is fully consistent with its solid-state structure, exhibiting three resonances at δ 4.19 (m, 4 H), 4.77 and 5.09 (m, 2 H each), assigned to the four inequivalent protons in the C$_5$H$_4$Te groups in addition to those signals attributed to the η[5]-C$_5$Me$_5$ (δ 1.67) and η[5]-C$_5$H$_5$ (δ 4.26) moieties. These indicate that rotation about the Te–C bond in **5** is restricted at room temperature in solution on a ^{1}H NMR timescale.

We have already shown that the dinuclear ruthenium(II) complex [{Ru(η[5]-C$_5$Me$_5$)(µ-SPr^i)}$_2$] readily incorporates

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* We cannot exclude the possibility that the diamagnetism of complex **5** is due to some exchange interaction *via* the orbitals of the bridging Te, since the Ru–Ru bond is unusually long.
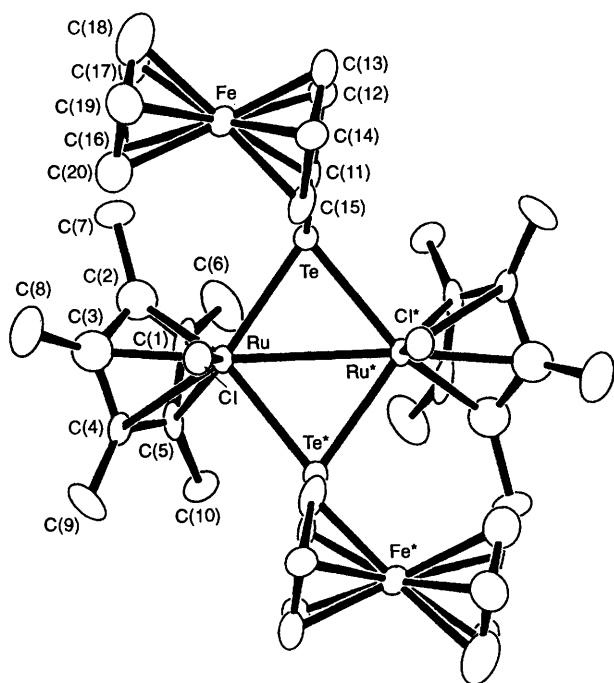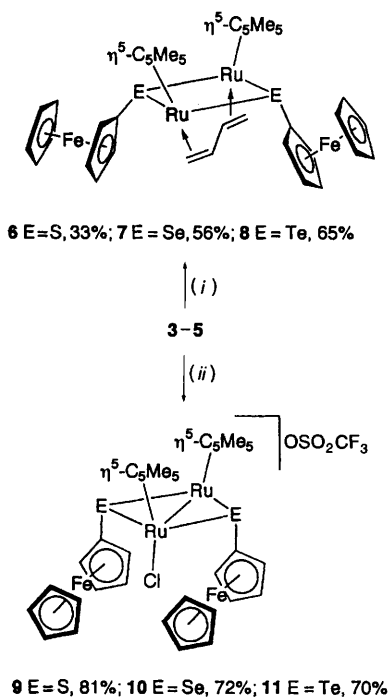
Fig. 3 An ORTEP drawing of complex 5 showing the atomic labelling scheme

6 E=S, 33%; 7 E = Se, 56%; 8 E = Te, 65%

(i)

3-5

(ii)

9 E = S, 81%; 10 E = Se, 72%; 11 E = Te, 70%

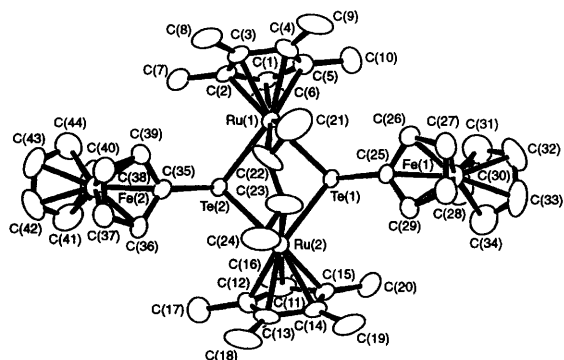**Scheme 2** (i) Na/Hg, buta-1,3-diene, thf; (ii) AgOSO$_2$CF$_3$, thf

Fig. 4 An ORTEP drawing of complex 8 showing the atomic labelling scheme

various organic substrates to its dinuclear site to form a wide variety of novel diruthenium complexes.[3c,8a,c,f,10] Thus, reduction of the ruthenium(III) complexes 3–5 was performed to obtain the corresponding dinuclear ruthenium(II) complexes [{Ru(η^5-C$_5$Me$_5$)(μ-ER)}$_2$] (E = S, Se or Te). However, we could not isolate these complexes by reduction with Na/Hg in thf. In contrast, similar reactions of 3–5 in the presence of buta-1,3-diene led to the formation of dinuclear ruthenium(II) complexes [{Ru(η^5-C$_5$Me$_5$)(μ-ER)}$_2$(μ-s-trans-η^2:$\eta^{2'}$-CH$_2$=C-HCH=CH$_2$)] (E = S 6, Se 7 or Te 8) in moderate yields (Scheme 2). Complexes 6–8 were obtained as orange microcrystalline solids characterized by ^{1}H NMR spectroscopy. The structure of 8 was crystallographically determined.

The molecular structure of complex 8 is depicted in Fig. 4 and selected bond distances and angles are listed in Table 2. Fig. 4 shows the dinuclear structure where the two (η^5-C$_5$Me$_5$)Ru units are bridged by both ferrocenyltellanyl ligands and by a buta-1,3-diene moiety.* Although the bond distances and angles of the butadiene moiety contain unusual values due to its slight disorder, there is no doubt that the buta-1,3-diene ligand is η^2-bound to each ruthenium atom in the s-trans conformation with the torsion angle C(1)–C(2)–C(3)–C(4) 162.8(10)°. Examples of transition-metal complexes with s-trans diene ligands are still relatively few in comparison with a large number of those with s-cis η^4-diene ligands.[15] Typical dinuclear examples are found in [{(Ph$_3$P)Pd(μ-X)PdX}$_2$(μ-s-trans-η^2:$\eta^{2'}$-CH$_2$=CHCH=CH$_2$)] (X = Cl, Br or I)[15a] and [{Ru(CO)(η^5-C$_5$H$_5$)}$_2$(μ-s-trans-η^2:$\eta^{2'}$-CH$_2$=CH-CH=CH$_2$)].[15c] The significantly longer Ru–Ru distance of 3.8538(8) Å in 8 compared with the values reported for diruthenium complexes with a Ru–Ru single bond (see above) clearly indicates the absence of any bonding interaction between the two ruthenium atoms. The ^{1}H NMR spectrum affords only one set of signals for each of the η^5-C$_5$Me$_5$, η^5-C$_5$H$_5$ and C$_5$H$_4$Te groups and the vinyl protons of the butadiene ligand. This clearly suggests that complex 8 has substantial C_2 symmetry in solution in full agreement with its solid-state structure. The ^{1}H NMR data obtained for complexes 6 and 7 are fully in accord with those of 8 implying C_2 symmetry, consequently their butadiene ligands also adopt the s-trans conformation.

We have previously reported that treatment of [{Ru(η^5-C$_5$Me$_5$)Cl(μ-SPr^i)}$_2$] with AgOSO$_2$CF$_3$ produces a highly reactive cationic complex [Cl(η^5-C$_5$Me$_5$)Ru(μ-SPr^i)$_2$Ru(η^5-C$_5$Me$_5$)][OSO$_2$CF$_3$] 12, which undergoes unique reactions with alkynes.[8e,g] Thus, it is of interest to investigate whether complexes 3–5 react with AgOSO$_2$CF$_3$ to form similar reactive species of the form [Cl(η^5-C$_5$Me$_5$)Ru(μ-ER)$_2$Ru(η^5-C$_5$-Me$_5$)][OSO$_2$CF$_3$] (E = S, Se or Te). Reactions of 3–5 with AgOSO$_2$CF$_3$ (1 equivalent) formed the cationic complexes [Cl(η^5-C$_5$Me$_5$)Ru(μ-ER)$_2$Ru(η^5-C$_5$Me$_5$)][OSO$_2$CF$_3$] (E = S 9, Se 10 or Te 11) in moderate yields (Scheme 2). The complexes were isolated as dark green crystalline solids and characterized by ^{1}H NMR measurements. The structure of 10 was crystallographically determined.

The structure of the cation of complex 10 is given in Fig. 5 and selected bond distances and angles are in Table 3. The cation comprises a doubly bridged diruthenium core with a Ru–Ru single bond distance of 2.6668(8) Å. The Cl ligand is terminally bound to Ru(1), and Ru(2) is apparently a 16-electron ruthenium(III) centre [Ru(1)–Cl 2.383(2), Ru(2)···Cl 4.15 Å]. The η^5-C$_5$Me$_5$ group attached to Ru(2) and the two ferrocenyl groups in the bridging ligands differ significantly in configuration from those observed in 4 (see Fig. 2). No appreciable distance characteristic of agostic interaction[16] was

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* Crystallographic analysis of complexes 6 and 7 was also attempted, but the disordered structures of their butadiene ligands prevented full refinement. Nevertheless, the molecular structures were confirmed to be essentially analogous to that of 8.

Table 2 Selected bond distances (Å) and angles (°) for [{Ru(η⁵-C₅Me₅)(μ-TeR)}₂(μ-s-*trans*-η²:η²′-CH₂=CHCH=CH₂)] **8**

Ru(1)–Te(1)	2.6511(7)	Ru(2)–C(11)	2.195(7)
Ru(1)–Te(2)	2.6688(8)	Ru(2)–C(12)	2.217(7)
Ru(1)–C(1)	2.191(6)	Ru(2)–C(13)	2.225(7)
Ru(1)–C(2)	2.210(7)	Ru(2)–C(14)	2.222(7)
Ru(1)–C(3)	2.217(7)	Ru(2)–C(15)	2.204(7)
Ru(1)–C(5)	2.230(7)	Ru(2)–C(23)	2.281(8)
Ru(1)–C(21)	2.183(8)	Ru(2)–C(24)	2.183(8)
Ru(1)–C(22)	2.266(8)	Te(1)–C(25)	2.115(7)
Ru(2)–Te(1)	2.6636(8)	Te(2)–C(35)	2.145(7)
Ru(2)–Te(2)	2.6535(7)		

Te(1)–Ru(1)–Te(2)	77.08(2)	Te(1)–Ru(1)–C(1)	100.5(2)
Te(1)–Ru(1)–C(2)	134.8(2)	Te(2)–Ru(1)–C(1)	99.4(2)
Te(2)–Ru(1)–C(2)	91.8(2)	C(1)–Ru(1)–C(2)	37.5(2)
Te(1)–Ru(2)–Te(2)	77.13(2)	Te(1)–Ru(2)–C(11)	100.4(2)
Te(1)–Ru(2)–C(12)	136.1(2)	Te(2)–Ru(2)–C(11)	99.8(2)
Te(2)–Ru(2)–C(12)	96.1(2)	C(11)–Ru(2)–C(12)	37.2(3)
Ru(1)–Te(1)–Ru(2)	92.96(2)	Ru(1)–Te(1)–C(25)	107.1(2)
Ru(2)–Te(1)–C(25)	107.2(2)	Ru(1)–Te(2)–Ru(2)	92.79(2)
Ru(1)–Te(2)–C(35)	106.9(2)	Ru(2)–Te(2)–C(35)	108.1(2)
Ru(1)–C(1)–C(2)	72.0(4)	Ru(1)–C(2)–C(1)	70.5(4)
Ru(1)–C(2)–C(3)	71.7(4)	C(1)–C(2)–C(3)	108.5(7)
Ru(2)–C(11)–C(12)	72.2(4)	Ru(2)–C(12)–C(11)	70.6(4)
C(11)–C(12)–C(13)	108.1(7)		

Table 3 Selected bond distances (Å) and angles (°) for [Cl(η⁵-C₅Me₅)Ru(μ-SeR)₂Ru(η⁵-C₅Me₅)][OSO₂CF₃] **10**

Ru(1)–Ru(2)	2.6668(8)	Ru(2)–Se(1)	2.4164(9)
Ru(1)–Se(1)	2.4341(9)	Ru(2)–Se(2)	2.4146(9)
Ru(1)–Se(2)	2.4245(9)	Ru(2)–C(11)	2.175(7)
Ru(1)–Cl	2.383(2)	Ru(2)–C(12)	2.171(6)
Ru(1)–C(1)	2.222(7)	Ru(2)–C(13)	2.221(6)
Ru(1)–C(2)	2.290(6)	Ru(2)–C(14)	2.173(6)
Ru(1)–C(3)	2.252(7)	Ru(2)–C(15)	2.211(7)
Ru(1)–C(4)	2.197(7)	Se(1)–C(21)	1.892(6)
Ru(1)–C(5)	2.197(7)	Se(2)–C(31)	1.893(7)

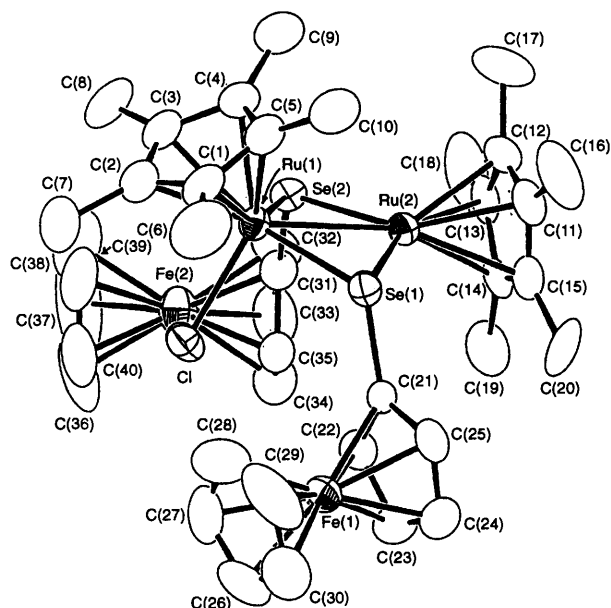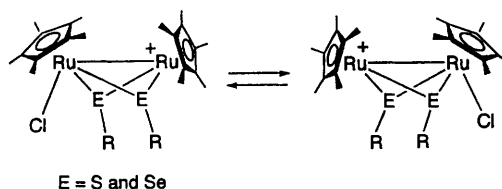|			
Ru(2)–Ru(1)–Se(1)	56.33(2)	Ru(2)–Ru(1)–Se(2)	56.38(3)
Ru(2)–Ru(1)–Cl	110.34(5)	Se(1)–Ru(1)–Se(2)	111.12(3)
Se(1)–Ru(1)–Cl	94.76(5)	Se(2)–Ru(1)–Cl	95.12(5)
Ru(1)–Ru(2)–Se(1)	56.96(2)	Ru(1)–Ru(2)–Se(2)	56.74(2)
Se(1)–Ru(2)–Se(2)	112.08(3)	Ru(1)–Se(1)–Ru(2)	66.71(3)
Ru(1)–Se(1)–C(21)	120.1(2)	Ru(2)–Se(1)–C(21)	105.5(2)
Ru(1)–Se(2)–Ru(2)	66.89(3)	Ru(1)–Se(2)–C(31)	121.2(2)
Ru(2)–Se(2)–C(31)	107.4(2)		

E = S and Se

Scheme 3 R = Ferrocenyl

Fig. 5 An ORTEP drawing of the cationic part of complex **10** showing the atomic labelling scheme

observed in the solid state among the non-bonding distances around Ru(2). Consequently, the 16-electron ruthenium(III) centre appears to be sterically stabilized by the bulky η⁵-C₅Me₅ and SeR groups. The average Ru(2)–Se–C bond angle [106°] is significantly smaller than the corresponding Ru(1)–Se–C angle [120°]. A variable-temperature ¹H NMR study revealed fluxional properties of **10**. The ¹H NMR spectrum in CDCl₃ at 20 °C shows only one set of signals due to the η⁵-C₅Me₅, η⁵-C₅H₅ and C₅H₄Se groups. Upon cooling to −60 °C the characteristic resonance at δ 1.54 due to the η⁵-C₅Me₅ groups broadened and then resolved into two broad singlets at δ 1.78 and 1.30, respectively. Similar behaviour was observed for complex **9**. Thus, a broad singlet peak assigned to the η⁵-C₅Me₅ group (δ 1.51) was observed at 30 °C, which split into two sharper peaks (δ 1.22 and 1.75) at lower temperatures (< 0 °C). These spectroscopic features can be rationalized by the fluxional process shown in Scheme 3. In sharp contrast to complexes **9** and **10**, a singlet observed in the ¹H NMR spectrum of **11**, assigned to the η⁵-C₅Me₅ group, failed to split

even at −60 °C. This result shows that the fluxionality of **11** is maintained even at low temperature.

In summary, the present study demonstrates the synthetic utility of the oxidative-addition reaction of REER (E = S, Se or Te; R = ferrocenyl) to complex **2** for the construction of diruthenium sites bridged by μ-ER ligands. Further studies to develop new types of transformations of organic substrates on these bimetallic centres are currently in progress.

Experimental

The compounds [{Ru(η⁵-C₅Me₅)(μ₃-Cl)}₄][12] and REER (E = S,[17] Se[17] or Te[18]) were prepared by the literature procedures. Buta-1,3-diene and AgOSO₂CF₃ were obtained commercially and used without further purification. Solvents were dried by refluxing over sodium–benzophenone (thf, benzene, hexane), P₂O₅ (CH₂Cl₂) or CaH₂ (acetonitrile) and freshly distilled prior to use. All manipulations were performed under N₂ with standard Schlenk-tube techniques. Infrared spectra were recorded on a Shimadzu FT-IR 8100M spectrometer, ¹H (270 MHz) NMR spectra on a JEOL EX-270 spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400II CHN analyser. The cyclic voltammograms for complexes **3–5** were measured in CH₂Cl₂–0.1 mol dm⁻³ [NBuⁿ₄][BF₄].

Preparations

[{Ru(η⁵-C₅Me₅)Cl(μ-SR)}₂] **3** (R = ferrocenyl). A brown suspension of [{Ru(η⁵-C₅Me₅)(μ₃-Cl)}₄] **2** (0.168 g, 0.155 mmol) in thf (6 cm³) immediately turned to a dark green solution and then gradually changed to a dark green suspension when RSSR (2 equivalents per **2**) in thf (5 cm³) was added. The reaction mixture was stirred overnight at room temperature. The dark green precipitate was filtered off, washed with thf, and recrystallized from CH₂Cl₂–hexane as dark green-black columnar crystals, which were washed with hexane and dried *in vacuo* (0.207 g, 63%); δ_H(C₆D₆) 4.77, 3.97 (t, 4 H each, J = 2.0 Hz, SC₅H₄), 4.26 (s, 10 H, C₅H₅) and 1.59 (s, 30 H, C₅Me₅) (Found: C, 46.05; H, 4.75. C₄₀H₄₈Cl₂Fe₂Ru₂S₂·CH₂Cl₂ requires C, 46.35; H, 4.75%). This complex showed two

reversible oxidation waves at $E_{\frac{1}{2}} = +0.64$ and $+0.96$ V and one irreversible reduction wave at $E_p = -0.88$ V (vs. saturated calomel electrode, SCE).

[{Ru(η⁵-C₅Me₅)Cl(μ-ER)}₂] (E = Se 4 or Te 5). Complexes 4 and 5 were obtained similarly except that the crude products were purified by chromatography on silica gel with EtOH (4) or thf (5), and recrystallized from CH₂Cl₂–hexane. Complex 4: yield 67%; $\delta_H(C_6D_6)$ 4.91, 4.02 (t, 4 H each, $J = 2.0$ Hz, SeC₅H₄), 4.30 (s, 10 H, C₅H₅) and 1.57 (s, 30 H, C₅Me₅) (Found: C, 41.85; H, 4.50. C₄₀H₄₈Cl₂Fe₂Ru₂Se₂·CH₂Cl₂ requires C, 42.6; H, 4.35%); two reversible oxidation waves at $E_{\frac{1}{2}} = +0.65$ and $+0.96$ V and two irreversible reduction waves at $E_p = -0.80$ and -1.54 V (vs. SCE). Complex 5: yield 77%; $\delta_H(C_6D_6)$ 5.09, 4.77 (m, 2 H each, TeC₅H₄), 4.26 (s, 10 H, C₅H₅), 4.19 (m, 4 H, TeC₅H₄) and 1.67 (s, 30 H, C₅Me₅) (Found: C, 41.0; H, 4.20. C₄₀H₄₈Cl₂Fe₂Ru₂Te₂ requires C, 41.1; H, 4.15%); one reversible oxidation wave at $E_{\frac{1}{2}} = +0.74$ V and four irreversible reduction waves at $E_p = -0.60, -0.91, -1.20$ and -1.45 V (vs. SCE).

[{Ru(η⁵-C₅Me₅)(μ-TeR)}₂(μ-s-trans-η²:η²′-CH₂=CH-CH=CH₂)] 8. A solution of complex 5 (0.095 g, 0.064 mmol) in thf (10 cm³) in the presence of Na/Hg (0.084 g, 3.65 mmol, 6.766 g) was cooled to -78 °C and buta-1,3-diene was condensed into the solution. The mixture was slowly warmed to room temperature with stirring, and stirred at room temperature for 3 h. The original brown suspension turned to an orange solution. After addition of hexane (20 cm³) the reaction mixture was filtered and the solvent evaporated. Recrystallization of the resultant solid from benzene–hexane gave 8 (0.052 g, 65%) as an orange solid; $\delta_H(C_6D_6)$ 4.76 (m, 2 H, diene), 4.27 (s, 10 H, η⁵-C₅H₅), 4.44, 4.17, 4.11, 3.72 (m, 2 H each, C₅H₄Te), 3.13 (d, 2 H, $J = 10.6$, diene), 2.86 (d, 2 H, $J = 7.9$ Hz, diene) and 1.86 (s, 30 H, η⁵-C₅Me₅) (Found: C, 48.75; H, 4.95. C₄₄H₅₄Fe₂Ru₂Te₂·C₆H₆ requires C, 48.8; H, 4.90%).

[{Ru(η⁵-C₅Me₅)(μ-ER)}₂(μ-s-trans-η²:η²′-CH₂=CH-CH=CH₂)] (E = S 6 or Se 7). Complexes 6 and 7 were obtained by a similar method and recrystallized from benzene–hexane. Complex 6: yield 33%; $\delta_H(C_6D_6)$ 4.84 (m, 2 H, diene), 4.22 (s, 10

H, η⁵-C₅H₅), 4.35, 4.04, 3.99, 3.52 (m, 2 H each, C₅H₄S), 3.82 (d, 2 H, $J = 7.9$, diene), 3.63 (d, 2 H, $J = 10.9$ Hz, diene) and 1.78 (s, 30 H, η⁵-C₅Me₅) (Found: C, 57.85; H, 6.15. C₄₄H₅₄Fe₂Ru₂S₂·C₆H₆ requires C, 57.8; H, 5.80%). Complex 7: yield 56%; $\delta_H(C_6D_6)$ 4.84 (m, 2 H, diene), 4.26 (s, 10 H, η⁵-C₅H₅), 4.38, 4.09, 4.04, 3.64 (m, 2 H each, C₅H₄Se), 3.56 (d, 2 H, $J = 7.9$, diene), 3.46 (d, 2 H, $J = 10.9$ Hz, diene) and 1.78 (s, 30 H, η⁵-C₅Me₅) (Found: C, 53.1; H, 5.70. C₄₄H₅₄Fe₂Ru₂Se₂·C₆H₆ requires C, 53.0; H, 5.35%).

[Cl(η⁵-C₅Me₅)Ru(μ-SeR)₂Ru(η⁵-C₅Me₅)][OSO₂CF₃] 10. A brown suspension of complex 4 (0.273 g, 0.255 mmol) in thf (25 cm³) immediately turned to a green solution upon addition of AgOSO₂CF₃ (0.066 g, 0.257 mmol). The reaction mixture was stirred overnight at room temperature and then filtered. After removal of the solvent, the resultant solid was recrystallized from CH₂Cl₂–hexane to give 10 as dark green crystals, which were washed with hexane and dried in vacuo (0.219 g, 72%); $\delta_H(CDCl_3)$ 4.48 (br, 18 H, η⁵-C₅H₅, C₅H₄Se) and 1.54 (s, 30 H, η⁵-C₅Me₅) (Found: C, 40.9; H, 4.20. C₄₁H₄₈ClF₃Fe₂O₃Ru₂SSe₂ requires C, 41.55; H, 4.10%).

[Cl(η⁵-C₅Me₅)Ru(μ-ER)₂Ru(η⁵-C₅Me₅)][OSO₂CF₃] (E = S 9 or Te 11). Complexes 9 and 11 were obtained by a similar method and recrystallized from CH₂Cl₂–hexane. Complex 9: yield 81%; $\delta_H(CDCl_3)$ 4.42 (br, 18 H, η⁵-C₅H₅, C₅H₄S) and 1.51 (s, 30 H, η⁵-C₅Me₅) (Found: C, 44.95; H, 4.40. C₄₁H₄₈ClF₃Fe₂O₃Ru₂S₃ requires C, 45.15; H, 4.45%). Complex 11: yield, 70%; $\delta_H(CDCl_3)$ 4.65 (br, 18 H, η⁵-C₅H₅, C₅H₄Te) and 1.62 (s, 30 H, η⁵-C₅Me₅) (Found: C, 36.5; H, 3.80. C₄₁H₄₈ClF₃Fe₂O₃Ru₂STe₂·CH₂Cl₂ requires C, 36.9; H, 3.70%).

Crystallography

Single crystals suitable for X-ray analysis were prepared by recrystallization from CH₂Cl₂–hexane (complexes 3, 4, 5 and 10) or benzene–hexane (8). Diffraction data were collected on a Rigaku AFC-7R four-circle automated diffractomater with Mo-Kα ($\lambda = 0.71069$ Å) radiation and a graphite monochromator at 20 °C using the ω–2θ scan technique (5 < 2θ < 55°). No

Table 4 Crystallographic data for complexes 3–5, 8 and 10

	3	4	5	8	10
Formula	C₄₁H₅₀Cl₄Fe₂Ru₂S₂	C₄₁H₅₀Cl₄Fe₂Ru₂Se₂	C₄₀H₄₈Cl₂Fe₂Ru₂Te₂	C₅₀H₆₀Fe₂Ru₂Te₂	C₄₁H₄₈ClF₃Fe₂O₃Ru₂SSe₂
M	1062.61	1156.41	1168.76	1230.06	1185.09
Crystal size/mm	0.2 × 0.2 × 0.3	0.35 × 0.20 × 0.35	0.10 × 0.40 × 0.20	0.20 × 0.20 × 0.20	0.50 × 0.14 × 0.20
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$C2/c$	$C2/c$	$C2/c$	$P\bar{1}$	$P2_1/c$
Crystal colour	Deep green	Deep green	Deep green	Orange	Deep green
a/Å	16.095(2)	16.309(1)	22.414(4)	12.743(2)	10.495(3)
b/Å	12.904(3)	12.953(2)	9.509(3)	15.424(1)	17.735(3)
c/Å	21.605(2)	21.734(1)	18.427(3)	12.088(1)	23.042(3)
α/°				93.840(9)	
β/°	109.415(9)	109.697(5)	104.50(1)	105.216(10)	95.50(2)
γ/°				85.281(9)	
U/Å³	4232(1)	4322.5(7)	3802(1)	2282.3(5)	4269(1)
Z	4	4	4	2	4
D_c/g cm⁻³	1.668	1.777	2.041	1.790	1.844
$F(000)$	2144	2288	2264	1208	2344
μ/cm⁻¹	17.51	33.03	32.00	25.58	32.27
No. unique data	5089	5197	4628	8026	10 129
No. data used [$I > 3\sigma(I)$]	2861	3483	2828	5054	5864
No. parameters refined	231	231	217	506	496
R	0.049	0.036	0.038	0.036	0.044
R'	0.036	0.027	0.027	0.022	0.029
Goodness of fit	1.57	2.57	1.74	1.59	2.22
Maximum residual/e Å⁻³	0.74	0.66	0.91	1.23	0.96

significant decay was observed for three standard reflections monitored every 150. Details of the X-ray diffraction study are summarized in Table 4.

For all structure analysis and refinement, computations were performed using TEXSAN.[19] Neutral atom scattering factors were taken from ref. 20. Anomalous dispersion effects were included in F_{calc};[21] the values for $\Delta f'$ and $\Delta f''$ were those of ref. 22. The structures were solved by Patterson methods. Full-matrix least-squares refinement (on F) was employed with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included but not refined. The weighting scheme $w = 1/\sigma^2(F_o)$, with $\sigma(F_o)$ from counting statistics, gave satisfactory agreement analyses.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/214.

References

1 J. M. Berg and R. H. Holm, in *Metal Ions in Biology*, ed. T. G. Spiro, Wiley, New York, 1982, vol. 4, p. 1; M. Rakowski Dubois, *Chem. Rev.*, 1989, **89**, 1; R. J. Angelici, *Acc. Chem. Res.*, 1988, **21**, 387.

2 T. D. Tilley, R. H. Grubbs and J. E. Bercaw, *Organometallics*, 1984, **3**, 274; N. Oshima, H. Suzuki and Y. Moro-oka, *Chem. Lett.*, 1984, 1161; U. Kölle, J. Kossakowski, N. Klaff, L. Wesemann, U. Engelert and G. E. Heberich, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 690.

3 (a) S. Dev, K. Imagawa, Y. Mizobe, G. Cheng, Y. Wakatsuki, H. Yamazaki and M. Hidai, *Organometallics*, 1989, **8**, 1232; (b) S. Dev, Y. Mizobe and M. Hidai, *Inorg. Chem.*, 1990, **29**, 4797; (c) A. Takahashi, Y. Mizobe, H. Matsuzaka, S. Dev and M. Hidai, *J. Organomet. Chem.*, 1993, **456**, 243; (d) M. Hidai, Y. Mizobe and H. Matsuzaka, *J. Organomet. Chem.*, 1994, **473**, 1.

4 H. Matsuzaka, T. Ogino, M. Nishio, M. Hidai, Y. Nishibayashi and S. Uemura, *J. Chem. Soc., Chem. Commun.*, 1994, 223.

5 (a) S. D. Killops and S. A. R. Knox, *J. Chem. Soc., Dalton Trans.*, 1978, 1260; (b) E. J. Houser, J. Amarasekera, T. B. Rauchfuss and S. R. Wilson, *J. Am. Chem. Soc.*, 1991, **113**, 7440; (c) J. Amarasekera, T. B. Rauchfuss and S. R. Wilson, *J. Chem. Soc., Chem. Commun.*, 1989, 14; (d) S. A. Koch and M. Millar, *J. Am. Chem. Soc.*, 1983, **105**, 3362; (e) M. M. Millar, T. O'Sullivan, N. Vries and S. A. Koch, *J. Am. Chem. Soc.*, 1985, **107**, 3714; (f) A. Shaver, P.-Y. Plouffe, D. C. Lilles and E. Singleton, *Chem. Ber.*, 1992, **31**, 997; (g) A. Hörnig, C. Rietmann, U. Englert, T. Wagner and U. Kölle, *Chem. Ber.*, 1993, **32**, 4069.

6 (a) E. D. Schermar and W. H. Baddley, *J. Organomet. Chem.*, 1971, **30**, 67; (b) P. L. Andreu, J. A. Cabeza, D. Miguel, V. Riera, M. A. Villa and S. Carcia-Granada, *J. Chem. Soc., Dalton Trans.*, 1991, 533; (c) J. Amarasekera, E. J. Houser, T. B. Rauchfuss and C. L. Stern, *Inorg. Chem.*, 1992, **31**, 1614; (d) J. Amarasekera, T. B. Rauchfuss and S. R. Wilson, *J. Chem. Soc., Chem. Commun.*, 1989, 14; (e) B. F. G. Johnson, T. M. Layer, J. Lewis, A. Martin and

P. R. Raithby, *J. Organomet. Chem.*, 1992, **429**, C41; (f) M. Draganjac, S. Dhingra, S.-P. Huang and M. Kanatzidis, *Inorg. Chem.*, 1990, **29**, 590; (g) R. S. Bates and A. H. Wrighty, *J. Chem. Soc., Chem. Commun.*, 1990, 1229; (h) W. N. Stassen and R. D. Heyding, *Can. J. Chem.*, 1968, **46**, 2159.

7 S.-P. Huang and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 1992, **114**, 5477.

8 (a) H. Matsuzaka, Y. Mizobe, M. Nishio and M. Hidai, *J. Chem. Soc., Chem. Commun.*, 1991, 1011; (b) H. Matsuzaka, Y. Hirayama, M. Nishio, Y. Mizobe and M. Hidai, *Organometallics*, 1993, **12**, 36; (c) M. Nishio, H. Matsuzaka, Y. Mizobe and M. Hidai, *J. Chem. Soc., Chem. Commun.*, 1993, 375; (d) H. Matsuzaka, H. Koizumi, Y. Takagi, M. Nishio and M. Hidai, *J. Am. Chem. Soc.*, 1993, **115**, 10396; (e) H. Matsuzaka, Y. Takagi and M. Hidai, *Organometallics*, 1994, **13**, 13; (f) M. Nishio, H. Matsuzaka, Y. Mizobe, T. Tanase and M. Hidai, *Organometallics*, 1994, **13**, 4214; (g) H. Matsuzaka, Y. Takagi, Y. Ishii, M. Nishio and M. Hidai, *Organometallics*, 1995, **14**, 2153.

9 A. Takahashi, Y. Mizobe and M. Hidai, *Chem. Lett.*, 1994, 371.

10 S. Kuwata, Y. Mizobe and M. Hidai, *Inorg. Chem.*, 1994, **33**, 3619.

11 H. J. Gysling, in *The Chemistry of Organic Selenium and Tellurium Compounds*, eds. S. Patai and Z. Rappoport, Wiley, New York, 1986, vol. 1, p. 679; F. J. Berry, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 2, p. 661.

12 P. J. Fagan, M. D. Ward and J. C. Calabrese, *J. Am. Chem. Soc.*, 1989, **111**, 1698; P. J. Fagan, W. S. Mahoney, J. C. Calabrese and I. D. Williams, *Organometallics*, 1990, **9**, 1843.

13 D. Seyferth, B. W. Hames, T. G. Rucker, M. Cowie and R. S. Dickson, *Organometallics*, 1983, **2**, 472; S. Akabori, T. Kumagai, T. Shirahige, S. Sato, K. Kawazoe, C. Tamura and M. Sato, *Organometallics*, 1987, **6**, 526; M. Sato, M. Sekino and S. Akabori, *J. Organomet. Chem.*, 1988, **344**, C31; W. R. Cullen, A. Talaba and S. J. Rettig, *Organometallics*, 1992, **11**, 3152; M. Herberhold, G.-X. Jiu and A. L. Rheingold, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 656.

14 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

15 (a) T. Murahashi, N. Kanehisa, Y. Kai, T. Otani and H. Kurosawa, *Chem. Commun.*, 1996, 825; (b) P. Leoni, M. Pasquali, M. Sommovigo, A. Albinati, F. Lianza, P. S. Pregosin and H. Rüegger, *Organometallics*, 1993, **12**, 4503; (c) G. S. Lewandos, S. A. R. Knox and A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1987, 2703; (d) C. G. Piapont, *Inorg. Chem.*, 1978, **17**, 1976; (e) P. F. Jackson, B. F. G. Johnson, J. Lewis, P. R. Raithby, G. J. Will, M. McPartlin and W. J. H. Nelson, *J. Chem. Soc., Chem. Commun.*, 1980, 1190; (f) M. Tachikawa, J. R. Shapley, R. C. Haltiwanger and C. G. Piapont, *J. Am. Chem. Soc.*, 1976, **98**, 4651; (g) H. Yasuda, K. Tatsumi and A. Nakamura, *Acc. Chem. Res.*, 1985, **18**, 120.

16 M. Brookhart and M. L. H. Green, *J. Organomet. Chem.*, 1983, **250**, 395.

17 M. Herberhold and P. Leitner, *J. Organomet. Chem.*, 1987, **336**, 153.

18 Y. Nishibayashi, T. Chiba, J.-D. Singh and S. Uemura, *J. Organomet. Chem.*, 1994, **473**, 205.

19 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corperation, Houston, TX, 1985 and 1992.

20 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, Table 2.2A.

21 J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 1964, **17**, 781.

22 D. C. Creagh and J. H. Hubbell, *International Tables for Crystallography*, ed. A. J. C. Wilson, Kluwer Academic Publishers, Boston, PA, 1992, vol. C, Table 4.2.4.3, pp. 200–206.