Structure and reactivity of η^4-cyclobutadiene and cisoid-η^4(5e)-butadienyl-substituted rhenium complexes formed by reaction of [$ReBr_2\{\eta^2(4e)$-alkyne$\}(\eta$-$C_5H_5)$] with alkynes or *o*-diphenylphosphinostyrene *

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When *cis*-/*trans*-[$ReBr_2(CO)_2(\eta$-$C_5H_5)$] and PhC_2Ph were heated together under reflux in toluene solution for 24 h the η^4-cyclobutadiene-substituted complex [$ReBr_2(\eta^4$-$C_4Ph_4)(\eta$-$C_5H_5)$] **1** was formed in good yield *via* the intermediate [$ReBr_2\{\eta^2(4e)$-$PhC_2Ph\}(\eta$-$C_5H_5)$]. A single-crystal X-ray diffraction study confirmed an overall pseudo-tetrahedral structure for **1**, establishing a Br–Re–Br angle of 83.9°. Treatment of **1** with PPh_3 or PMe_3 (L) in the presence of $AgBF_4$ afforded the cations [$ReBr(L)(\eta^4$-$C_4Ph_4)(\eta$-$C_5H_5)$][BF_4] **2** (L = PPh_3) and **3** (L = PMe_3). Reaction of **1** with an excess of Li[AlH_4] gave the dihydride [$ReH_2(\eta^4$-$C_4Ph_4)(\eta$-$C_5H_5)$] **4** characterised by X-ray crystallography, whereas, 1 equivalent of Li[AlH_4] afforded [$ReH(Br)(\eta^4$-$C_4Ph_4)(\eta$-$C_5H_5)$] **5**. In contrast with predictions from the Davis–Green–Mingos rules, reaction of **2** with Li[$BHEt_3$] afforded **5** (major) and the minor product [$ReH(PPh_3)(\eta^4$-$C_4Ph_4)(\eta$-$C_5H_5)$]Br **6**. Extended Hückel molecular orbital calculations suggested that protonation of **4** should give the cationic trihydride [$ReH_3(\eta^4$-$C_4Ph_4)(\eta$-$C_5H_5)]^+$, however a novel ring-opening reaction occurred with CF_3CO_2H to give the crystallographically characterised η^4-1,3-diene complex [$ReH\{OC(O)CF_3\}\{\eta^2,\eta^2$-*Z*,*Z*-PhCH=C(Ph)C(Ph)=C(Ph)H$\}(\eta$-$C_5H_5)$] **7**. When [$ReBr_2\{\eta^2(4e)$-$PhC_2R\}(\eta$-$C_5H_5)$] (R = Me or Ph) was treated with $AgBF_4$ (2 equivalents) and *o*-diphenylphosphinostyrene (dpps) a carbon–carbon coupling reaction between the co-ordinated alkyne and alkene part of the dpps ligand took place followed by a deprotonation reaction to give the cisoid-η^4(5e)-butadienyl-substituted complexes [Re{=C(Ph)-η^3-C(R)CHCH-$C_6H_4PPh_2$-*o*}$(\eta$-$C_5H_5)$][BF_4] **8** (R = Me) and **9** (R = Ph); the structure of **8** being confirmed by single-crystal X-ray crystallography. Treatment of **9** with K[$BHBu^s_3$] led to the selective delivery of 'H^-' to the Re=C_α carbon of the η^4(5e)-butadienyl ligand and formation of the crystallographically identified d^6 η^4-1,3-diene complex [Re{η^4-CH(Ph)=C(Ph)CH=CHC$_6H_4PPh_2$-*o*}$(\eta$-$C_5H_5)$] **10**. Interestingly, reaction of **10** with [Ph_3C][BF_4] led to regeneration of the parent cisoid-η^4(5e)-butadienyl complex **9** confirming the relationship between η^4(5e)-butadienyl and η^4-1,3-diene ligands.

We recently[2] reported that the η^2(4e)-bonded alkyne complexes [$ReBr_2\{\eta^2(4e)$-alkyne$\}(\eta$-$C_5H_5)$] are formed in good yield when a toluene solution of *cis*-/*trans*-[$ReBr_2(CO)_2(\eta$-$C_5H_5)$] and the alkynes PhC≡CPh and PhC≡CMe are heated under reflux for 2 h. In an initial study[2] of the reactivity of these alkyne-substituted complexes it was observed that treatment with phosphines (L) or the bis(phosphine) $Ph_2PCH_2CH_2PPh_2$ (dppe) in the presence of halide-abstracting reagents $AgBF_4$ or $TlPF_6$ led to the formation respectively of the cations [$ReBr\{\eta^2(4e)$-alkyne$\}L(\eta$-$C_5H_5)]^+$ or dications [$Re\{\eta^2(4e)$-alkyne$\}$(dppe)$(\eta$-$C_5H_5)]^{2+}$. However, when the corresponding reactions with *o*-diphenylphosphinostyrene (dpps) were explored[3] we were surprised to observe an alkyne/alkene coupling reaction resulting in the formation of cisoid-η^4(5e)-butadienyl-substituted rhenium cations. This observation led us to examine the reaction of *cis*-/*trans*-[$ReBr_2(CO)_2(\eta$-$C_5H_5)$] and [$ReBr_2\{\eta^2(4e)$-$PhC_2Ph\}(\eta$-$C_5H_5)$] with diphenylacetylene under more forcing conditions, in the belief that alkyne-coupling reactions might occur. This paper describes the results of this investigation and provides details of the cisoid-η^4(5e)-butadienylrhenium cation-forming reactions, and a study of their reactivity towards a source of 'H^-'.

Results and Discussion

When a solution of [$ReBr_2\{\eta^2(4e)$-$PhC_2Ph\}(\eta$-$C_5H_5)$] and PhC≡CPh in deuteriotoluene contained in a sealed NMR tube was heated (80 °C) it was observed the signal at δ 219.2 in the ^{13}C-{^1H} NMR spectrum attributable to the contact PhC_2Ph carbons gradually decreased in intensity over a period of 15 h. In view of this observation a solution of *cis*-/*trans*-[$ReBr_2(CO)_2(\eta$-$C_5H_5)$] and an excess of diphenylacetylene in toluene was heated under reflux for 24 h. Work-up by column chromatography and elution with dichloromethane–hexane gave a good yield (68%) of a deep red crystalline material, which was identified by elemental analysis, ^1H and ^{13}C-{^1H} NMR spectroscopy as the η^4-tetraphenylcyclobutadiene-substituted complex [$ReBr_2(\eta^4$-$C_4Ph_4)(\eta$-$C_5H_5)$] **1**. This was confirmed by single-crystal X-ray crystallography; the molecular structure is illustrated in Fig. 1, and selected bond lengths and angles are listed in Table 1.

The ORTEX[4] diagram shows a pseudo-tetrahedral geometry in which two bromo ligands and the centroids of the η-C_5H_5 and η^4-C_4Ph_4 rings occupy the vertices. In the C_4Ph_4 ligand the phenyl rings adopt a propeller orientation with respect to one another with average Re–C distances for the η^4-C_4Ph_4 and η-C_5H_5 ligands of 2.23(3) and 2.24(3) Å respectively, and Re–Br bond distances of 2.581(4) and 2.574(4) Å. The Br–Re–Br and Ca–Re–Cb) (Ca = C_5H_5 centroid, Cb = C_4Ph_4 centroid) angles are 83.9(1) and 133(1)° respectively. The overall geometry of **1** is similar to that reported[5] for the paramagnetic complex [$MoCl_2(\eta^4$-$C_4Ph_4)(\eta$-$C_5H_5)$], however it is interesting that in the molybdenum system a Cl–Mo–Cl angle of 90° is observed in the solid state. A similar difference in X–M–X bond angles has also been previously noted[5] and discussed for the species [$MX_2(\eta^4$-$C_4Ph_4)(\eta$-$C_5H_5)$] (M = Nb, Cl–Nb–Cl 97.3°; M = Mo,

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* Reactions of co-ordinated ligands. Part 66.[1]

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**

Re–C(4)	2.18(3)	C(1)–C(4)	1.51(4)
Re–C(1)	2.18(3)	C(1)–C(2)	1.52(4)
Re–C(2)	2.24(3)	C(2)–C(3)	1.45(4)
Re–C(3)	2.31(3)	C(2)–C(11)	1.52(4)
Re–Br(2)	2.574(4)	C(3)–C(17)	1.44(4)
Re–Br(1)	2.581(4)	C(3)–C(4)	1.53(4)
C(1)–C(5)	1.49(4)	C(4)–C(23)	1.49(4)
Br(2)–Re–Br(1)	83.86(12)	C(17)–C(3)–C(4)	132(3)
C(4)–C(1)–C(2)	87(2)	C(23)–C(4)–C(1)	133(3)
C(3)–C(2)–C(1)	94(2)	C(23)–C(4)–C(3)	127(3)
C(2)–C(3)–C(4)	88(2)	C(1)–C(4)–C(3)	91(2)
C(3)–C(2)–C(11)	133(3)	C(10)–C(5)–C(6)	121(3)
C(11)–C(2)–C(1)	131(3)	C(10)–C(5)–C(1)	123(3)
C(17)–C(3)–C(2)	138(3)	Ca–Re–Cb	133(1)

Ca and Cb are the centroids of the cyclopentadienyl and cyclobutadienyl rings respectively.

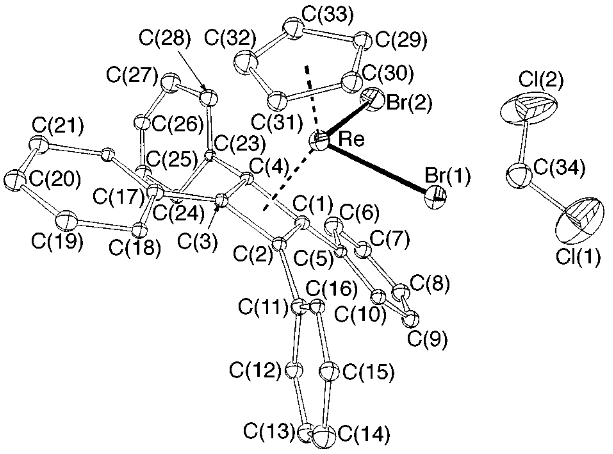
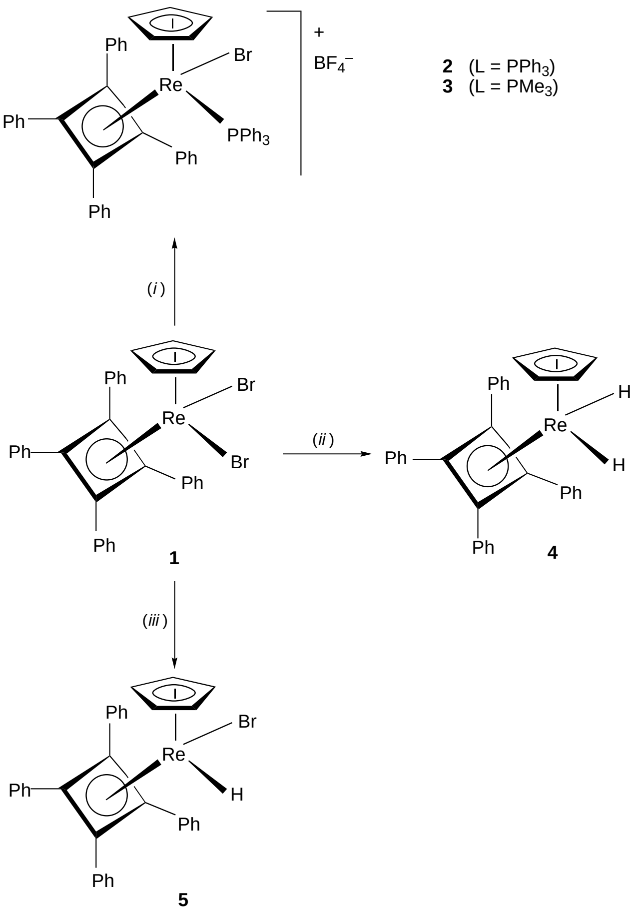


Fig. 1 Molecular structure of [$ReBr_2(\eta^4-C_4Ph_4)(\eta-C_5H_5)$] **1**

Cl–Mo–Cl 90.0°). In this study extended-Hückel molecular orbital (EHMO) calculations showed that the frontier orbitals of the $Mo(\eta-C_5H_5)_2$ and $Mo(\eta^4-C_4H_4)(\eta-C_5H_5)$ fragments are nearly identical and that the η^4-cyclobutadiene moiety is best represented as a dinegative ligand, implying that the niobium and molybdenum species can be viewed as d^0 and d^1 complexes respectively. The EHMO calculations showed that in agreement with experiment the Cl–M–Cl angle decreases as the d-electron count increases, and leads to the prediction that the d^2 complex [$ReBr_2(\eta^4-C_4Ph_4)(\eta-C_5H_5)$] **1** should exhibit, as in fact is observed, a X–M–X bond angle close to that reported[6] (82°) for the d^2 molybdenum complex [$MoCl_2(\eta-C_5H_5)_2$].

The formation of complex **1** represents a new example of the formation of an η^4-cyclobutadiene-substituted transition-metal complex by reactions of an alkyne with a labile metal species.[7] It is likely that the η^2(4e)-bonded alkyne complex [$ReBr_2\{\eta^2(4e)-PhC_2Ph\}(\eta-C_5H_5)$] is formed initially[†] in this reaction and that a second PhC_2Ph ligand is accommodated by a switch [$\eta^2(4e) \longrightarrow \eta^2(2e)$] in the bonding mode of the already coordinated PhC_2Ph. Coupling of the alkyne ligands to form a rhenacyclopentadiene followed by reductive elimination then leads to the formation of the η^4-cyclobutadiene complex **1**.

As a first step in the development of the reaction chemistry of complex **1** attention was focused on the Re–Br bonds. When 1 equivalent of both $AgBF_4$ and PPh_3 were added to a stirred dichloromethane solution of [$ReBr_2(\eta^4-C_4Ph_4)(\eta-C_5H_5)$] an orange cationic crystalline complex was obtained in good yield (70%), and this was identified by analysis and NMR spectroscopy (see Experimental section) as the complex [$ReBr(PPh_3)(\eta^4-C_4Ph_4)(\eta-C_5H_5)$][$BF_4$] **2** (Scheme 1). A similar reaction between **1**, $AgBF_4$ and PMe_3 afforded orange [$ReBr(PMe_3)(\eta^4-C_4Ph_4)(\eta-C_5H_5)$][$BF_4$] **3**, albeit in lower (35%) yield. Secondly, because of the structural relationship discussed earlier between **1** and [$MoCl_2(\eta-C_5H_5)_2$], the possibility of synthesizing the species [$ReH_2(\eta^4-C_4Ph_4)(\eta-C_5H_5)$] was examined with a view to comparing its chemistry with that of the molybdenum complex [$MoH_2(\eta-C_5H_5)_2$]. Addition (−78 °C) of an excess of Li[AlH_4] to a tetrahydrofuran (thf) solution of **1** resulted in an immediate change from orange to bright yellow, and on work-up of the reaction mixture by column chromatography a yellow crystalline complex was obtained (80% yield). This was characterised by elemental analysis, NMR spectroscopy [^1H (δ −13.07, ReH) and $^{13}C-\{^1H\}$ (δ 89.3, C_5H_5; 66.9, C_4Ph_4)] as the rhenium dihydride [$ReH_2(\eta^4-C_4Ph_4)(\eta-C_5H_5)$] **4** (Scheme 1). The structure was confirmed by single-crystal X-ray crystallography. It contained two molecules in the asymmetric unit. One of these is illustrated in Fig. 2, while selected bond lengths and angles are listed in Table 2.



Scheme 1 (*i*) $AgBF_4$, L, CH_2Cl_2; (*ii*) excess of Li[AlH_4]; (*iii*) 1 equivalent Li[AlH_4]

The hydrogens attached to the rhenium centres were located in this structure, at an advanced stage of the refinement. The H–Re–H angles at the two metal centres in the unique portion of the unit cell were 79(3) and 80(2)° which, as expected, are similar to the Br–Re–Br angle in complex **1**. However, the corresponding Ca–Re–Cb angles for both molecules in **4** are greater than in **1**, having values of 146.8(2) and 146.5(2)°. This is in fact expected given the minimum steric bulk of the hydride ligands, and it is interesting that these angle data for **4** are in agreement with those reported by Schultz *et al.*[8] in a neutron study of the d^2 complex [$MoH_2(\eta-C_5H_5)_2$], in which H–Mo–H and Ca–Mo–Ca angles of 75.52 and 151.47° respectively were observed.

[†] Reaction of [$ReBr_2\{\eta^2(4e)-PhC_2Ph\}(\eta-C_5H_5)$] with PhC_2Ph in toluene at 100 °C forms complex **1** as the only product.

Table 2 Selected bond lengths (Å) and angles (°) for complex **4**

Re–H(1A)	1.65(4)	Re(2)–H(2B)	1.66(5)
Re–H(1B)	1.65(4)	Re(2)–C(39)	2.164(6)
Re–C(7)	2.162(6)	Re(2)–C(40)	2.169(6)
Re–C(8)	2.218(5)	Re(2)–C(41)	2.169(5)
Re–C(9)	2.180(5)	Re(2)–C(42)	2.236(5)
C(6)–C(7)	1.463(8)	C(39)–C(40)	1.486(8)
C(6)–C(9)	1.485(7)	C(39)–C(42)	1.457(8)
C(6)–C(10)	1.481(6)	C(39)–C(43)	1.517(6)
C(7)–C(8)	1.473(7)	C(40)–C(41)	1.471(8)
C(7)–C(16)	1.482(6)	C(40)–C(49)	1.468(6)
C(8)–C(9)	1.456(7)	C(41)–C(42)	1.471(7)
C(8)–C(22)	1.491(6)	C(41)–C(55)	1.513(6)
C(9)–C(28)	1.497(6)	C(42)–C(61)	1.467(6)
Re(2)–H(2A)	1.62(5)		
C(6)–C(7)–C(8)	89.1(4)	C(49)–C(40)–C(39)	131.0(5)
C(6)–C(7)–C(16)	132.4(5)	C(41)–C(40)–C(39)	89.5(4)
C(8)–C(7)–C(16)	135.1(5)	C(40)–C(41)–C(42)	89.9(4)
C(9)–C(8)–C(7)	91.3(4)	C(40)–C(41)–C(55)	132.7(5)
C(9)–C(8)–C(22)	135.9(5)	C(42)–C(41)–C(55)	134.6(5)
C(7)–C(8)–C(22)	131.6(5)	C(39)–C(42)–C(61)	133.1(5)
C(8)–C(9)–C(6)	88.9(4)	C(39)–C(42)–C(41)	90.6(4)
C(8)–C(9)–C(28)	135.0(5)	C(61)–C(42)–C(41)	136.1(5)
C(6)–C(9)–C(28)	134.6(5)	Ca–Re(1)–Cb	146.8(2)
C(42)–C(39)–C(40)	89.9(4)	Ca–Re(2)–Cb	146.5(2)
C(42)–C(39)–C(43)	134.1(5)	H(1B)–Re(1)–H(1A)	80(2)
C(40)–C(39)–C(43)	131.1(5)	H(2B)–Re(2)–H(2A)	79(3)
C(49)–C(40)–C(41)	136.7(5)		

Ca and Cb are respectively the centroids of the cyclopentadienyl and cyclobutadienyl rings attached to each rhenium centre.

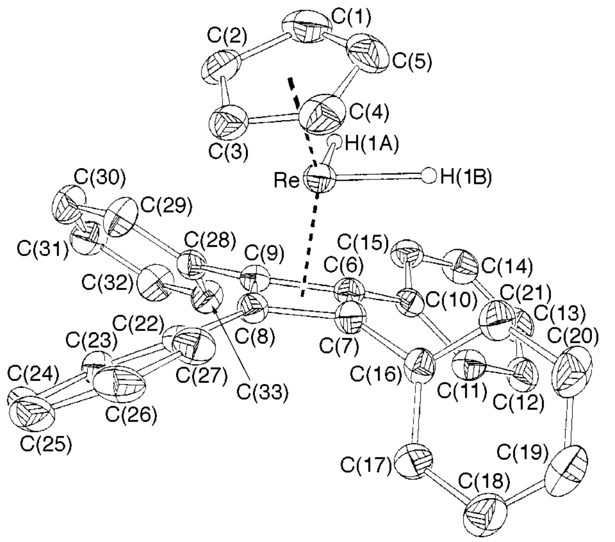
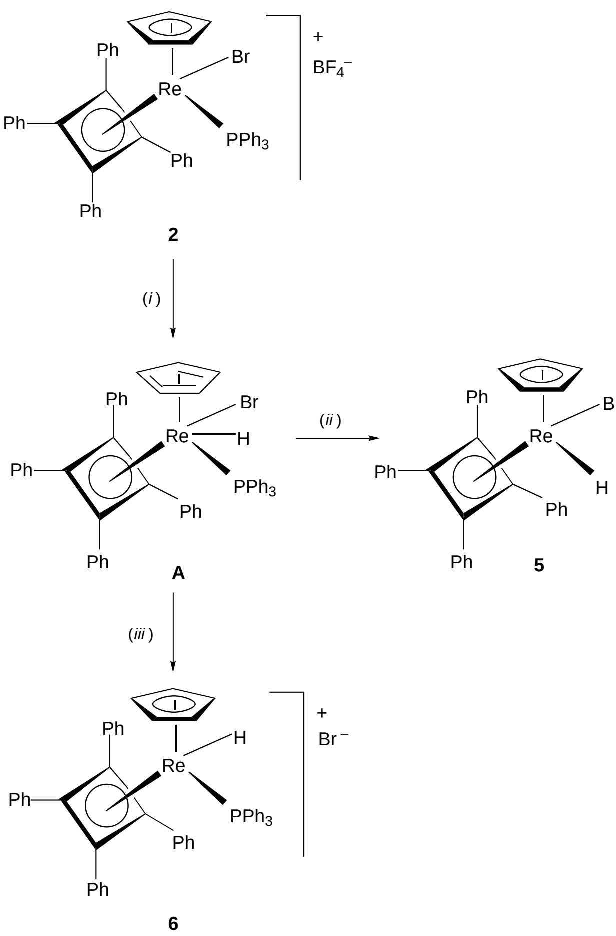


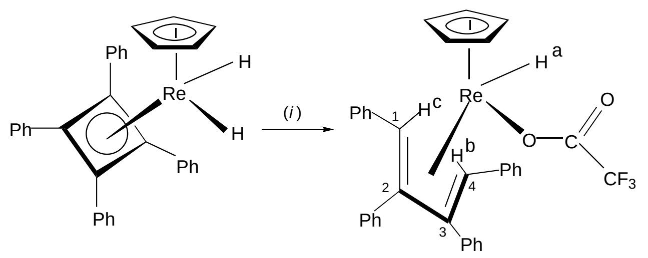
Fig. 2 Molecular structure of $[ReH_2(\eta^4-C_4Ph_4)(\eta-C_5H_5)]$ **4**



Scheme 2 (*i*) $Li[BHEt_3]$, thf; (*ii*) $-PPh_3$; (*iii*) $-Br^-$

When 1 molar equivalent instead of an excess of lithium aluminium hydride was added to a cooled solution of complex **1** in thf the colour changed from red to orange. On chromatographic work-up a low yield (20%) of an orange crystalline complex was obtained. This was characterised by analysis and NMR spectroscopy as the species $[ReH(Br)(\eta^4-C_4Ph_4)(\eta-C_5H_5)]$ **5** (Scheme 2). Interestingly this complex was also formed by reaction of the cation $[ReBr(PPh_3)(\eta^4-C_4Ph_4)(\eta-C_5H_5)][BF_4]$ **2** with $Li[BHEt_3]$. Examination of the NMR spectra of the reaction mixture showed that it was a mixture (20:1) of **5** (major) and a minor product the cationic species $[ReH(PPh_3)(\eta^4-C_4Ph_4)(\eta-C_5H_5)]Br$ **6**. This is not consistent with the Davis–Green–Mingos rules,[9] which predict that a source of 'H^-' should react with **2** *via* attack on a η^4-cyclobutadiene ring carbon. It is suggested that instead $[BHEt_3]^-$ delivers 'H^-' to the rhenium centre assisted by a η^5 to η^3 slippage[10] in the bonding mode of the cyclopentadienyl ligand; the resulting (Scheme 2) intermediate **A** can then either undergo dissociative loss of PPh_3 to form the major product **5**, or lose Br^- to give the minor cationic product.

Since it is known[11] that protonation of $[MoH_2(\eta-C_5H_5)_2]$ leads to the formation of the cationic trihydride $[MoH_3(\eta-C_5H_5)_2]^+$, it was interesting to examine the corresponding reaction of $[ReH_2(\eta^4-C_4Ph_4)(\eta-C_5H_5)]$ **4**. Addition of CF_3CO_2H to a cooled (−78 °C) solution of **4** in CH_2Cl_2 afforded on chromatographic work-up an orange crystalline complex **7**. Elemental analysis and a mass spectrum indicated that **7** was a 1:1 adduct of the reactants; also the appearance in the $^{13}C-\{^1H\}$ NMR spectrum of resonances at δ 165.0 (q) and 112.3 (q) due to the $CF_3\mathit{C}$ and $\mathit{C}F_3C$ carbons respectively and a singlet in the ^{19}F spectrum at δ −74.9 confirmed the presence in the adduct of a trifluoroacetate group. In the $^{13}C-\{^1H\}$ spectrum there was also the expected cyclopentadienyl signal at δ 88.7 and phenyl group signals at δ 126.5–143.1, but there were three anomalous signals apparent at δ 113.1, 61.5 and 57.8. In the ^1H NMR spectrum there was a high-field signal at δ −7.87 (H^a), which integrated for one proton with respect to the five hydrogens of the cyclopentadienyl ring at δ 4.52, however this high-field signal was a doublet of doublets (J = 3.0 and 5.6 Hz) and from a H–H correlation spectroscopy (COSY) study it was apparent that H^a was coupled to H^b at δ 3.40 [H^b, 1 H, $J(H^aH^b)$ 5.6 Hz] and H^c at δ 4.04 [H^c, 1 H, $J(H^aH^c)$ 3.0 Hz]. This suggested that an unexpected reaction had occurred and that possibly ring opening of the tetraphenylcyclobutadiene moiety had taken place to afford, as is illustrated in Scheme 3, a η^4-buta-1,3-diene substituted complex. In agreement a C–H correlation NMR study revealed that H^c was bonded to the carbon at δ 61.5 and H^b to the carbon at δ 57.8, consistent with the presence of two CH groups within the molecule. In order to confirm the molecular geometry of **7** a single-crystal X-ray diffraction study was undertaken. The asymmetric unit was seen to contain three



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Scheme 3 (*i*) $+CF_3CO_2H$

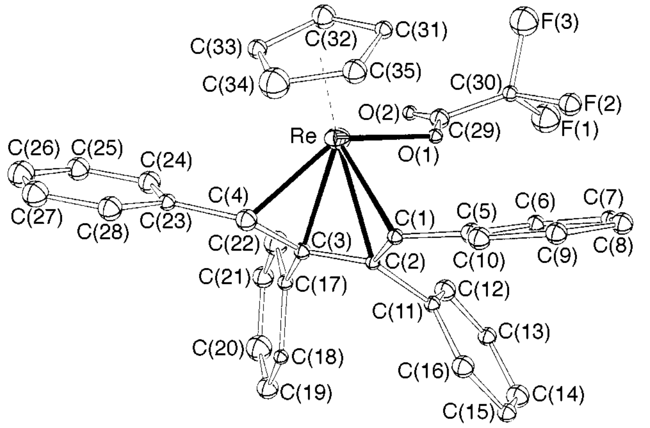


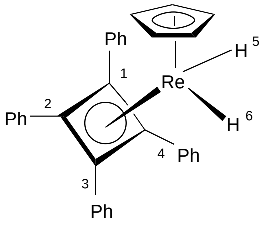
Fig. 3 Molecular structure of $[ReH\{OC(O)CF_3\}\{\eta^2,\eta^2\text{-}Z,Z\text{-}PhC(H){=}C(Ph)C(Ph){=}C(Ph)H\}(\eta\text{-}C_5H_5)]$ **7**

molecules, one of which is shown in Fig. 3. Difficulties during data collection, which are outlined later, unfortunately mean that the derived bond distances and angles from this structure determination are not reliable for comparison purposes. However, the diffraction study does confirm the overall geometry of the complex, and identifies the complex as $[ReH\{OC(O)CF_3\}\{\eta^2,\eta^2\text{-}Z,Z\text{-}PhC(H){=}C(Ph)C(Ph){=}C(Ph)H\}(\eta\text{-}C_5H_5)]$.

In order to gain an insight into this interesting reaction a deuterium-labelling experiment was carried out. Reaction of complex **4** with CF_3CO_2D in CH_2Cl_2 resulted in the formation of a deuterio-substituted version of **7**. Examination of the ^2D NMR spectrum revealed only one signal at *ca.* δ −7.5 suggesting that the deuterio-complex had the structure $[ReD\{OC(O)CF_3\}\{\eta^2,\eta^2\text{-}Z,Z\text{-}PhC(H){=}C(Ph)C(Ph){=}C(H)Ph\}(\eta\text{-}C_5H_5)]$. In order further to clarify the early stages of this protonation reaction $\mathbf{4} \longrightarrow \mathbf{7}$ an EHMO calculation was also carried out using the molecular parameters established by the crystal structure study on complex **4**. Since the ReH_2 environment was not precisely defined by the diffraction study the rhenium–hydrogen distance was set at 1.68 Å and the H–Re–H angle was varied until the total energy of the molecule was minimised. As is shown in Table 3 the lowest energy is at 80°, which is close to the angle found in the structure determination. Significantly the calculations showed that the carbon atoms of the C_4 ring are all positive (0.151, 0.036, 0.124 and 0.040) and a large negative charge (−0.225) resides at the rhenium centre. The calculations also showed (Fig. 4) that the highest occupied molecular orbital (HOMO) located on the rhenium centre lies between the two hydride ligands similar to what was previously observed by Lauher and Hoffmann[11] for $[MoH_2(\eta\text{-}C_5H_5)_2]$. The EHMO calculations therefore suggest that protonation of **4** should occur at the rhenium centre assisted by the charge and directed between the two hydride ligands.

Thus, in contrast with the molybdenum system, the initial product of protonation of complex **4** is evidently unstable, the formation of the cationic trihydride $[ReH_3(\eta^4\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)][CF_3CO_2]$ **B** (Scheme 4) triggering a ring-opening reaction of the $\eta^4\text{-}C_4Ph_4$ ligand. This can be explained by the facile migration of a ReH hydrogen from the metal onto a carbon of the cyclobutadiene ring resulting in formation of $[ReH_2(\eta^3\text{-}C_4Ph_4H)(\eta\text{-}C_5H_5)][CF_3CO_2]$. A switch $[\eta^3(3e) \longrightarrow \eta^1,\eta^2(3e) \longrightarrow \eta^1(1e)]$ in the bonding mode of the η^3-cyclobutenyl ligand then provides a pathway *via* **C** to the η^1,η^2-butadienyl-substituted species **D**, in which the stereochemistry (*E*) of the co-ordinated alkene derives from a conrotatory[12–14] ring-opening of a $[ReH_2(\eta\text{-}C_5H_5)]^+$-substituted cyclobutene. At this stage in the reaction sequence intermediate **D** could, in principle, undergo a reductive elimination with concomitant attack by the $CF_3CO_2^-$ anion (see Scheme 5); however, since such a step would be expected[15] to proceed with retention of the alkenyl configuration, a co-ordinated buta-1,3-diene would be formed with a stereochemistry different from that observed, *i.e.* with the terminal CH hydrogens in *syn* and *anti* positions. This suggests that a rapid stereomutation of the stereochemistry of the terminal =CHPh group in intermediate **D** intervenes, and a possible insight into such a process was provided by our earlier observation[16] that reaction of the cisoid-η^4(5e)-butadienyl ruthenium complex $[Ru\{{=}C(Ph)\text{-}\eta^3\text{-}C(Ph)C(Ph)CH(Ph)\}(\eta\text{-}C_5H_5)]$ with $P(OMe)_3$ afforded the η^3(3e)-butadienyl-substituted species $[Ru\{\eta^1,\eta^2\text{-}C(Ph){=}C(Ph)C(Ph){=}C(Ph)H\}\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ with a change in the stereochemistry of the end =CH(Ph) group. It was suggested that this thermodynamically driven stereomutation involved a reaction pathway related to that postulated by Taylor and Maitlis[14] to

Table 3 Atom charges and *E*(total) for complex **4** at various H–Re–H angles



Atom	Charge at H–Re–H angle (°) 80	 70	 100
Re	−0.225	−0.236	−0.240
C(1)	0.151	0.168	0.110
C(2)	0.063	0.051	0.088
C(3)	0.124	0.127	0.115
C(4)	0.040	0.029	0.063
H(5)	−0.212	−0.200	−0.209
H(6)	−0.233	−0.215	−0.246
E(total)	−2930.25	−2930.10	−2930.09

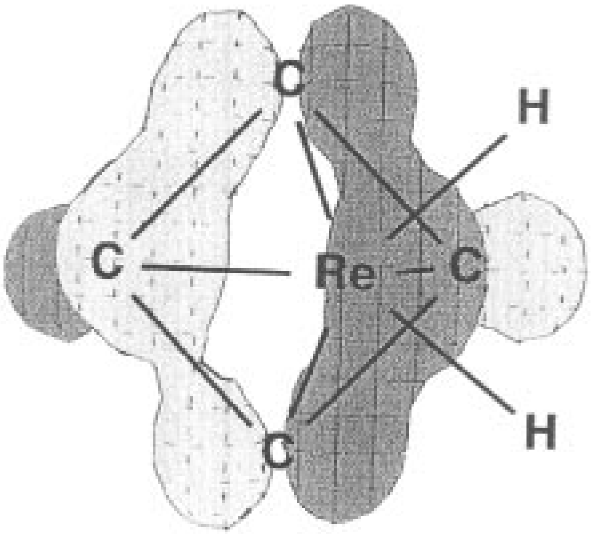
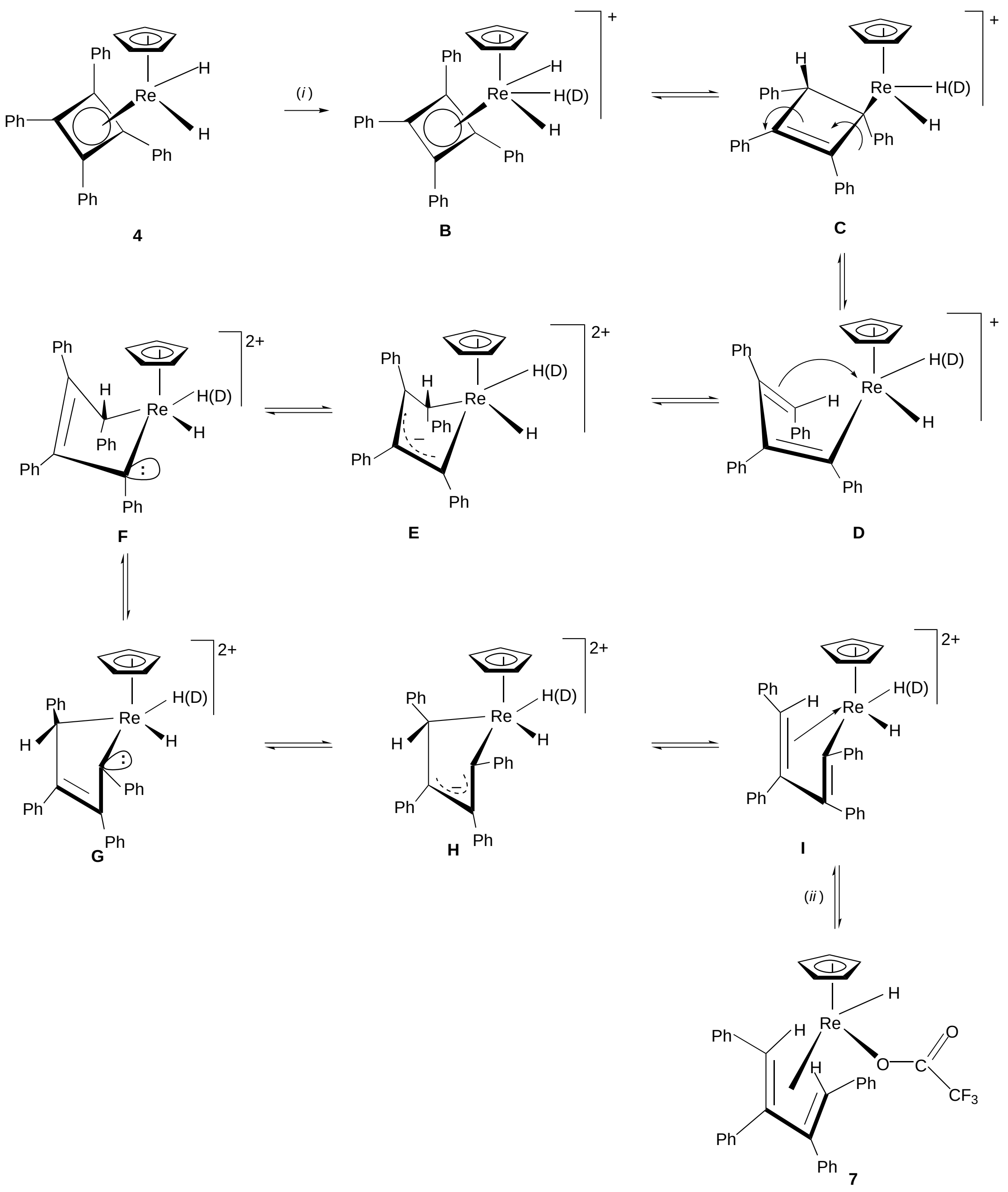
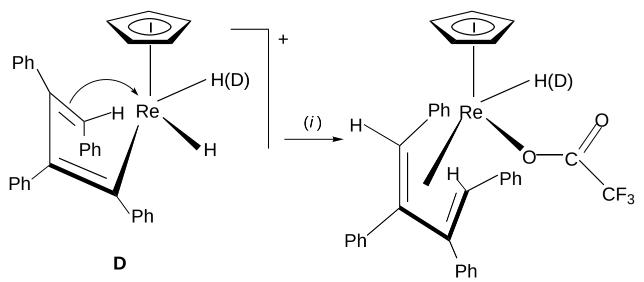


Fig. 4 The HOMO centred on the rhenium of complex **4**



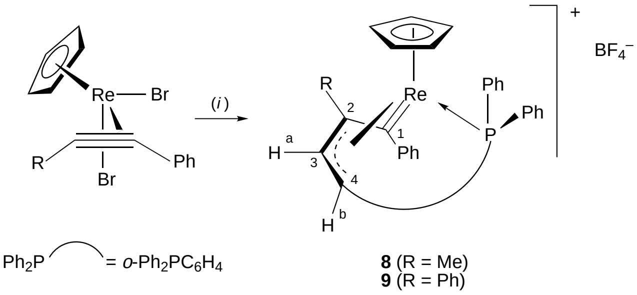
Scheme 4 (*i*) +$CF_3CO_2H(D)$, (*ii*) +$CF_3CO_2^-$



Scheme 5 (*i*) +$CF_3CO_2^-$

explain the isomerisation reactions of the complexes [Pd{η^1,η^2-C(R)=C(R)C(R)=C(R)Ph}(S_2CNR_2)] (R = aryl), and, as illustrated in Scheme 4, this idea can be extended to explain the formation of **7**. Thus, the η^1,η^2-butadienyl-substituted intermediate **D** reversibly transforms into the metalla-C_5 ring species **E**, which can switch into the metallacyclopent-3-ene **F** with a carbanion (lone pair) located on an α-carbon. Then, if a 'ring-flip' process occurs, *i.e.* **F** ⟶ **G**, similar to that postulated by Faller and Rosan[17] to explain the synchronous *exo*/*endo* and *cis*/*trans* isomerisation of η^4-co-ordinated penta-1,3-dienes, stereomutation takes place at the CH(Ph) centre allowing the successive formation of the intermediates **H** and **I**, thus leading on reductive elimination to the isolated product **7**. Finally, as shown in Scheme 4, this reaction pathway provides an understanding as to why deuterium is delivered selectively to a ReH site on treatment of **4** with CF_3CO_2D.

In exploring the chemistry of cationic molybdenum η^2(4e)-bonded alkyne complexes we had observed[18] that when the X-ray crystallographically characterised η^2(2e)-alkene/η^2(4e)-alkyne complex [Mo(dpps){η^2(4e)-MeC_2Me}(η-C_5H_5)][BF_4] was refluxed in acetonitrile a carbon–carbon coupling reaction followed by a 1,3-H shift process occurred, resulting in the formation of the 1,3-diene complex [Mo(NCMe){η^4-MeCH=C(Me)CH=CH$C_6H_4PPh_2$-*o*}(η-C_5H_5)][BF_4]. Following this study a related reaction in rhenium chemistry was observed.[19] It was found that the complex [$ReCl_2${η^2(4e)-MeC_2Me}-(η-C_5Me_5)] on treatment with ethylene and a catalytic amount of HBF_4 afforded the 1,3-diene-substituted complex [$ReCl_2$-



Scheme 6 (*i*) dpps, 2AgBF$_4$, thf, −2AgBr, −HBF$_4$

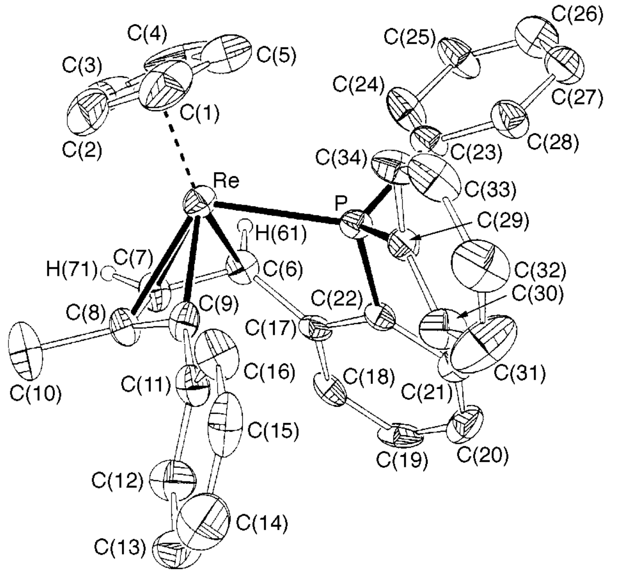


Fig. 5 Molecular structure of the cation present in the complex [Re{=C(Ph)-η^3-C(Me)CHCHC$_6$H$_4$PPh$_2$-*o*}(η-C$_5$H$_5$)][BF$_4$] **8**

{η^4-CH$_2$=CHC(Me)=CH(Me)}(η-C$_5$Me$_5$)]. In view of these findings and our observation[2] that reaction of [ReBr$_2${η^2(4e)-PhC$_2$R}(η-C$_5$H$_5$)] (R = Ph or Me) with dppe and AgBF$_4$ (2 molar equivalents) gave the dications [Re(dppe){η^2(4e)-PhC$_2$R}(η-C$_5$H$_5$)][BF$_4$]$_2$, we examined the corresponding reactions with dpps in the belief that a dicationic alkene/alkyne-substituted complex would be formed.[3]

Addition of 2 molar equivalents of AgBF$_4$ to a tetrahydrofuran solution of [ReBr$_2${η^2(4e)-PhC$_2$Me}(η-C$_5$H$_5$)] and dpps led to the precipitation of AgBr (2 molar equivalents) and the formation of a deep green solution. Work-up of the reaction mixture by filtration and removal of the solvent *in vacuo* and recrystallisation from CH$_2$Cl$_2$–Et$_2$O gave green crystals of a cationic complex **8** (93% yield). Surprisingly, the elemental analysis and a FAB mass spectrum indicated that the complex was a monocation, and significantly resonances characteristic of a co-ordinated η^2(4e)- or η^2(2e)-bonded alkyne were absent from the ^{13}C-{^{1}H} NMR spectrum. The spectrum did, however, show one low-field doublet [*J*(CP) 16.3 Hz] signal at δ 257.7 characteristic of a rhenium alkylidene carbon. The ^{31}P-{^{1}H} spectrum showed a single resonance at δ 41.0 confirming that one dpps molecule had been incorporated into the product **8**. This was also supported by the ^{1}H NMR spectrum which showed aryl resonances, a η-C$_5$H$_5$ signal at δ 5.46, a methyl singlet at δ 2.17 and interestingly an AB spectrum consistent with the presence of a CMeCH^{a}CH^b fragment. This latter feature taken together with the observation that **8** is a monocationic species suggested that not only had carbon–carbon bond coupling occurred between the co-ordinated alkyne and the dpps alkene, but also that a molecule of HBF$_4$ had been eliminated. Indeed tests confirmed the acidity of the tetrahydrofuran reaction mixture.

Table 4 Selected bond lengths (Å) and angles (°) for complex **8**

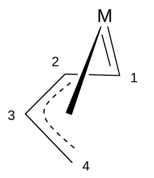
Re–P	2.375(2)	Re–C(9)	1.950(9)
Re–C(6)	2.172(9)	P–C(23)	1.811(9)
Re–C(7)	2.220(9)	P–C(22)	1.813(8)
Re–C(8)	2.227(9)	C(6)–C(17)	1.496(12)
C(7)–C(6)–C(17)	122.5(8)	C(7)–C(8)–C(10)	118.3(8)
C(8)–C(7)–C(6)	121.7(8)	C(9)–C(8)–C(10)	122.8(8)
C(7)–C(8)–C(9)	117.6(8)	C(11)–C(9)–C(8)	128.4(9)

It was found that a similar reaction occurred with the diphenylacetylene-substituted system, treatment of [ReBr$_2${η^2(4e)-PhC$_2$Ph}(η-C$_5$H$_5$)] with dpps and AgBF$_4$ (2 molar equivalents) in thf affording a high yield (90%) of the corresponding monocation **9**. Examination of the NMR spectra revealed similar features to those observed with **8** suggesting the presence in these cations of the arrangement Re=C(Ph)C(R)CHCHC$_6$H$_4$PPh$_2$-*o* (R = Me or Ph), *i.e.* a η^4(5e)-butadienyl system Re{=C(Ph)-η^3-C(R)CHCHC$_6$H$_4$PPh$_2$-*o*} (see Scheme 6). This was confirmed by a single-crystal X-ray diffraction study of **8**; the molecular geometry of the cation is shown in Fig. 5, selected bond lengths and angles being listed in Table 4.

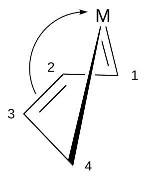
The cationic complex contains a cisoid-η^4(5e)-butadienyl ligand formed by coupling of the co-ordinated PhC$_2$Me and alkene part of the dpps ligand. The C$_4$ chain adopts an essentially coplanar geometry with a C^1–C^2–C^3–C^4 [C(9)–C(8)–C(7)–C(6) crystallographic numbering] dihedral angle of 11.42°. All of the carbons are bonded to the rhenium centre, but the Re–C(9) bond distance is significantly shorter at 1.950(9) Å, whereas, Re–C(6), Re–C(7) and Re–C(8) are at distances of 2.172(9), 2.220(9) and 2.227(9) Å respectively, a feature in common with other[16,20–22] crystallographically identified η^4(5e)-butadienyls (see Table 5). As is summarised in the table the carbon–carbon distances within the C$_4$ fragment are similar to those found[16] for the ruthenium complex [Ru{=C(Ph)-η^3-C(Ph)C(Ph)CHPh}(η-C$_5$H$_5$)] and are consistent with a major contribution from the canonical form **I** rather than **II** (see Table 5), the latter form describing more accurately the bonding in the tungsten complex [WO{=C(Ph)-η^1,η^2-C(Ph)C(Ph)CHPh}-(S$_2$CNEt$_2$)].[21]

The formation of the cations **8** and **9** is especially interesting in that this represents a new synthetic pathway to cisoid-η^4(5e)-butadienyl ligands, which have previously been synthesized either by conrotatory ring opening of a ruthenium substituted η^1,η^2-cyclobutene ring,[16] coupling of η^2(3e)-vinyl and alkyne ligands,[20,21,23] or by coupling of an η^1-allyl fragment with a co-ordinated alkyne followed by a hydrogen shift.[22] It is suggested (see Scheme 7) that in the formation of **8** and **9** the sought for dicationic η^2(2e)-alkene/η^2(4e)-alkyne complex **J** is formed initially. However, an oxidative (Re$^{\text{III}}$ ⟶ Re$^{\text{V}}$) carbon–carbon coupling reaction intervenes to form the dicationic rhenacyclopent-2-ene[18,19,24] species **K**, which then undergoes proton loss from the δ-carbon accompanied by a double bond shift (C=C to C=Re) to form the monocationic alkylidene rhenium species **L**, an obvious precursor of the isolated η^4(5e)-butadienyl-substituted monocations **8** and **9**. Although it is known that alkylidenemetal complexes are susceptible to attack by a proton on the α-carbon, it is likely that the intermediate **L** is protected from such an attack by the positive charge on the complex. A further interesting aspect of this new synthetic pathway is that it is stereoselective, only one product, *i.e.* **8**, being formed in the reaction with the unsymmetrical alkyne (PhC$_2$Me)-substituted system. It is likely that the selectivity has its origin in an electronic effect arising from the fact that the π* orbital of the co-ordinated alkyne has the largest lobe on the methyl-substituted carbon. Following Stockis and Hoffmann's[25] analysis of metalla-C$_4$ ring-forming reactions this leads to the predicted selective formation of the intermediate **K**

Table 5 Bond lengths (Å) for η^4(5e)-butadienyl ligands



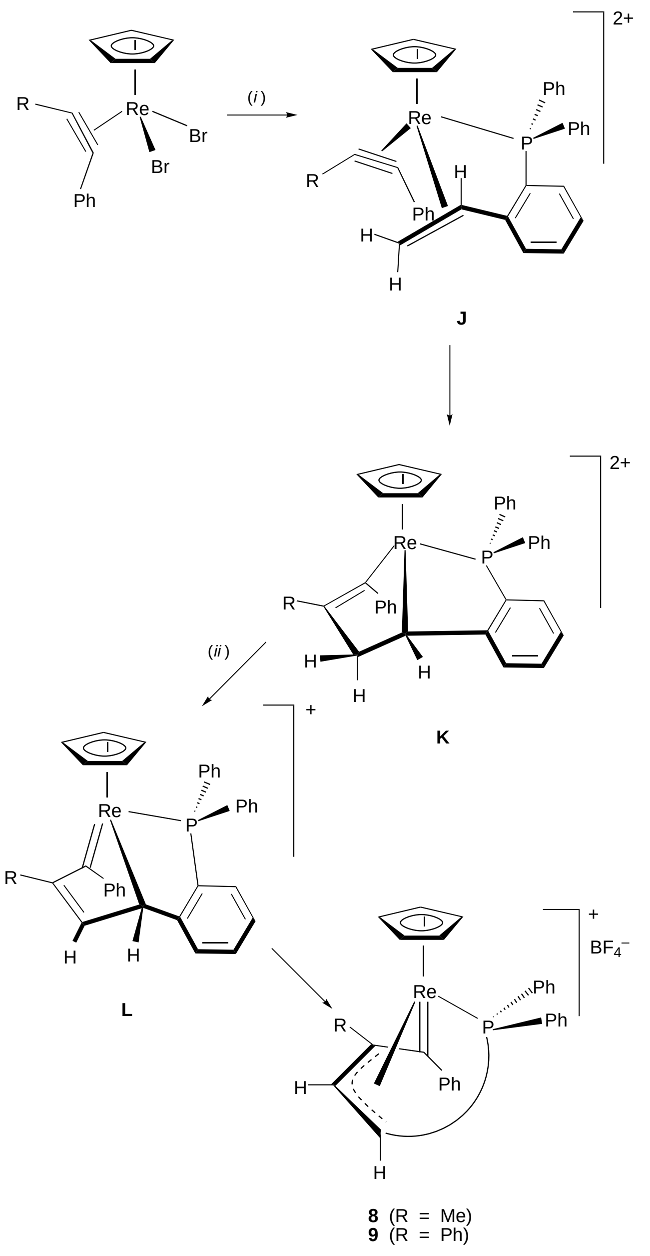
I



II

Complex	M–C(1)	M–C(2)	M–C(3)	M–C(4)	C(1)–C(2)	C(2)–C(3)	C(3)–C(4)
8	1.950(9)	2.227(9)	2.220(9)	2.172(9)	1.429(12)	1.418(13)	1.448(13)
[Ru{=C(Ph)-η^3-C(Ph)C(Ph)CHPh}(η-C_5H_5)][a]	1.896(5)	2.204(5)	2.152(4)	2.154(6)	1.419(5)	1.436(7)	1.445(7)
[Mo{=C(Me)-η^3-C(Me)C(Me)CHMe}Br-{P(OMe)$_3$}(η-C_5H_5)]$^+$ [b]	1.938(16)	2.352(19)	2.443(22)	2.336(23)	1.40(3)	1.40(3)	1.34(3)
[WO{=C(Ph)-η^1,η^2-C(Ph)C(Ph)CHPh}(S_2CNEt_2)][c]	1.96(1)	2.52(1)	2.61(1)	2.25(1)	1.44(1)	1.43(1)	1.49(1)
[Nb{=C(Ph)-η^3-C(Ph)CHCHMe}{HB(dmpz)$_3$}][d]	1.993(4)	2.334(4)	2.370(5)	2.277(5)	1.439(7)	1.418(6)	1.392(7)

[a] Ref. 16. [b] Ref. 20. [c] Ref. 21. [d] Ref. 22, dmpz = 3,5-dimethylpyrazoyl.



Scheme 7 (*i*) 2AgBF$_4$, dpps, −2AgBr; (*ii*) −HBF$_4$

with the methyl substituent on the β position of the rhenacyclopent-2-ene.

The discovery of a new pathway to the η^4(5e)-butadienyl ligand is also interesting in the context of 1,3-diene synthesis by the formal addition of an alkene carbon–hydrogen bond to an alkyne. As described earlier such reactions have been observed[18,19] at molybdenum and rhenium centres, and in both systems metallacyclopent-2-enes have been proposed as intermediates. However, in order to transform such species into coordinated 1,3-dienes the metallacyclopent-2-ene must undergo a 1,3-hydrogen shift process. This requirement generates a problem because a suprafacial 1,3-H shift is a disallowed process.[12] Moreover, a β-H elimination requiring a *cis*-coplanar transition state, followed by a reductive elimination, also poses a major difficulty. The formation of **8** and **9** *via* the elimination of HBF$_4$ suggests an alternative reaction pathway, which avoids these difficulties. This involves δ-proton loss from a metallacyclopent-2-ene to give a η^4(5e)-butadienyl moiety, which is then converted into a 1,3-diene *via* protonation of the alkylidene α-carbon. A precedent for this latter step is provided by the observation[26] that protonation of [Ru{=C(Ph)-η^3-C(Ph)-C(Ph)CH(Ph)}(η-C_5H_5)] with [(MeO)$_3$PH][BF$_4$] affords the 1,3-diene complex [Ru{η^4-(*E*,*Z*)-CH(Ph)=C(Ph)C(Ph)=CH(Ph)}{P(OMe)$_3$}(η-C_5H_5)][BF$_4$], and it is evident that further studies in this area are merited.

The availability of the cations **8** and **9** presented the opportunity further to explore the reactivity of cationic η^4(5e)-butadienyl ligands towards nucleophiles. We had previously[20] observed that treatment of the cation [Mo{=C(Me)-η^3-C(Me)C(Me)CHMe}X{P(OMe)$_3$}(η-C_5H_5)][BF$_4$] (X = Cl or Br) with BH_4^-, [BHBu$^s_3$]$^-$ or [BHEt$_3$]$^-$ led to two competing reactions, namely deprotonation from the β-methyl group Mo=C(Me) to form a η^4-vinylallene and nucleophilic attack on the Mo=C$_\alpha$ carbon to form a η^4-1,3-diene. However, it was found that, by treating these cations with the reagents Li[N(SiMe$_3$)$_2$] or AlHBu$^i_2$ the vinylallene [MoCl{η^4-CH(Me)=C(Me)C(Me)=C=CH$_2$}{P(OMe)$_3$}(η-C_5H_5)] or 1,3-diene complex [MoBr{η^4-CH(Me)=C(Me)C(Me)=CH(Me)}-{P(OMe)$_3$}(η-C_5H_5)] is formed selectively. In the case of the rhenium-substituted cations the alkylidene α-carbon carries a phenyl substituent and therefore the deprotonation reaction pathway is shut down. However, an EHMO calculation using the bond parameters established in the crystal structure of the cation in **8** showed that there is a positive charge on the Re–C$_\alpha$ carbon C(1) [Re (−0.495), C(1) (0.125), C(2) (0.136), C(3) (0.058), C(4) (−0.036), P (0.719)], and that the lowest unoccupied molecular orbital (LUMO) of the complex (Fig. 6) resides mainly on C(1) and not on C(2) or C(3), indicating that hydride attack should occur under frontier-orbital control on the Re=C alkylidene carbon.

Addition (−78 °C) of K[BHBu$^s_3$] to a thf solution of complex **9** resulted on work-up by column chromatography in the isolation in good yield (60%) of a neutral orange crystalline

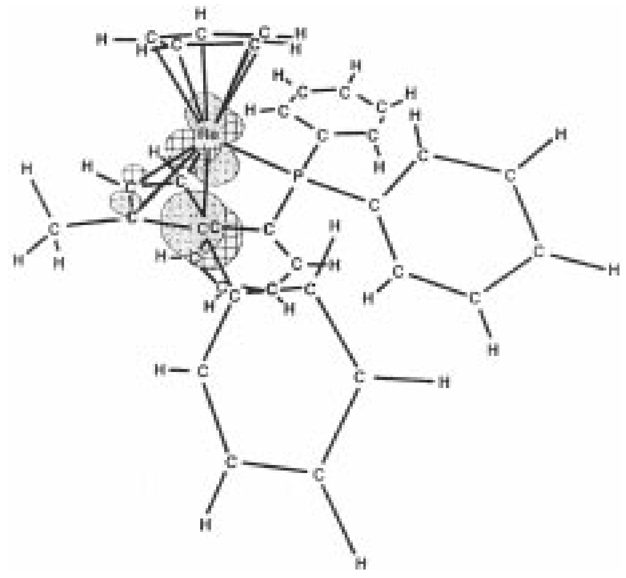


Fig. 6 The LUMO of complex **8**

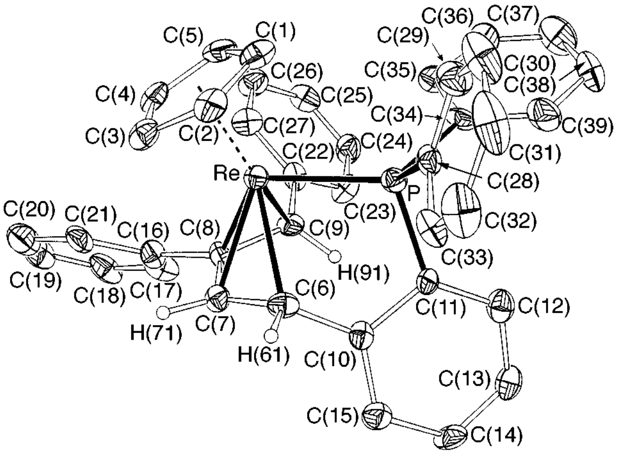
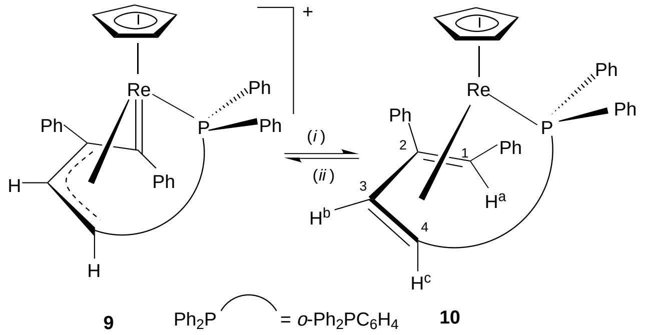


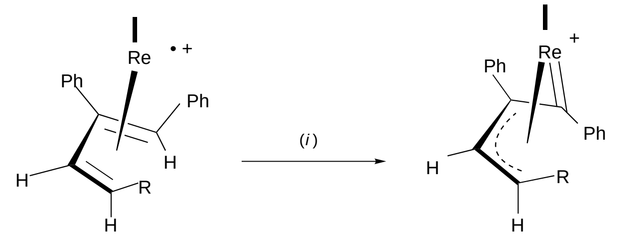
Fig. 7 Molecular structure of [Re{η^4-CH(Ph)=C(Ph)CH=CHC$_6$H$_4$-PPh$_2$-*o*}(η-C$_5$H$_5$)] **10**



Scheme 8 (*i*) K[BHBu$^s_3$]; (*ii*) [Ph$_3$C][BF$_4$]

Table 6 Selected bond lengths (Å) and angles (°) for complex **10**

Re–C(6)	2.229(11)	Re–C(8)	2.199(10)
Re–C(7)	2.184(11)	Re–C(9)	2.264(9)
C(7)–C(6)–C(10)	124.4(10)	C(9)–C(8)–C(16)	124.4(10)
C(6)–C(7)–C(8)	123.9(9)	C(7)–C(8)–C(16)	118.5(9)
C(9)–C(8)–C(7)	116.7(9)	C(8)–C(9)–C(22)	120.9(10)



Scheme 9 Ligands omitted for clarity, R = C$_6$H$_4$PPh$_2$-*o*. (*i*) +Ph$_3$C$^•$, −Ph$_3$CH

complex **10**. Elemental analysis and the FAB mass spectrum indicated the product was the expected η^4-1,3-diene complex, and in agreement the ^{31}P-{^{1}H} NMR spectrum showed one singlet at δ 61.8. In the ^{1}H spectrum H^b and H^c (Scheme 8) appeared as an AB pattern (δ 5.02 and 5.14) with a similar coupling constant [*J*(H^{b}H^c) 7.8 Hz] to that observed for the parent complex **9**. The ^{13}C-{^{1}H} NMR spectrum did not display a low-field signal characteristic of an α-alkylidene carbon suggesting that 'H$^-$' had indeed been delivered to the alkylidene carbon. Furthermore, a C–H correlation NMR study revealed that H^b was attached to C^3 (δ 64.2), H^c to C^4 (δ 52.2) and H^a, which resonated as a singlet at δ 0.93 in the ^{1}H spectrum, was connected to C^1 (δ 43.2). Although these data were fully consistent with the η^4-1,3-diene structure shown in Scheme 8, the stereochemistry at C^1 in complex **10** could not be determined from the NMR spectra. Therefore, in order to elucidate this structural feature and to confirm the overall molecular geometry a single-crystal X-ray diffraction study was carried out on a suitable crystal of **10**. The resulting structure is shown in Fig. 7, and selected bond lengths and angles are listed in Table 6.

The complex contains a η^4-bonded 1,3-diene ligand which adopts the expected cisoid geometry as is exemplified by the torsion angle C(6)–C(7)–C(8)–C(9) (6.37°). The hydride anion delivered by [BHBu$^s_3$]$^-$ is attached to the 'inside', *i.e. anti* position, such that the two phenyl substituents are *cis* to each other [C(22)–C(9)–C(8)–C(16) 14.44°]. The C(6)–C(7), C(7)–C(8) and C(8)–C(9) bond distances are very similar at *ca.* 1.43 Å, with the internal diene carbons, C(7) and C(8), being slightly closer to the rhenium [2.184(11) and 2.199(10) Å, respectively] than C(6) and C(9) [2.229(11) and 2.264(9) Å]. This is indicative of π complexation of the 1,3-diene rather than metallacyclopentene co-ordination of the diene.

Interestingly, when the d^6 1,3-diene complex [Re{η^4-CH(Ph)=C(Ph)CH=CHC$_6$H$_4$PPh$_2$-*o*}(η-C$_5$H$_5$)] **10** was treated at room temperature with [Ph$_3$C][BF$_4$] in dichloromethane the reaction mixture rapidly changed from orange to dark green, and on addition of diethyl ether the η^4(5e)-butadienyl cation **9** was obtained in high yield (80%) (Scheme 8). This type of reaction has only been previously observed[20] with the d^4 molybdenum complex [MoBr{η^4-CH(Me)=C(Me)C(Me)=CH(Me)}-{P(OMe)$_3$}(η-C$_5$H$_5$)], and involves, as has now been established for the rhenium system, the formal abstraction of 'H$^-$' by the Ph$_3$C$^+$ cation from the terminal *anti* position of the co-ordinated 1,3-diene. As with the molybdenum system we suggest (see Scheme 9) that Ph$_3$C$^+$ abstracts an electron from a metal-centred HOMO, and that the resulting 17e radical cation then undergoes a hydrogen (H$^•$) abstraction reaction by the Ph$_3$C$^•$ radical, facilitated by spin delocalisation *via* the developing Re=C(Ph) bond. From a synthetic standpoint this is an important result, suggesting that it might be possible to transform other electron-rich 1,3-diene complexes into η^4(5e)-butadienyls with their potential for unusual reactivity patterns.

Experimental

The ^{1}H, ^{13}C-{^{1}H} and ^{19}F NMR spectra were recorded on JEOL GX270 and EX400 spectrometers. Data are given for room-temperature measurements. Chemical shifts are referenced relative to SiMe$_4$ for ^{1}H and ^{13}C, H$_3$PO$_4$ (85% external) for ^{31}P, and CCl$_3$F (external) for ^{19}F. Coupling constants are in Hz. Infrared spectra were recorded on a Nicolet 580P FTIR spectrometer. All reactions were carried out in Schlenk tubes under atmospheres of dry oxygen-free nitrogen, using freshly distilled and degassed solvents. Column chromatography was performed using BDH alumina, Brockman activity II as solid support.

Preparations

[ReBr$_2$(η^4-C$_4$Ph$_4$)(η-C$_5$H$_5$)] 1. A solution of a mixture of *cis*- and *trans*-[ReBr$_2$(CO)$_2$(η-C$_5$H$_5$)][27] (2.00 g, 4.28 mmol) and an excess of diphenylacetylene (7.63 g, 42.8 mmol) in toluene (100 cm^3) was heated under reflux for 24 h. The reaction mixture was allowed to cool and the volatile material removed *in vacuo*. The residue was dissolved in the minimum volume of dichloromethane and chromatographed on alumina (30 × 3 cm column). Elution with hexane gave a trace of unchanged starting materials, and further elution with CH$_2$Cl$_2$–hexane (1 : 5) gave a single red band. This was collected and recrystallised from CH$_2$Cl$_2$–hexane to give deep red air stable *crystals* of complex **1** (2.23 g, 68%) (Found: C, 51.5; H, 3.3. C$_{33}$H$_{25}$Br$_2$Re requires C, 51.6; H, 3.3%). NMR (CD$_2$Cl$_2$): ^{1}H, δ 7.75–6.35 (m, 20 H, Ph) and 5.68 (s, 5 H, C$_5$H$_5$); ^{13}C-{^{1}H}, δ 136.0–122.0 (C$_6$H$_5$) and 96.1 (C$_5$H$_5$).

[ReBr(PPh$_3$)(η^4-C$_4$Ph$_4$)(η-C$_5$H$_5$)][BF$_4$] 2. Addition of triphenylphosphine (0.36 g, 1.38 mmol) and silver tetrafluoroborate (0.35 g, 1.8 mmol) to a stirred (room temperature) solution of complex **1** (1.05 g, 1.38 mmol) in dichloromethane (20 cm^3) resulted in the rapid formation of a precipitate of AgBr. After 12 h the reaction mixture was filtered through Celite and the solvent removed *in vacuo*. Recrystallisation of the solid residue from CH$_2$Cl$_2$–Et$_2$O afforded orange *crystals* of **2** (0.62 g, 70%) (Found: C, 59.2; H, 4.0. C$_{51}$H$_{40}$BBrF$_4$PRe requires C. 59.1; H, 3.9%). NMR (CD$_2$Cl$_2$): ^{1}H, δ 7.55–6.25 (m, 35 H, Ph) and 5.89 (s, 5 H, C$_5$H$_5$); ^{13}C-{^{1}H}, δ 133.9–125.8 (Ph) and 96.0 (C$_5$H$_5$); ^{19}F, δ −154.0 (s, BF$_4^-$); ^{31}P-{^{1}H}, δ 15.0 (s, PPh$_3$).

[ReBr(PMe$_3$)(η^4-C$_4$Ph$_4$)(η-C$_5$H$_5$)][BF$_4$] 3. A similar reaction between complex **1** (0.14 g, 0.184 mmol), PMe$_3$ (0.014 g, 0.184 mmol) and silver tetrafluoroborate (0.036 g, 0.184 mmol) in dichloromethane (20 cm^3) gave orange *crystals* of **3** (0.06 g, 35%) (Found: C, 50.3; H, 3.4. C$_{36}$H$_{34}$BBrF$_4$PRe requires C, 50.8; H, 4.0%). NMR (CD$_2$Cl$_2$): ^{1}H, δ 7.60–7.00 (m, 20 H, Ph), 5.69 [d, 5 H, C$_5$H$_5$, *J*(HP) 1.0] and 1.11 [d, 9 H, PMe, *J*(HP) 14.0]; ^{13}C-{^{1}H}, δ 133.0–122.5 (Ph), 94.4 (C$_5$H$_5$) and 16.5 [d, PMe, *J*(CP) 39.0 Hz]; ^{31}P-{^{1}H}, δ 55.3 (s, PMe$_3$).

[ReH$_2$(η^4-C$_4$Ph$_4$)(η-C$_5$H$_5$)] 4. Addition (−78 °C) of an excess of lithium aluminium hydride (4.20 cm^3 of a 1 M solution in tetrahydrofuran) to a stirred solution of complex **1** (1.23 g, 1.61 mmol) in thf (20 cm^3) resulted in a change from red to yellow on warming to room temperature. The volatiles were removed *in vacuo* and the yellow residue chromatographed. Elution with thf afforded a yellow band, which on recrystallisation (−20 °C) from CH$_2$Cl$_2$–hexane gave yellow *crystals* of **4** (0.79 g, 80%) (Found: C, 64.9; H, 4.4. C$_{33}$H$_{27}$Re requires C, 65.0; H, 4.5%). NMR (CD$_2$Cl$_2$): ^{1}H, δ 7.36–7.14 (m, 20 H, Ph), 4.85 (s, 5 H, C$_5$H$_5$), −13.07 (s, 2 H, ReH); ^{13}C-{^{1}H}, δ 136.6, 130.6, 128.0, 126.4 (Ph), 89.3 (C$_5$H$_5$) and 66.9 (CPh).

[ReH(Br)(η^4-C$_4$Ph$_4$)(η-C$_5$H$_5$)] 5. Dropwise addition (−78 °C) of Li[AlH$_4$] in thf (1.6 cm^3 of a 1 M solution in thf) to a stirred solution of complex **1** (1.23 g, 1.61 mmol) in thf (20 cm^3) resulted in a change in colour on warming to room temperature. The volatiles were removed *in vacuo* and the residue chromatographed. Elution with pentane gave a trace of the yellow complex **4**. Further elution with CH$_2$Cl$_2$–pentane (1 : 5) gave an orange band which was collected and recrystallised (−10 °C) from CH$_2$Cl$_2$–pentane to give orange *crystals* of **5** (0.22 g, 20%) (Found: C, 57.0; H, 6.2. C$_{33}$H$_{26}$BrRe requires C, 57.5; H, 6.6%). NMR (CD$_2$Cl$_2$): ^{1}H, δ 7.24–7.16 (m, 20 H, Ph), 5.17 (s, 5 H, C$_5$H$_5$) and −12.15 (s, 1 H, ReH); ^{13}C-{^{1}H}, δ 133.6, 131.4, 128.1, 127.7 (Ph), 89.9 (C$_5$H$_5$) and 67.1 (CPh). FAB mass spectrum: *m/z* 688 (*M*$^+$) and 608 ([*M* − Br]$^+$).

Reaction of complex 2 with lithium triethylhydroborate. A solution of Li[BHEt$_3$] (160 μl, 1 M solution in thf, 0.16 mmol) was added with stirring to a cooled (−78 °C) solution of complex **2** (0.16 g, 0.15 mmol) in thf (20 cm^3). On warming to room temperature the solution changed from orange to black. After 2 h the reaction mixture was filtered through a plug of silica gel. The volatiles were removed *in vacuo* and the orange residue crystallised (−10 °C) from thf–diethyl ether (1 : 1) to afford a mixture (20 : 1) of **5** and [ReH(PPh$_3$)(η^4-C$_4$Ph$_4$)(η-C$_5$H$_5$)]Br **6** (0.06 g, 40%). NMR (CD$_2$Cl$_2$): ^{1}H, δ 7.48–7.14 (m, 35 H, Ph), 5.19 (s, 5 H, C$_5$H$_5$, major), 5.07 [d, 5 H, C$_5$H$_5$, minor *J*(HP) 1.4], −11.81 [d, 1 H, ReH, minor, *J*(HP) 25.2 Hz] and −12.14 (s, 1 H, ReH, major); ^{13}C-{^{1}H}, δ 134.1–127.7 (Ph) and 89.9 (C$_5$H$_5$, major); ^{31}P-{^{1}H}, δ 27.3 (s, PPh$_3$, minor).

Reaction of complex 4 with trifluoroacetic acid. An excess of CF$_3$CO$_2$H (84 μl, 1.09 mmol) was added at −78 °C to a yellow solution of complex **4** (0.22 g, 0.36 mmol) in CH$_2$Cl$_2$ (20 cm^3). After 12 h at room temperature the volatiles were removed *in vacuo* and the resulting dark orange solid was chromatographed on alumina. Elution with CH$_2$Cl$_2$ gave a single orange band, which was collected and recrystallised (0 °C) from toluene–hexane to give orange *crystals* of [ReH{OC(O)CF$_3$}{η^4-PhCH=C(Ph)C(Ph)=C(Ph)H}(η-C$_5$H$_5$)] **7** (0.22 g, 85%) (Found: C, 58.2; H, 4.0. C$_{35}$H$_{28}$F$_3$O$_2$Re requires C, 58.1; H 3.9%). NMR (CD$_2$Cl$_2$): ^{1}H, δ 8.42–6.74 (m, 20 H, Ph), 4.52 (s, 5 H, C$_5$H$_5$), 4.04 [d, 1 H, H^c, *J*(H^{c}H^a) 3.0], 3.40 [d, 1 H, H^b, *J*(H^{a}H^b) 5.6] and −7.87 [dd, 1 H, ReH^a, *J*(H^{a}H^c) 3.0, *J*(H^{a}H^b) 5.6]; ^{13}C-{^{1}H}, δ 165.0 [q, *C*CF$_3$, *J*(CF) 36], 143.1–126.5 (Ph), 113.1 (C^2 or C^3), 112.3 [q, *C*F$_3$, *J*(CF) 291 Hz], 88.7 (C$_5$H$_5$), 61.5 (CH, C^4 or C^1) and 57.8 (CH, C^1 or C^4); ^{19}F, δ −74.9 (CF$_3$). FAB mass spectrum: *m/z* 723 (*M*$^+$) and 610 (*M* − CF$_3$Cl$_2$]$^+$).

[Re{=C(Ph)-η^3-C(Me)CHCHC$_6$H$_4$PPh$_2$-*o*}(η-C$_5$H$_5$)][BF$_4$] 8. Silver tetrafluoroborate (0.21 g, 1.1 mmol) was added to a solution (thf, 20 cm^3) of *o*-diphenylphosphinostyrene (0.16 g, 0.55 mmol) and [ReBr$_2${η^2(4e)-MeC$_2$Ph}(η-C$_5$H$_5$)] (0.294 g, 0.54 mmol). After stirring at room temperature for 4 h, the solvent was removed *in vacuo* and the product extracted into CH$_2$Cl$_2$ and filtered through Celite. Removal of the solvent followed by recrystallisation from CH$_2$Cl$_2$–Et$_2$O gave green *crystals* of complex **8** (0.36 g, 93%) (Found: C, 55.1; H, 3.8. C$_{34}$H$_{29}$BF$_4$PRe requires C, 55.1; H, 3.9%). NMR (CD$_2$Cl$_2$): ^{1}H, δ 7.65–6.46 (m, 19 H, Ph), 6.59–6.55 [AB spectrum, 2 H, H^a and H^b, *J*(H^{a}H^b) 8.0], 5.46 [d, 5 H, C$_5$H$_5$, *J*(HP) 1.65] and 2.17 (s, 3 H, Me); ^{13}C-{^{1}H}, δ 257.7 [d, Re=C, *J*(CP) 16.3 Hz], 152.0–126.7 (Ph), 88.1 (C$_5$H$_5$), 78.3 (C^3 or C^4), 69.2 (C^2), 57.3 (C^3 or C^4) and 17.0 (Me); ^{31}P-{^{1}H}, δ 41.0. FAB mass spectrum: *m/z* 655 (*M*$^+$).

[Re{=C(Ph)-η^3-C(Ph)CHCHC$_6$H$_4$PPh$_2$-*o*}(η-C$_5$H$_5$)][BF$_4$] 9. Similarly, reaction of [ReBr$_2${η^2(4e)-PhC$_2$Ph}(η-C$_5$H$_5$)] (0.25 g, 0.42 mmol) with dpps (0.127 g, 0.4 mmol) and AgBF$_4$ (0.166 g, 0.85 mmol) in thf (20 cm^3) gave a green product, which on recrystallisation (CH$_2$Cl$_2$–Et$_2$O) afforded green *crystals* of **9** (0.30 g, 90%) (Found: C, 58.3; H, 3.9. C$_{39}$H$_{31}$BF$_4$PRe requires C, 58.3; H, 3.9%). NMR (CD$_2$Cl$_2$): ^{1}H, δ 7.70–6.51 (m, 24 H, Ph), 6.81–6.69 [AB spectrum, 2 H, H^a and H^b, *J*(H^{a}H^b) 8.3] and 5.42 [d, 5 H, C$_5$H$_5$, *J*(HP) 1.65]; ^{13}C-{^{1}H}, δ 252.9 [d, Re=C, *J*(CP) 14.9 Hz], 151.5, 125.8 (Ph), 89.3 (C$_5$H$_5$), 73.5 (C^3 or C^4), 71.3 (C^2) and 57.7 (C^3 or C^4); ^{31}P-{^{1}H}, δ 39.9. FAB mass spectrum: *m/z* 717 (*M*$^+$).

Reaction of complex 9 with K[BHBu$^s_3$]. A solution of K[BHBu$^s_3$] (0.38 cm^3, 1 M thf solution, 0.38 mmol) was added

Table 7 Crystallographic details for compounds **1**, **4**, **7**, **8** and **10**

	1	**4**	**7**	**8**	**10**
Empirical formula	$C_{34}H_{27}Br_2Cl_2Re$	$C_{33}H_{27}Re$	$C_{35}H_{28}F_3O_2Re$	$C_{34}H_{29}BF_4PRe$	$C_{39}H_{32}PRe$
M	852.48	1219.49	723.77	741.55	717.82
Crystal size/mm	0.2 × 0.15 × 0.15	0.2 × 0.2 × 0.1	0.3 × 0.3 × 0.35	0.2 × 0.2 × 0.15	0.2 × 0.2 × 0.25
Colour	Dark red	Yellow	Orange	Green	Orange
T/K	293(2)	293(2)	170(2)	293(2)	293(2)
λ/Å	0.710 69	0.709 30	0.709 30	0.709 30	0.709 30
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$Pbca$	$P2_1/n$	$P\bar{1}$ (no. 2)	$P2_1/c$	$P2_1/c$
a/Å	11.629(4)	10.037(1)	13.466(4)	11.324(1)	11.100(3)
b/Å	19.450(9)	26.110(4)	18.894(5)	15.033(1)	17.539(4)
c/Å	26.961(6)	18.967(3)	22.210(7)	17.598(2)	16.023(4)
α/°	—	—	109.75(2)	—	—
β/°	—	98.34(2)	98.95(3)	98.08(1)	105.78(2)
γ/°	—	—	107.18(3)	—	—
U/Å^3	6098(4)	4918.0(12)	4872(3)	2966.0(5)	3001.8(13)
D_c/g cm^{-3}	1.857	1.647	0.987	1.661	1.588
μ(Mo-Kα)/mm^{-1}	6.804	4.961	2.524	4.198	4.128
Z	8	8	6	4	4
F(000)	3280	2400	1424	1456	1424
θ Range/°	2.23–21.99	2.17–23.92	2.03–23.99	2.26–23.92	2.23–23.92
Index ranges	$0 \leqslant h \leqslant 12$, $0 \leqslant k \leqslant 20$, $0 \leqslant l \leqslant 27$	$0 \leqslant h \leqslant 11$, $-29 \leqslant k \leqslant 0$, $-21 \leqslant l \leqslant 21$	$-14 \leqslant h \leqslant 0$, $-20 \leqslant k \leqslant 0$, $-22 \leqslant l \leqslant 25$	$0 \leqslant h \leqslant 12$, $0 \leqslant k \leqslant 17$, $-19 \leqslant l \leqslant 19$	$-12 \leqslant h \leqslant 12$, $0 \leqslant k \leqslant 20$, $0 \leqslant l \leqslant 18$
No. data collected	4195	8186	6823	4883	4691
Independent reflections	1899	7700	6802	4624	4691
No. reflections with $I > 2\sigma(I)$	1899	5348	3097	2737	3613
Absorption correction	DIFABS	DIFABS	—	DIFABS	DIFABS
Maximum, minimum absorption corrections	1.254, 0.788	1.153, 0.829	—	1.357, 0.898	1.00, 0.467[a]
Data, restraints, parameters	1899, 0, 183	7700, 4, 534	5240, 9, 338	4622, 17, 373	4684, 3, 380
Goodness of fit on F	1.180	1.019	1.067[b]	1.035	1.083
$R1$, $wR2[I > 2\sigma(I)]$	0.0642, 0.1582	0.0303, 0.0681	0.1042, 0.2544	0.0459, 0.1010	0.0402, 0.1397
$R1$, $wR2$ (all data)	0.0642, 0.1582	0.0649, 0.0741	0.2605, 0.3844	0.1058, 0.1145	0.0663, 0.1678
Maximum, minimum residual electron density/e Å^{-3}	1.102, −1.405	0.758, −0.690	1.500, −1.379	1.494, −1.007	1.631, −0.830
Weighting scheme, w, where $P = (F_o^2 + 2F_c^2)/3$	$1/[\sigma^2(F_o^2) + (0.0389P)^2 + 482.7171P]$	$1/[\sigma^2(F_o^2) + (0.0437P)^2]$	$1/[\sigma^2(F_o^2) + (0.1456P)^2 + 206.0368P]$	$1/[\sigma^2(F_o^2) + (0.0629P)^2]$	$1/[\sigma^2(F_o^2) + (0.0991P)^2 + 19.2856P]$
Extinction coefficient[c]	0.000 08(4)	0.000 65(5)	0.0010(3)	0.000 02(10)	0.0003(3)

[a] Maximum, minimum transmission factors quoted. [b] Refinement based on F^2 rather than F. [c] Extinction expression $F_c^* = kF_c[1 + (0.001 \times F_c^2\lambda^3/\sin 2\theta)]^{-\frac{1}{4}}$.

(−78 °C) to a stirred solution of complex **9** (0.38 g, 0.37 mmol) in thf (10 cm^3). After 12 h at room temperature the resulting orange solution was pre-adsorbed onto alumina and chromatographed on a short column (4 × 1 cm). Elution with hexane–CH_2Cl_2 (3 : 1) gave an orange band, which on recrystallisation (0 °C, hexane–CH_2Cl_2) afforded orange *crystals* of [Re{η^4-CH(Ph)=C(Ph)CH=CHC$_6$H$_4$PPh$_2$-*o*}(η-C_5H_5)] **10** (0.16 g, 60%) (Found: C, 64.9; H, 4.4. $C_{39}H_{32}PRe$ requires C, 65.3; H, 4.5%). NMR (C_6D_6): ^{1}H, δ 7.70–6.51 (m, 20 H, Ph), 5.14–5.02 [AB spectrum 2 H, H^b and H^c, *J*(H^{b}H^c) 7.8], 4.34 (s, 5 H, C_5H_5) and 0.93 (s, 1 H, H^a); ^{13}C-{^{1}H}, δ 153.4–122.8 (Ph), 82.4 (C^2), 80.5 (C_5H_5), 64.2 (C^3), 52.2 [d, C^4, *J*(CP) 3.3] and 43.2 [d, C^1, *J*(CP) 7.7 Hz]; ^{31}P-{^{1}H}, δ 61.8. FAB mass spectrum: *m*/*z* 718 (*M*$^+$).

Reaction of complex 10 with [Ph$_3$C][BF$_4$]. Addition of [Ph$_3$C][BF$_4$] (0.03 g, 0.08 mmol) to a stirred solution of complex **10** (0.60 g, 0.08 mmol) in CH_2Cl_2 (10 cm^3) at room temperature led to a rapid change from orange to dark green. Removal of the solvent *in vacuo* and recrystallisation from CH_2Cl_2–Et_2O afforded green *crystals* of **9** (0.50 g, 80%), identified by ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR spectroscopy.

Crystallography

Many of the details of the structure analyses carried out on compounds **1**, **4**, **7**, **8** and **10** are listed in Table 7. Crystallographic measurements for **1** were made on a Hilger and Watts Y290 four-circle diffractometer whereas data collections for **4**, **7**, **8** and **10** were carried out on a CAD4 diffractometer. Corrections for Lorentz-polarisation effects and extinction were applied in all cases. Absorption corrections were applied using DIFABS[28] as noted in Table 7. The structures were solved by Patterson methods and refined using the SHELX[29,30] suite of programs. Structural diagrams were generated using ORTEX.[4]

The asymmetric unit in complex **1** consisted of one molecule of the cyclobutadienerhenium complex along with one molecule of the recrystallisation solvent, dichloromethane. In the dihydride complex, **4**, the unique portion of the unit cell comprised of two molecules of the dihydride complex, whereas in **7** three molecules of the trifluoroacetate complex were correspondingly present. Finally, the asymmetric unit in **8** consisted of one molecule of the rhenium salt while in **10** the unique portion of the unit cell consisted of one molecule of the neutral dienyl rhenium complex.

For complex **1** only the rhenium, bromine and chlorine atoms were anisotropically refined. The remaining atoms necessitated isotropic treatment in order to maintain satisfactory thermal displacement parameters. All non-hydrogen atoms were refined anisotropically for **4** and also **8**, with the single exception of the boron atom in the latter which was treated isotropically due to smearing of the electron density in the region of the tetrafluoroborate anion. Diligent efforts made to model this disorder met with failure. Ultimately, the most satisfactory refinement of the anionic moiety in **8** was achieved by restraining all B–F bond lengths to be the same, and by similarly treating F···F distances.

Hydrogen atoms were included throughout at calculated positions where relevant, except in the case of the hydride protons of complex **4** where H(1A) and H(1B) [attached to Re(1)] along with H(2A) and H(2B) [attached to Re(2)] were located in the penultimate Fourier-difference electron-density map, and refined at a fixed distance of 1.70 Å from the appropriate rhenium centres. The Re–H distances in fact converged to an average value of 1.65 Å in this structure. The hydrogens attached to C(6) and C(7) in **8**, and to C(6), C(7) and C(9) in **10**, were similarly located, and refined at a fixed distance of 0.98 Å from the appropriate parent atoms.

Unfortunately, as mentioned earlier, refinement of the crystal structure for complex **7** was not satisfactory and was severely hampered by many factors. In the first instance the crystals appeared to self destruct as they grew in solution, by developing cracks, in what were initially very small gem-like blocks. The crystal batch had inherent handling difficulties, and the only remotely suitable sample for a single-crystal structure determination was substandard. Poor quality was quickly manifested in broad scan widths during early search routines on the diffractometer. In addition, the diffracting ability of the sample fell off rapidly with increasing Bragg angle, and much of the higher angle data collected were flagged as weak and bore negative intensity. As a consequence of a poor data set, convergence was inhibited, but improved by omitting reflections with negative intensity from the final refinement cycles, treating phenyl and cyclopentadienyl rings as rigid groups, and by restricting the C–C distances in the butadienyl moieties to a value of 1.42 Å. Blocked-matrix refinement attempts proved unstable, and attempts to treat more atoms anisotropically were unsuccessful. Bond distances and angles are not reliable for comparison purposes and hence not quoted. However, the structural analysis *did* attain one of its objectives by providing proof of a novel cyclobutadienyl ring-opening reaction, while also confirming the relative configuration of the organic fragments attached to the rhenium centres.

CCDC reference number 186/684.

Extended Hückel molecular orbital calculations

The EHMO calculations employed the CACA02 program package developed by Mealli and Proserpio.[31]

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