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Synthesis and reactivity of η^2(4e)-alkyne and η^2(3e)-vinyl complexes of rhenium†

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Reaction of *cis*-/*trans*-$[ReBr_2(CO)_2(\eta\text{-}C_5H_5)]$ with PhC_2Ph and MeC_2Ph in refluxing toluene afforded good yields of the η^2(4e)-donor alkyne complexes $[ReBr_2(\eta^2\text{-}PhC_2Ph)(\eta\text{-}C_5H_5)]$ **1** and $[ReBr_2(\eta^2\text{-}MeC_2Ph)(\eta\text{-}C_5H_5)]$ **2**, respectively. Treatment of **1** and **2** with either $AgBF_4$ or $TlPF_6$ in the presence of PPh_3, $PMePh_2$ or $P(OMe)_3$ (L) gave monocations $[ReBr\{\eta^2(4e)\text{-alkyne}\}L(\eta\text{-}C_5H_5)]^+$, whereas a similar reaction with 2 equivalents of $AgBF_4$ and 1 equivalent of $Ph_2PCH_2CH_2PPh_2$ (dppe) afforded dications $[Re(\eta^2\text{-}PhC_2Ph)(dppe)(\eta\text{-}C_5H_5)][BF_4]_2$ and $[Re(\eta^2\text{-}MeC_2Ph)(dppe)(\eta\text{-}C_5H_5)][BF_4]_2$. The structural identity of $[ReBr(\eta^2\text{-}PhC_2Ph)(PMePh_2)(\eta\text{-}C_5H_5)][PF_6]$ was confirmed by single-crystal X-ray crystallography. The alkyne C–C vector lies parallel to the Re–Br bond and the alkyne C–C bond length [C(1)–C(2) 1.26(4) Å] is relatively short. Treatment of $[ReBr(\eta^2\text{-}PhC_2Ph)(PPh_3)(\eta\text{-}C_5H_5)][BF_4]$ and $[ReBr(\eta^2\text{-}PhC_2Ph)(PMePh_2)(\eta\text{-}C_5H_5)][PF_6]$ with $K[BHBu^s_3]$ in dichloromethane at −78 °C led to neutral η^2(3e)-vinyl complexes $[Re\{=C(Ph)CHPh\}Br(PPh_3)(\eta\text{-}C_5H_5)]$ and $[Re\{=C(Ph)CHPh\}Br(PMePh_2)(\eta\text{-}C_5H_5)]$. The crystal structure of the latter showed that the C–C vector of the vinyl moiety lies almost parallel to the Re–Br bond. The stereochemistry of these reactions is discussed in the light of extended-Hückel molecular orbital calculations. Reaction (−78 °C) of $[Re(\eta^2\text{-}PhC_2Ph)(dppe)(\eta\text{-}C_5H_5)][BF_4]_2$ with 1 equivalent of $K[BHBu^s_3]$ in tetrahydrofuran afforded the X-ray crystallographically identified monocationic η^2(3e)-vinyl complex $[Re\{=C(Ph)CHPh\}(dppe)(\eta\text{-}C_5H_5)][BF_4]$, which reacted at room temperature with a further equivalent of $K[BHBu^s_3]$ to give the *cis*-stilbene-substituted complex $[Re(\eta^2\text{-}Z\text{-}PhCH{=}CHPh)(dppe)(\eta\text{-}C_5H_5)]$. The structure of the latter showed that the alkene phenyl substituents are orientated towards the cyclopentadienyl ring. In contrast, a similar reaction between $K[BHBu^s_3]$ and $[Re(\eta^2\text{-}MeC_2Ph)(dppe)(\eta\text{-}C_5H_5)][BF_4]_2$ gave initially the η^2(3e)-vinyl complex $[Re\{=C(Me)CHPh\}(dppe)(\eta\text{-}C_5H_5)][BF_4]$; a further equivalent of $K[BHBu^s_3]$ led to deprotonation and formation of the η^2-allene complex $[Re\{\eta^2\text{-}CH(Ph){=}C{=}CH_2\}(dppe)(\eta\text{-}C_5H_5)]$, in which the substituted allenic bond is co-ordinated to the rhenium. The dinuclear complex $[Re_2Br_2(PPh_3)_2(\mu\text{-}O)(\eta\text{-}C_5H_5)_2][BF_4]_2$ was also prepared and shown crystallographically to possess a single rhenium–rhenium bond [2.731(5) Å].

There has been a revival of interest in alkyne organotransition-metal chemistry, stimulated in part by the realisation that the alkyne ligand in mononuclear complexes can adopt an η^2(4e)-bonding mode with interesting consequences for reactivity studies.[2] Although these developments have mainly focused on molybdenum and tungsten species it was clearly important to establish whether a related chemistry could be developed for other transition-metal systems. The report by Herrmann *et al.*[3] that the interesting molecules $[ReX_2(\eta^2\text{-}MeC_2Me)(\eta\text{-}C_5Me_5)]$ (X = Cl, Br or I) can be synthesised by a relatively complex oxidation/reduction sequence, $[Re(CO)_3(\eta\text{-}C_5Me_5)] \longrightarrow [ReO_3(\eta\text{-}C_5Me_5)] \longrightarrow [ReX_4(\eta\text{-}C_5Me_5)] \longrightarrow [ReX_3(\eta\text{-}C_5Me_5)]$, followed by a non-selective reaction with but-2-yne, stimulated our interest, and prompted us to seek a more direct synthetic approach to complexes of this type with a view to exploring their reaction chemistry.

Results and Discussion

Our synthetic entry point was suggested by an earlier observation[4,5] in molybdenum chemistry where it was found that PhC_2Ph reacts thermally with $[MoCl(CO)_3(\eta\text{-}C_5H_5)]$ to form the four-electron donor diphenylacetylene complex $[MoCl(\eta^2\text{-}PhC_2Ph)(CO)(\eta\text{-}C_5H_5)]$. This suggested that an analogous reaction between alkynes and the complex $[ReBr_2(CO)_2(\eta\text{-}C_5H_5)]$, formed[6] as a mixture of *cis* and *trans* isomers by the oxidative addition of Br_2 to $[Re(CO)_3(\eta\text{-}C_5H_5)]$, might provide a direct approach to the d^4 complexes $[ReBr_2\{\eta^2(4e)\text{-alkyne}\}(\eta\text{-}C_5H_5)]$. This idea proved to be correct. When a toluene solution of *cis*-/*trans*-$[ReBr_2(CO)_2(\eta\text{-}C_5H_5)]$ and a 5 molar excess of PhC_2Ph was heated under reflux for 2 h carbon monoxide was displaced and the complex $[ReBr_2(\eta^2\text{-}PhC_2Ph)(\eta\text{-}C_5H_5)]$ **1** (Scheme 1) was formed as red crystals in 78% yield. A similar reaction with 1-phenylprop-1-yne afforded (75% yield) brown crystals of $[ReBr_2(\eta^2\text{-}MeC_2Ph)(\eta\text{-}C_5H_5)]$ **2**. Both complexes were characterised by elemental analysis and NMR spectroscopy. The $^{13}C\text{-}\{^1H\}$ spectra showed alkyne contact-carbon resonances at δ 219.2 (**1**) and 229.8, 209.2 (**2**) consistent with an η^2(4e)-bonding mode,[2,7] the appearance of only one resonance in the case of the diphenylacetylene-substituted complex **1** confirming that at ambient temperature the alkyne is freely rotating around the metal–ligand axis. In the solid state it is reasonable to assume that the alkyne C–C vector lies parallel to a rhenium–halogen vector, as has been previously[3] established by X-ray crystallography for the related complex $[ReCl_2(\eta^2\text{-}EtC_2Et)(\eta\text{-}C_5Me_5)]$.

In order to assess the reactivity of these complexes towards donor ligands a molar equivalent of triphenylphosphine was added at room temperature to a solution of **1** in CD_2Cl_2 contained in an NMR tube. There was an immediate change from red to green and examination of the $^{13}C\text{-}\{^1H\}$ NMR spectrum revealed that the resonance at δ 219.2 assigned to the

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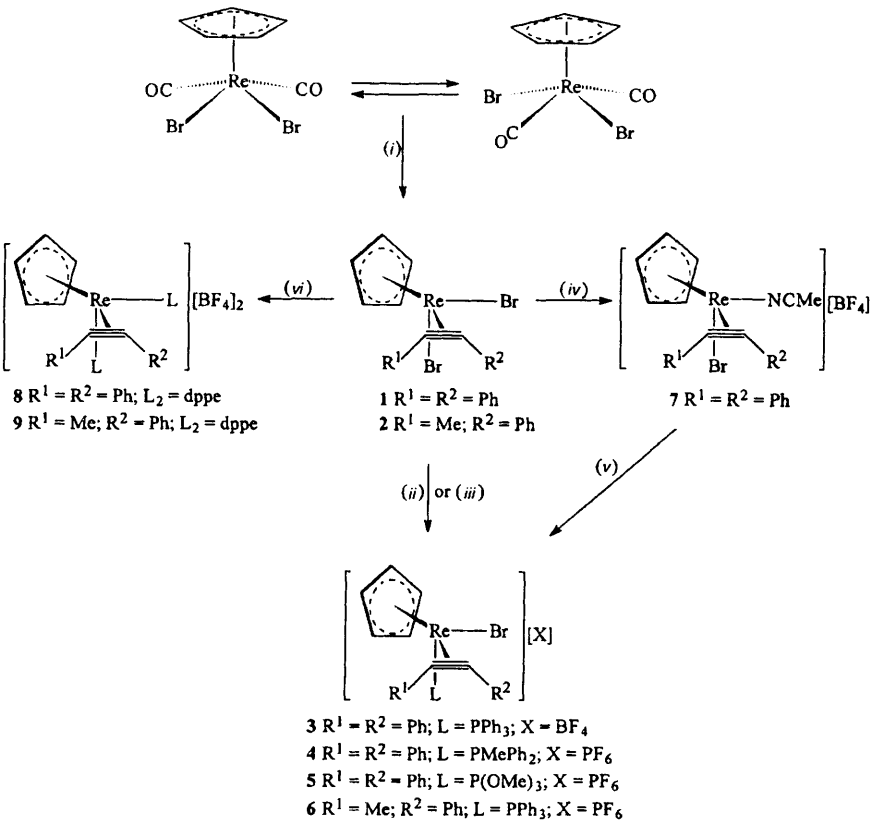


Scheme 1 (*i*) $R^1C_2R^2$, reflux, toluene; (*ii*) $AgBF_4$, L, CH_2Cl_2; (*iii*) $TlPF_6$, L, CH_2Cl_2; (*iv*) $AgBF_4$, MeCN; (*v*) L; (*vi*) $AgBF_4$, $Ph_2PCH_2CH_2PPh_2$ (dppe), CH_2Cl_2

diphenylacetylene contact carbons had been replaced by a singlet at δ 225.0. In addition the ^{31}P-{^1H} spectrum showed a singlet at δ 0.38 characteristic of a co-ordinated triphenylphosphine. These observations suggested that in solution the cationic species [ReBr(η²-PhC_2Ph)(PPh_3)(η-C_5H_5)]Br was formed, however attempts to isolate it by precipitation with diethyl ether simply regenerated the starting materials. This problem was solved by treating **1** with PPh_3 and $AgBF_4$ in dichloromethane, which resulted in the precipitation of AgBr and the formation in good yield of the cation [ReBr(η²-PhC_2Ph)(PPh_3)(η-C_5H_5)][BF_4] **3** (Scheme 1) as a stable pale green complex.

This synthetic methodology was readily extended to the preparation of the related complexes [ReBr(η²-PhC_2Ph)($PMePh_2$)(η-C_5H_5)][PF_6] **4**, [ReBr(η²-PhC_2Ph){$P(OMe)_3$}(η-C_5H_5)][PF_6] **5**, and [ReBr(η²-MeC_2Ph)(PPh_3)(η-C_5H_5)][PF_6] **6**, except that it was found, as detailed in the Experimental section, that the use of $TlPF_6$ instead of a silver(I) salt resulted in improved yields. The substitution-labile acetonitrile complex [ReBr(NCMe)(η²-PhC_2Ph)(η-C_5H_5)][BF_4] **7** was also prepared by treating **1** with $AgBF_4$ in acetonitrile, and it was found that the nitrile could readily be displaced by the appropriate phosphorus ligand thus accessing the cations present in **3**–**5**; however, the yields of the acetonitrile-substituted cations were low using either silver(I) or thallium(I) salts, and therefore the direct route to these cations was preferred. It was also found that the dications **8** and **9** could be prepared in good yield by treating **1** and **2** respectively with 1,2-bis(diphenylphosphino)ethane (dppe) and 2 molar equivalents of silver tetrafluoroborate in dichloromethane as solvent.

All of these complexes were isolated as air-stable crystalline materials and characterised by elemental analysis and NMR spectroscopy, the appearance of only one low-field acetylene contact carbon indicating, that as with **1** and **2**, there is a low barrier to rotation for the η²(4e)-bonded alkyne. Attempts to 'freeze out' this process by cooling to −90 °C were unsuccessful.

In order to confirm the structural identity of these complexes an X-ray diffraction study was undertaken with a crystal of **4** obtained by layered diffusion of hexane into a dichloromethane solution. The molecular geometry of the cation is illustrated in Fig. 1, and fractional coordinates, selected bond lengths and angles are listed in Tables 1 and 2 respectively. The rhenium-centred cation carries η⁵-C_5H_5, $PMePh_2$, bromo and η²-PhC_2Ph ligands, the alkyne C–C vector lying parallel to the rhenium–bromide bond, thus maximising back bonding from the metal fragment HOMO (highest occupied molecular orbital) to the alkyne antibonding orbitals. It is interesting that the alkyne C–C bond length [C(1)–C(2) 1.26(4) Å] is short, being similar to that reported[8] for the oxorhenium complexes [Re(O)I(η²-MeC_2Me)$_2$] [average 1.283(7) Å], [ReO(η²-MeC_2Me)$_2$(py)][SbF_6] (py = pyridine) [average 1.285(6) Å], and the cationic nitrosyl complex [Re(NO)(η²-EtC_2Et)(PPh_3)(η-C_5H_5)][BF_4] [1.24(1) Å],[9] but significantly (0.07 Å) shorter than that found[3] in the η²(4e)-bonded hex-3-yne complex [$ReCl_2$(η²-EtC_2Et)(η-C_5Me_5)] [1.326(4) Å]. Examination of the bond-length data shows that the η-C_5H_5 ligand is tilted relative to the rhenium atom as is reflected in the atom separations Re–C(28) 2.21(3), Re–C(29) 2.14(3), Re–C(30) 2.33(3), Re–C(31) 2.37(3), and Re–C(32) 2.34(3) Å. It is suggested that this effect is of steric origin and arises because of the proximity of one of the $PMePh_2$ ligand phenyl groups to the cyclopentadienyl ligand. The cations **3**–**6** clearly contain a chiral rhenium centre and indeed the unit cell contained both *R* and *S* isomers. Application of Stanley and Baird's pseudo-atom convention[10] leads to the priority sequence Br(80) > η-C_5H_5(60) > $PMePh_2$(31) > η²-PhC_2Ph(24), and hence the *R* configuration to the enantiomer shown in Fig. 1.

We have previously shown[11,12] that treatment of the four-electron alkyne complex [Mo(η²-PhC_2Ph){$P(OMe)_3$}$_2$(η-C_5H_5)][BF_4] with K[$BHBu^s_3$] leads to formation of the η²(3e)-vinyl complex [Mo{=C(Ph)CHPh}{$P(OMe)_3$}$_2$(η-C_5H_5)], and therefore it followed that the reaction of a source of 'H^-' with the rhenium cations shown in Scheme 1 might lead

Table 1 Fractional atomic coordinates ($\times 10^4$) with estimated standard deviations (e.s.d.s) in parentheses for [ReBr(η^2-PhC$_2$Ph)(PMePh$_2$)(η-C$_5$H$_5$)][PF$_6$] **4**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re	1012(1)	522(1)	2380(1)	C(12)	2925(1)	884(9)	−342(1)
Br	1985(3)	1852(2)	2259(2)	C(13)	2268(1)	851(9)	240(1)
P(1)	2611(6)	199(4)	3679(5)	C(14)	2215(1)	145(9)	741(1)
P(2)	1898(7)	2240(5)	6325(6)	C(15)	3248(2)	991(2)	4483(2)
F(1)	2443(30)	2067(21)	7412(15)	C(16)	2356(2)	−609(1)	4420(1)
F(2)	1886(25)	3136(13)	6613(17)	C(17)	1911(2)	−1334(1)	3996(1)
F(3)	1890(24)	1331(13)	6031(19)	C(18)	1637(2)	−1933(1)	4543(1)
F(4)	1336(26)	2419(18)	5263(16)	C(19)	1808(2)	−1809(1)	5515(1)
F(5)	831(23)	2146(29)	6509(22)	C(20)	2253(2)	−1084(1)	5939(1)
F(6)	2955(21)	2330(20)	6113(23)	C(21)	2527(2)	−484(1)	5392(1)
C(1)	953(2)	−430(2)	1579(2)	C(22)	3683(1)	−156(1)	3190(1)
C(2)	1514(2)	110(2)	1361(2)	C(23)	3981(1)	−967(1)	3228(1)
C(3)	441(1)	−1231(1)	1258(1)	C(24)	4850(1)	−1198(1)	2936(1)
C(4)	533(1)	−1527(1)	400(1)	C(25)	5420(1)	−618(1)	2607(1)
C(5)	100(1)	−2277(1)	58(1)	C(26)	5122(1)	193(1)	2570(1)
C(6)	−425(1)	−2733(1)	572(1)	C(27)	4253(1)	424(1)	2861(1)
C(7)	−517(1)	−2437(1)	1430(1)	C(28)	−487(2)	1183(2)	2248(2)
C(8)	−84(1)	−1686(1)	1772(1)	C(29)	−578(3)	281(2)	2397(2)
C(9)	2819(1)	−528(9)	659(1)	C(30)	−82(2)	48(2)	3241(2)
C(10)	3476(1)	−495(9)	78(1)	C(31)	448(2)	709(2)	3745(2)
C(11)	3529(1)	211(9)	−423(1)	C(32)	133(2)	1403(2)	3127(2)

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

Br–Re	2.581(6)	P(1)–Re	2.429(9)
C(1)–Re	1.96(3)	C(2)–Re	1.95(3)
C(28)–Re	2.21(3)	C(29)–Re	2.14(3)
C(30)–Re	2.33(3)	C(31)–Re	2.37(3)
C(32)–Re	2.34(3)	C(15)–P(1)	1.79(3)
C(16)–P(1)	1.82(2)	C(22)–P(1)	1.87(2)
C(2)–C(1)	1.26(4)	C(1)–C(3)	1.50(3)
C(2)–C(14)	1.49(3)		
Re–C(1)–C(2)	71(2)	Re–C(2)–C(1)	72(2)
Re–C(1)–C(3)	147(2)	Re–C(2)–C(14)	153(2)
P(1)–Re–Br	85.1(3)	C(1)–Re–Br	125.0(9)
C(1)–Re–P(1)	99.4(8)	C(2)–Re–Br	87.2(9)
C(2)–Re–P(1)	96.5(9)	C(2)–Re–C(1)	38(1)
C(3)–C(1)–C(2)	142(2)	C(14)–C(2)–C(1)	135(3)

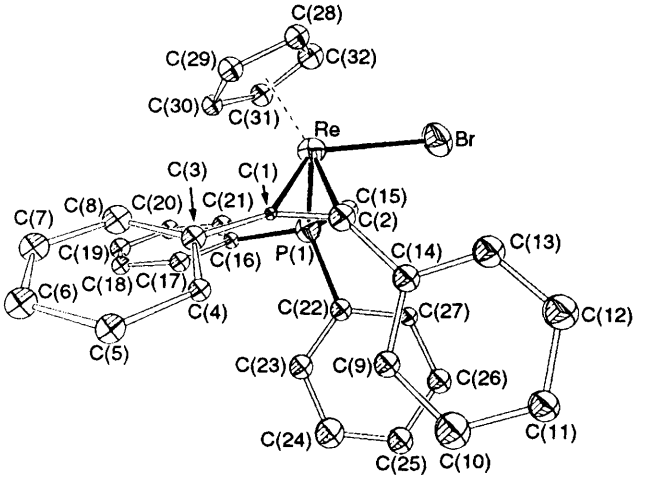


Fig. 1 Molecular structure of the cation associated with the complex [ReBr(η^2-PhC$_2$Ph)(PMePh$_2$)(η-C$_5$H$_5$)][PF$_6$] **4**

to η^2(3e)-vinyl-substituted rhenium complexes. There is only one previously reported η^2-vinyl-substituted rhenium complex, namely [Re{=C(CH$_2$Ph)CH$_2$}Cl(dppe)$_2$][BF$_4$] formed[13] by protonation (HBF_4) of the η^2-allene complex [Re(η^2-CH$_2$=C=CHPh)Cl(dppe)$_2$]. Owing to the asymmetric environment of the co-ordinated η^2(4e)-PhC$_2$Ph ligand present in the cations **3**–**6**, nucleophilic attack by 'H^-' could, therefore, lead to the formation of diastereoisomers, and also isomers

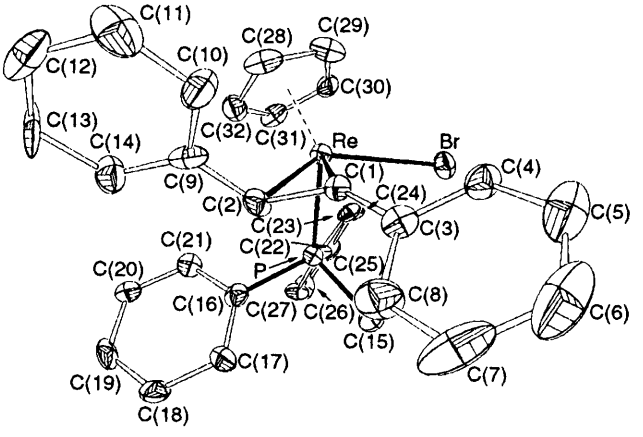


Fig. 2 Molecular structure of the complex [Re{=C(Ph)CHPh}Br(PMePh$_2$)(η-C$_5$H$_5$)] **11**

differing with respect to the orientation of the η^2(3e)-vinyl fragment.

Treatment (−78 to +25 °C) of a dichloromethane solution of complex **3** with a molar equivalent of K[BHBu$^s_3$] resulted in a change from pale to dark green, and column chromatography of the reaction mixture gave on elution with hexane one green band, which on crystallisation afforded a good yield (70%) of the dark green hexane-soluble crystalline complex **10**. A similar reaction between **4** and K[BHBu$^s_3$] gave the dark green complex **11**. Both complexes were characterised by elemental analysis and by NMR spectroscopy, the latter confirming that only one of the possible diastereomeric pairs was formed. The ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} spectra showed the features expected for complexes with the molecular formula [Re{=C(Ph)CHPh}Br(L)(η-C$_5$H$_5$)] (L = PPh$_3$ or PMePh$_2$), and in particular the ^{13}C-{^{1}H} spectra of **10** and **11** exhibited characteristic low-field singlets at δ 258.3 and 253.6, respectively, which can be assigned[11–13] to the carbon atoms doubly bonded to the rhenium. The spectra did not, however, define the stereochemistry and the orientation of the η^2-vinyl ligand.

In order to solve this structural problem a single-crystal X-ray diffraction study was undertaken with a suitable crystal of complex **11**. This established the molecular structure illustrated in Fig. 2, fractional coordinates and selected bond lengths and angles being listed in Tables 3 and 4, respectively; the unit cell

Table 3 Fractional atomic coordinates ($\times 10^4$) with e.s.d.s in parentheses for [Re{=C(Ph)CHPh}Br(PMePh$_2$)(η-C$_5$H$_5$)] **11**

Atom	*x*	*y*	*z*
Re	1275(1)	1733(1)	1960(1)
Br	1424(1)	1055(2)	−81(2)
P	1811(3)	791(4)	2879(5)
C(1)	2326(11)	2619(13)	1680(15)
C(2)	2237(11)	2676(14)	2924(16)
C(3)	3080(9)	3013(10)	886(13)
C(4)	2983(9)	3024(10)	−365(13)
C(5)	3669(9)	3439(10)	−1099(13)
C(6)	4452(9)	3843(10)	−581(13)
C(7)	4549(9)	3832(10)	669(13)
C(8)	3863(9)	3417(10)	1403(13)
C(9)	2112(10)	3415(12)	3484(11)
C(10)	2076(10)	4060(12)	2774(11)
C(11)	1954(10)	4725(12)	3317(11)
C(12)	1869(10)	4744(12)	4568(11)
C(13)	1904(10)	4099(12)	5278(11)
C(14)	2026(10)	3434(12)	4736(11)
C(15)	2708(11)	741(13)	2145(18)
C(16)	2139(7)	1081(10)	4439(11)
C(17)	2980(7)	1441(10)	4738(11)
C(18)	3221(7)	1700(10)	5921(11)
C(19)	2620(7)	1598(10)	6805(11)
C(20)	1779(7)	1238(10)	6506(11)
C(21)	1538(7)	979(10)	5323(11)
C(22)	1141(8)	−310(9)	3026(11)
C(23)	482(8)	−687(9)	2230(11)
C(24)	−11(8)	−1531(9)	2343(11)
C(25)	156(8)	−1998(9)	3251(11)
C(26)	815(8)	−1622(9)	4047(11)
C(27)	1307(8)	−777(9)	3934(11)
C(28)	421(12)	2338(14)	2382(25)
C(29)	133(13)	1865(17)	1291(26)
C(30)	−150(13)	1004(19)	1591(21)
C(31)	−43(12)	971(15)	2859(23)
C(32)	334(13)	1752(17)	3316(22)

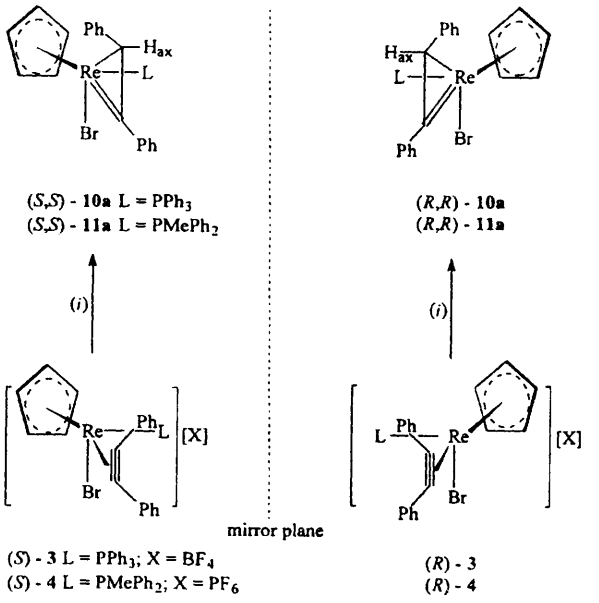
Table 4 Selected bond distances (Å) and angles (°) for complex **11**

Br–Re	2.610(5)	P–Re	2.412(8)
C(1)–Re	1.91(2)	C(2)–Re	2.13(2)
C(28)–Re	2.19(2)	C(29)–Re	2.22(2)
C(30)–Re	2.35(2)	C(31)–Re	2.38(2)
C(32)–Re	2.24(2)	C(15)–P	1.80(2)
C(16)–P	1.83(2)	C(22)–P	1.83(2)
C(2)–C(1)	1.39(3)	C(3)–C(1)	1.51(3)
C(9)–C(2)	1.52(3)		
P–Re–Br	85.5(2)	C(1)–Re–Br	89.6(6)
C(1)–Re–P	96.6(7)	C(2)–Re–Br	126.7(6)
C(2)–Re–P	85.3(7)	C(2)–Re–C(1)	39.9(7)
C(2)–C(1)–Re	79(1)	C(3)–C(1)–Re	149(1)
C(3)–C(1)–C(2)	130(2)	C(1)–C(2)–Re	62(1)
C(9)–C(2)–Re	122(1)	C(9)–C(2)–C(1)	121(2)

contains a 1:1 mixture of two diastereoisomers, related by an inversion centre.

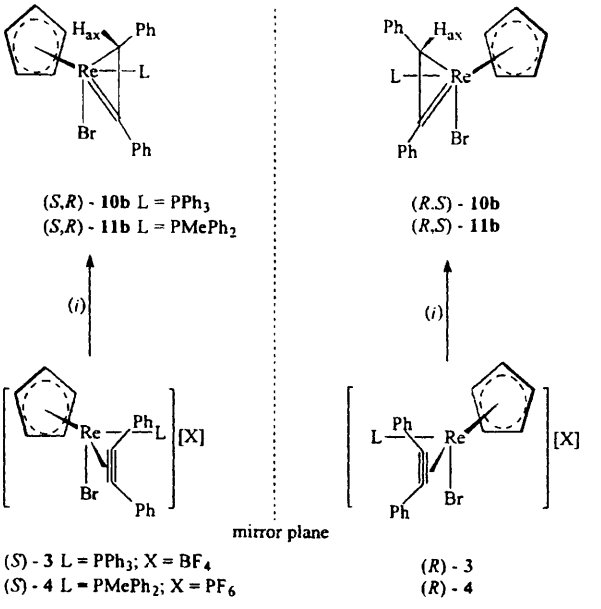
The molecule contains a rhenium atom to which is co-ordinated η^5-cyclopentadienyl, PMePh$_2$, Br and η^2(3e)-bonded vinyl ligands. The C–C vector of the vinyl moiety lies almost parallel to the Re–Br bond as reflected in the dihedral angles P–Re–C(1)–C(2) and Br–Re–C(1)–C(2) of −76.44 and 161.72° respectively. Such a stereochemistry is, of course, to be expected in view of the structure established for the parent complex **4** and the isolobal relationship η^2(4e)-HC$_2$H $\longleftrightarrow$ η^2(3e)-CH=CH$_2^-$.[11] The η^2(3e)-vinyl ligand is orientated such that the rhenium to carbon double bond is *cis* to the bromide ligand and is co-ordinated to the metal centre *via* one short [Re–C(1) 1.91(2) Å] and one long [Re–C(2) 2.13(2) Å] bond characteristic of double and single Re–C bonds, respectively. The carbon atom C(2) also carries phenyl and hydrogen substituents, the former occupying a pseudo-equatorial position.

Axial delivery of H$^-$ *cis* to the ligand L



Scheme 2 (*i*) K[BHBu$^s_3$], CH_2Cl_2, −78 to +25 °C

Axial delivery of H$^-$ *trans* to the ligand L



Scheme 3 (*i*) K[BHBu$^s_3$], CH_2Cl_2, −78 to +25 °C

Thus, as illustrated in Scheme 2, the reaction between the η^2(4e)-bonded alkyne-substituted cation **3** or **4** and K[BHBu$^s_3$] is stereoselective. Since both of these cations exist as a 50:50 mixture of *R* and *S* enantiomers the selective delivery of 'H$^-$' to one of the alkyne contact carbons generates a new chiral centre, and as is illustrated the products of these reactions, **10** and **11**, are obtained as a 50:50 mixture of the *S,S* and *R,R* enantiomeric diastereoisomers. Clearly it was interesting to examine the possible origins of this stereoselectivity, and in particular to explain why **10a** and **11a** are formed rather than **10b** and **11b** (Scheme 3).

An initial step was to carry out a standard extended-Hückel MO calculation[14] using the crystallographic bond parameters found for complex **4** simplified by replacing the phosphorus and alkyne substituents with H atoms at idealised distances of 1.45 and 1.10 Å, respectively. This established the composition of the LUMO (lowest unoccupied molecular orbital) displayed in Fig.

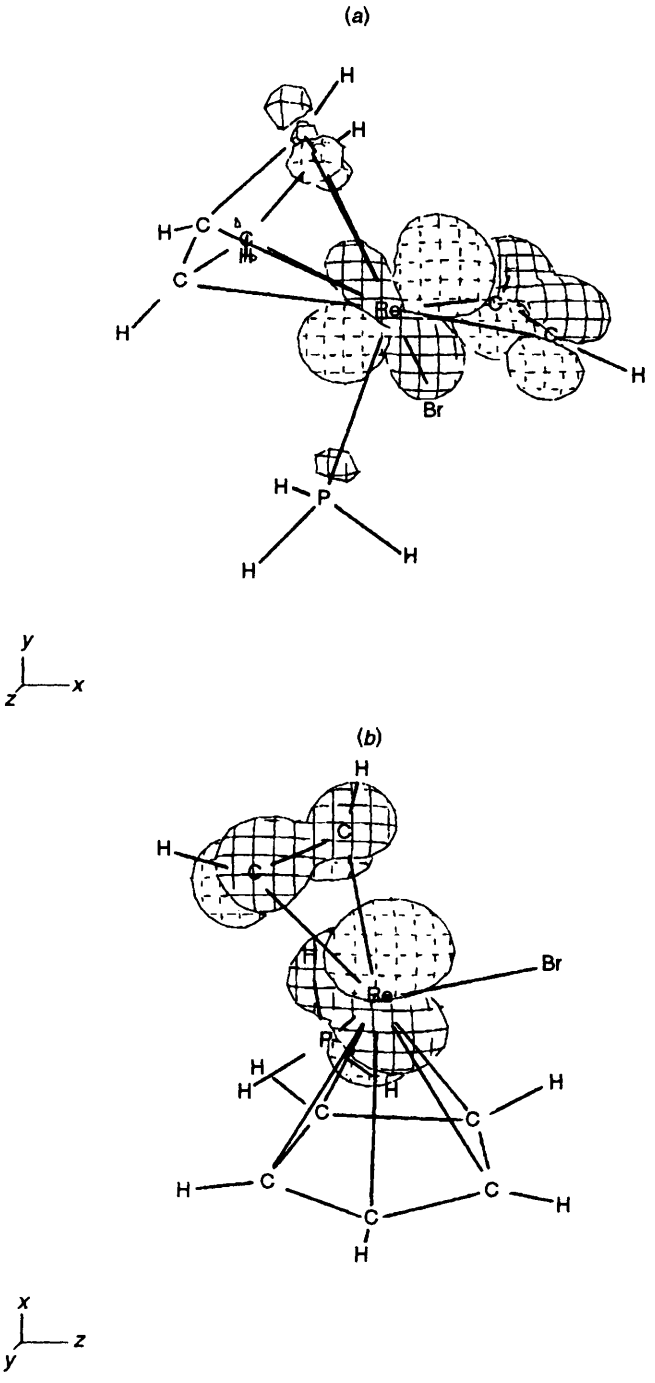


Fig. 3 Alternative views (*a*) and (*b*) of the LUMO associated with the complex $[ReBr(\eta^2\text{-}PhC_2Ph)(PMePh_2)(\eta\text{-}C_5H_5)][PF_6]$ **4**

3(*a*) and 3(*b*). The only significant contributions arise from the metal (*ca.* 40%) and the two alkyne contact-carbon atoms [*ca.* 20% for the C atom furthest from the Br ligand, C(1) (crystallographic numbering), and *ca.* 10% for the other C(2)]. This suggests that there are two possible reaction pathways to the complexes **10** and **11**, one involves a FMO (frontier molecular orbital)-controlled attack by $[BHBu^s_3]^-$ on the diphenylacetylene ligand resulting in the delivery, presumably *via* a pseudo-axial trajectory,* of 'H^-' to the alkyne carbon C(1) furthest from the Br ligand, a process facilitated by a small

* Although a pseudo-axial trajectory might seem the obvious direction of approach by an incoming nucleophile the work of Dunitz and co-workers[15] on the 'Stereochemistry of reaction paths at carbonyl centres' suggests that a more detailed theoretical study of the direction of attack on co-ordinated η^2(4e)-alkynes might provide further insight.

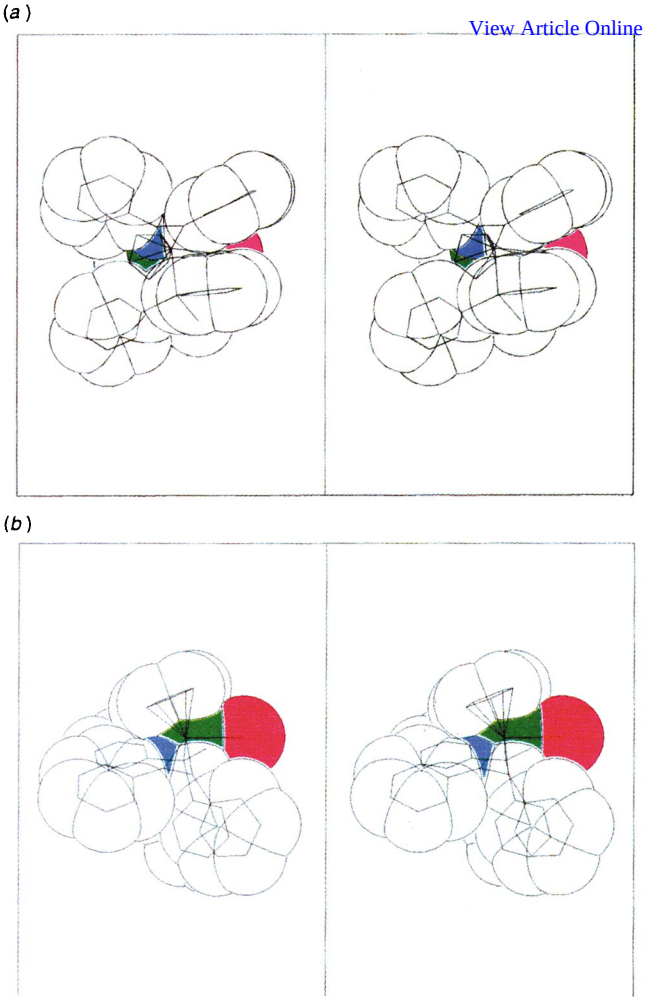


Plate 1 Stereographic space-filling models for complex **4** viewed from below (*a*) and above (*b*); green = Re, cyan = C(1) and magenta = Br

positive charge of 0.017 on C(1), which compares with a larger but negative charge on C(2) of −0.070. The second possible pathway would proceed by FMO-controlled nucleophilic attack at the rhenium centre facilitated by the largest LUMO coefficient and greatest positive charge of 0.154. There is, in fact, some experimental evidence for this second pathway in that in the reaction **3** ⟶ **10** a red intermediate is formed, whereas in the corresponding reaction **4** ⟶ **11** there was no evidence for a similar red species.

In the case of the pathway involving FMO-controlled attack on one of the alkyne contact carbons the EHMO calculations do not, of course, predict the direction of attack, *i.e. cis* or *trans* to the phosphorus ligand L (see Schemes 2 and 3). Moreover, examination of space-filling models (Plate 1) shows that it is not possible to differentiate between these two directions of attack, although detailed calculations might allow this. Thus, the present calculations do not provide us with an explanation for the observed diastereoselectivity. There is, of course, the possibility of the diastereoselectivity being thermodynamically controlled, and indeed our previous theoretical study[11] of the complexes $[Mo\{=C(R^1)CR^2R^3\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ ($R^1 = R^2 = R^3$ = aryl or alkyl) showed that the η^2(3e)-vinyl fragment can undergo a facile (*ca.* 20 kJ mol^{-1}) 90° 'windscreen-wiper' motion. However, examination of Schemes 2 and 3 shows that such a process cannot equilibrate the isomeric pairs **10a/10b** and **11a/11b**. This leads us to make the tentative suggestion that if the reaction does indeed involve direct attack on the co-ordinated diphenylacetylene then the origin of the observed selectivity lies in the ability of the π cloud of one of the phosphorus ligand aryl groups to interact with the Lewis

acid BBu^s_3, which is liberated on transfer of 'H^-', thus directing the nucleophile to attack from the direction *cis* to the PPh_3 or $PMePh_2$ ligand.

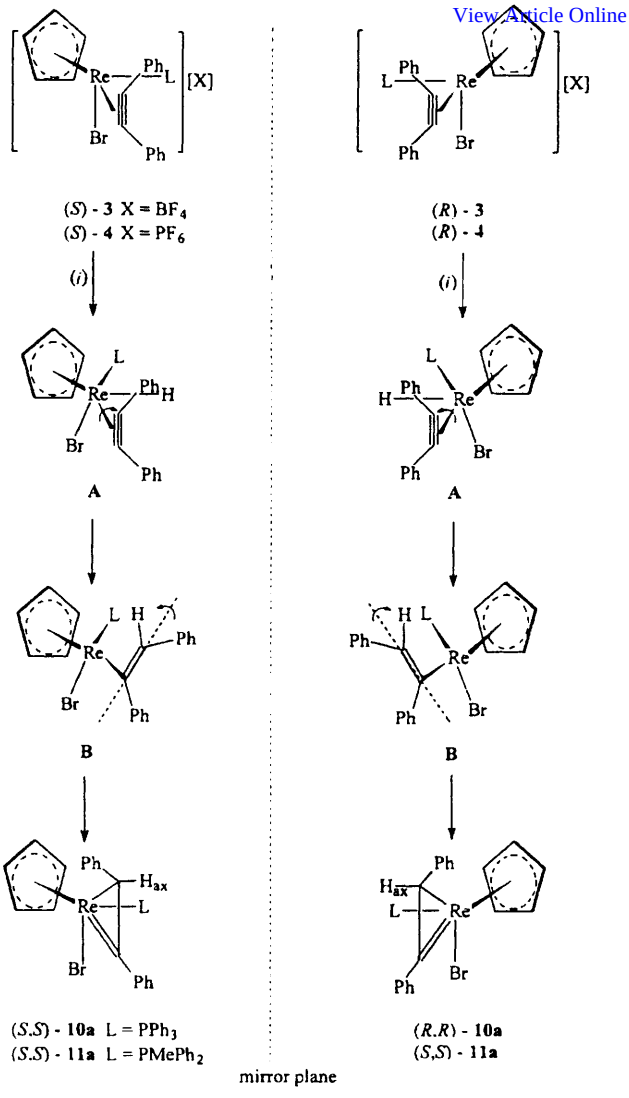
Alternatively, if assumptions are made about the stereochemistry then as is shown in Scheme 4 the diastereoselective formation of complexes **10a** and **11a** can be understood if the reaction involves delivery of 'H^-' to the rhenium centre, *i.e.* **3** or **4** ⟶ **A**. Then rotation of the PhC_2Ph ligand followed by migration of the hydride ligand *via* a *cis*-coplanar transition state could afford the 16e η^1-vinyl species **B**, a precursor of **10a** or **11a** if we assume that the rotational switch [η^1(1e) ⟶ η^2(3e)] in the bonding mode of the vinyl fragment is monodirectional. Clearly further theoretical and experimental work is needed if we are fully to understand the origins of the selectivity exhibited in these reactions.

The reactivity of the dicationic η^2(4e)-bonded diphenylacetylene complex **8** towards a source of 'H^-' was next explored to investigate the possibility of being able to effect the sequential reduction of a co-ordinated alkyne, first into a monocationic η^2(3e)-vinyl complex, and then into a neutral co-ordinated alkene with potentially interesting stereochemical consequences. As noted earlier there is one previous example[13] of the characterisation of a cationic η^2(3e)-vinyl complex, the rhenium cation $[Re\{=C(CH_2Ph)CH_2\}Cl(dppe)_2][BF_4]$. However, a study of the reactivity of this species towards nucleophilic reagents has not been reported.

Treatment (−78 to +25 °C) of a stirred suspension of complex **8** in tetrahydrofuran (thf) with 1 molar equivalent of the hydride anion donor $K[BHBu^s_3]$ led to the formation (57% yield) of the dark green crystalline monocationic complex **12**, which was characterised by elemental analysis and NMR spectroscopy. Whilst the NMR spectra showed that the reaction was regioselective producing only one of the possible isomeric rhena-η^2(3e)-vinyls (Re=C, δ 260.9), the data did not establish the stereochemistry at the β-carbon, *i.e.* Re=C(Ph)CHPh, or the orientation of the η^2(3e)-vinyl fragment. Answers to these structural questions were, however, provided by a single-crystal X-ray diffraction study which established the molecular geometry shown in Fig. 4 for one of the diastereoisomeric cations (related, as previously stated, by an inversion centre), both cations being present in the unit cell. Fractional coordinates, selected bond lengths and angles are listed in Tables 5 and 6, respectively.

This confirmed that **12** was a cationic η^2(3e)-vinyl complex and showed that the hydrogen atom delivered by the borohydride occupies a pseudo-axial site on the rhena-η^2(3e)-vinyl as was also the case for the neutral complex **11**. The C(6)–C(7) vector of the η^2(3e)-vinyl ligand lies parallel to the Re–P(1) bond with the rhenium to carbon double bond [Re–C(6) 1.93(1) Å] *trans* to P(1). Thus, the η^2(3e)-vinyl fragment present in **12** has a different orientation from that found in **11**.

An insight into the structural consequences of these observations is provided by Scheme 5 where it can be seen that in solution the diphenylacetylene-substituted dication **8** exists as a pair of enantiomers, which can be readily interconverted by a 'windscreen-wiper' motion, a simpler situation than with the unsymmetrical cations **3** and **4**. An X-ray crystallographic study was not carried out with **8**, and therefore molecular parameters were not available for an EHMO study. However, it is reasonable to assume that because of the symmetrical environment of the dication it would be difficult to distinguish between direct attack by the $[BHBu^s_3]^-$ anion under FMO control on the α or β contact carbon of the co-ordinated alkyne, and therefore both possibilities are illustrated in Scheme 5. Of course, as is the case for the corresponding reactions of **3** and **4**, nucleophilic attack on the alkyne α- and β-carbons from a direction *trans* to the phosphorus ligand is also possible, and this is depicted in Scheme 6. As is shown in Scheme 5, reaction



Scheme 4 (*i*) $K[BHBu^s_3]$, CH_2Cl_2, −78 to +25 °C

at the α-carbon affords the enantiomers **C** and **D**, which are those found in the crystal structure of the η^2(3e)-vinyl complex **12**. These same enantiomers can also be obtained *via* nucleophilic attack on the β-alkyne carbon followed by a 90° 'windscreen-wiper' rotation of the type which had been previously[11] shown to occur with the related complexes $[Mo(=CHCH_2)\{P(OH)_3\}_2(\eta\text{-}C_5H_5)]$, with a barrier to rotation of 20 kJ mol^{-1}. Thus, **E** can be transformed reversibly into **D** *via* clockwise rotation and then back into **E** by an anticlockwise 90° rotation. A similar anticlockwise rotation converts **F** into **C**, the process being reversed by a clockwise rotation. A similar relationship, *i.e.* **G** ⟷ **J** and **H** ⟷ **I**, is also apparent on examination of Scheme 6. However, especially important is the fact that a 90° clockwise rotation of the η^2(3e)-vinyl fragment in the isomer **H** (Scheme 6) results in the formation of **C** (Scheme 5), and similarly an anticlockwise rotation of **G** (Scheme 6) gives **D** (Scheme 5). What this means is that in the case of the Re(dppe)(η-C_5H_5)-substituted system it is not possible to distinguish between attack on the α- or β-carbons and to differentiate between approach of the nucleophile from a direction *cis* or *trans* to the dppe ligands. Moreover, even if initial attack by 'H^-' occurs at the rhenium centre, once the η^2(3e)-vinyl-substituted manifold is entered an equilibrium process can determine the stereochemical outcome of the reaction. In other words the stereochemistry of **12** could result from thermodynamic control.

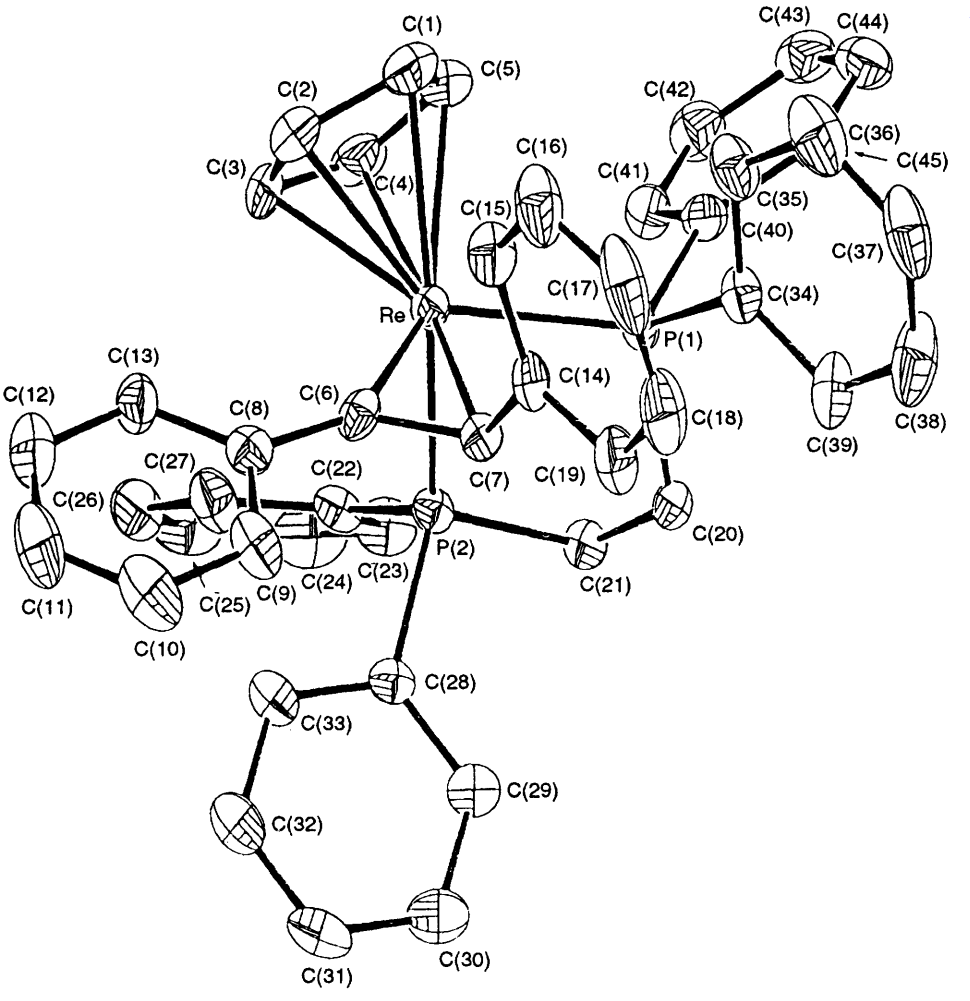


Fig. 4 Molecular structure of the cation associated with the complex $[Re\{=C(Ph)CHPh\}(dppe)(\eta\text{-}C_5H_5)][BF_4]$ **12**

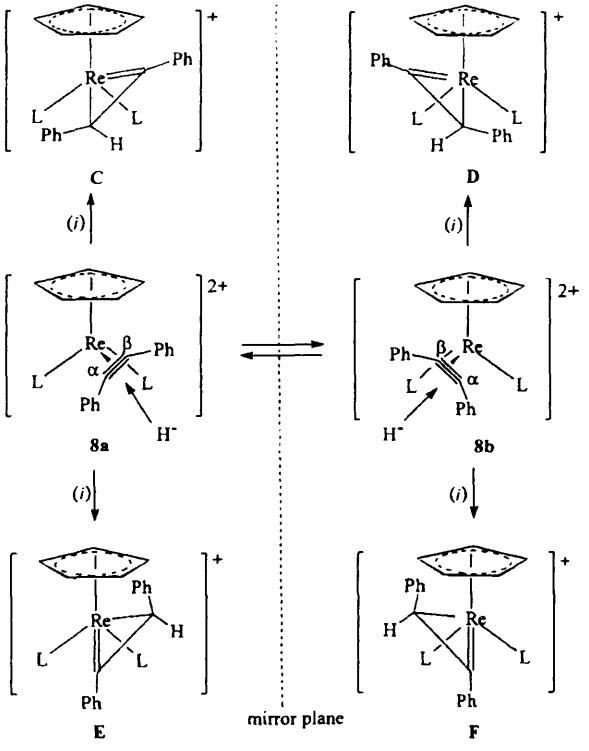
Table 5 Fractional atomic coordinates ($\times 10^4$) with e.s.d.s in parentheses for $[Re\{=C(Ph)CHPh\}(dppe)(\eta\text{-}C_5H_5)][BF_4]$ **12**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re	−2 240.3(4)	−1 453.0(1)	−10 210.9(3)	C(25)	−6 839(7)	−2 675(2)	−13 344(5)
P(1)	−1 320(2)	−1 718(1)	−8 185(2)	C(26)	−6 586(7)	−2 255(2)	−13 585(5)
P(2)	−4 232(2)	−1 753(1)	−10 235(2)	C(27)	−5 762(7)	−1 984(2)	−12 640(5)
C(1)	−376(10)	−1 466(4)	−10 580(9)	C(28)	−5 543(6)	−1 364(2)	−10 299(5)
C(2)	−1 482(11)	−1 295(4)	−11 614(9)	C(29)	−5 895(6)	−1 319(2)	−9 355(5)
C(3)	−2 471(12)	−1 618(4)	−12 096(9)	C(30)	−6 897(6)	−1 025(2)	−9 453(5)
C(4)	−1 971(12)	−1 990(4)	−11 383(10)	C(31)	−7 546(6)	−777(2)	−10 496(5)
C(5)	−694(11)	−1 895(4)	−10 471(10)	C(32)	−7 193(6)	−822(2)	−11 441(5)
C(6)	−3 049(9)	−887(3)	−10 519(8)	C(33)	−6 192(6)	−1 116(2)	−11 342(5)
C(7)	−2 441(9)	−863(3)	−9 234(8)	C(34)	−97(6)	−1 406(2)	−6 954(6)
C(8)	−3 724(7)	−552(2)	−11 410(5)	C(35)	1 066(6)	−1 266(2)	−7 027(6)
C(9)	−4 107(7)	−173(2)	−11 037(5)	C(36)	2 068(6)	−1 042(2)	−6 064(6)
C(10)	−4 868(7)	137(2)	−11 887(5)	C(37)	1 907(6)	−958(2)	−5 029(6)
C(11)	−5 246(7)	68(2)	−13 109(5)	C(38)	744(6)	−1 098(2)	−4 957(6)
C(12)	−4 863(7)	−311(2)	−13 482(5)	C(39)	−258(6)	−1 322(2)	−5 919(6)
C(13)	−4 102(7)	−621(2)	−12 633(5)	C(40)	−516(5)	−2 261(2)	−7 922(5)
C(14)	−1 340(7)	−545(2)	−8 552(6)	C(41)	−1154(5)	−2 596(2)	−8 729(5)
C(15)	−1 280(7)	−364(2)	−7 498(6)	C(42)	−560(5)	−3 004(2)	−8 523(5)
C(16)	−279(7)	−62(2)	−6 853(6)	C(43)	672(5)	−3 076(2)	−7 511(5)
C(17)	661(7)	60(2)	−7 263(6)	C(44)	1 310(5)	−2 741(2)	−6 703(5)
C(18)	600(7)	−121(2)	−8 318(6)	C(45)	716(5)	−2 333(2)	−6 909(5)
C(19)	−400(7)	423(2)	−8 962(6)	B	−3 951(12)	−3 704(4)	−10 421(8)
C(20)	−2 717(8)	−1 817(3)	−7 794(8)	F(1)	−4 632(9)	−3 606(4)	−9 871(8)
C(21)	−3 836(9)	−2 049(3)	−8 825(7)	F(2)	−2 931(12)	−4 001(3)	−9 679(8)
C(22)	−5 192(7)	−2 135(2)	−11 453(5)	F(3)	−4 660(14)	−3 862(3)	−11 474(7)
C(23)	−5 445(7)	−2 556(2)	−11 212(5)	F(4)	−3 352(8)	−3 376(3)	−10 515(8)
C(24)	−6 268(7)	−2 826(2)	−12 157(5)				

With a cationic η^2(3e)-vinyl complex of defined stereochemistry and geometry to hand we could now, however, examine the reactivity of **12** towards nucleophilic reagents. Room-temperature addition of a molar equivalent of $K[BHBu^s_3]$ to a thf solution of **12** led (20 min) to a change from green to yellow, and work-up by column chromatography on

Table 6 Selected bond distances (Å) and angles (°) for complex **12**

P(1)–Re	2.391(4)	P(2)–Re	2.374(5)
C(1)–Re	2.30(2)	C(2)–Re	2.29(2)
C(3)–Re	2.29(1)	C(4)–Re	2.32(2)
C(5)–Re	2.32(2)	C(6)–Re	1.93(1)
C(7)–Re	2.26(1)	C(20)–P(1)	1.84(1)
C(34)–P(1)	1.800(8)	C(40)–P(1)	1.864(9)
C(21)–P(2)	1.84(1)	C(22)–P(2)	1.836(8)
C(28)–P(2)	1.857(9)	C(6)–C(7)	1.43(1)
C(8)–C(6)	1.46(1)	C(14)–C(7)	1.50(1)
C(21)–C(20)	1.50(1)		
P(2)–Re–P(1)	80.5(2)	C(6)–Re–P(1)	117.5(4)
C(6)–Re–P(2)	90.6(4)	C(7)–Re–P(1)	79.3(3)
C(7)–Re–P(2)	90.7(4)	C(7)–Re–C(6)	38.8(3)
C(7)–C(6)–Re	83.3(6)	C(8)–C(6)–Re	146.6(7)
C(8)–C(6)–C(7)	129.3(9)	C(6)–C(7)–Re	57.9(6)
C(14)–C(7)–Re	125.9(8)	C(14)–C(7)–C(6)	122(1)

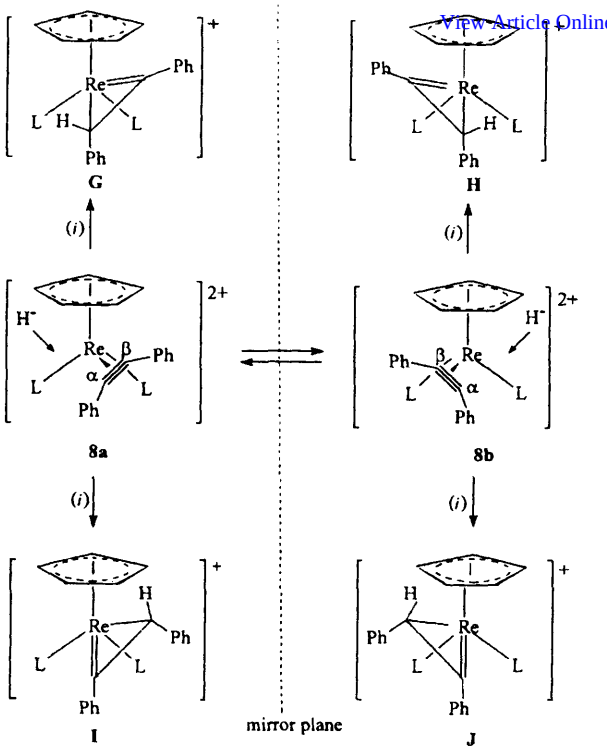


Scheme 5 L_2 = dppe. (*i*) K[BHBu$^s_3$], thf

alumina with elution by CH_2Cl_2–hexane afforded (40% yield) yellow crystals of the neutral complex **13**. Although the NMR data (see Experimental section) for **13** showed that the product of nucleophilic attack was a [Re(η^2-PhCH=CHPh)(dppe)(η-C_5H_5)] complex, the spectra did not differentiate between a *cis*- or *trans*- (rotating) alkene ligand. However, a single-crystal X-ray study clarified this question.

As is shown in Fig. 5 (fractional coordinates, selected bond lengths and angles are listed in Tables 7 and 8, respectively) **13** is a d^6 *cis*-stilbene complex with characteristic[16] bond lengths and angles, in which the vector C(6)–C(7) of the alkene lies parallel to the η-C_5H_5 plane, the phenyl substituents on the stilbene ligand being directed towards the cyclopentadienyl ligand.* This latter feature is unusual in that it might have been expected that the *cis*-stilbene ligand could rotate so as to minimise steric interaction between the η-C_5H_5

* Examination of the low-temperature (−100 °C) ^{1}H NMR spectrum provided no evidence for restricted rotation (see ref. 17) of the unsubstituted cyclopentadienyl ligand.



Scheme 6 L_2 = dppe. (*i*) K[BHBu$^s_3$], thf

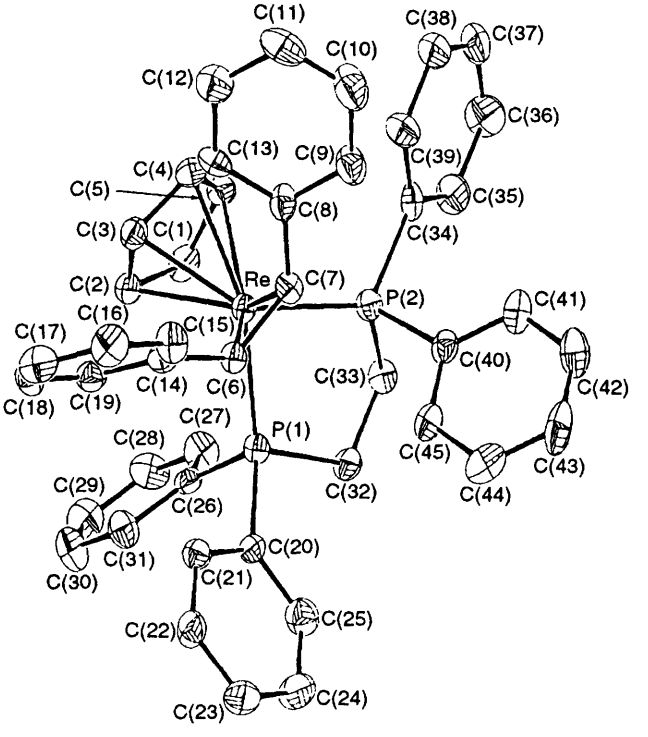


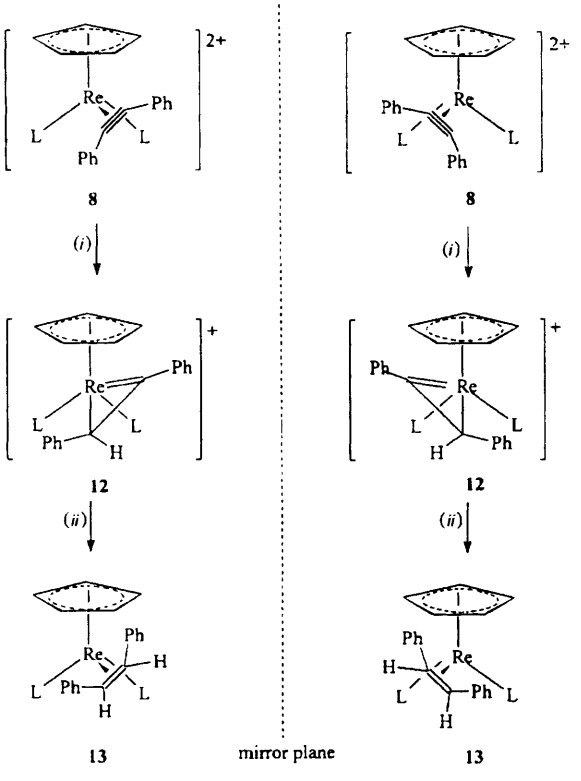
Fig. 5 Molecular structure of the complex [Re(η^2-*Z*-PhCH=CHPh)-(dppe)(η-C_5H_5)] **13**

ligand and the stilbene phenyl substituents. Moreover, as is illustrated in Scheme 7, the *cis*-stilbene might also have been predicted to orientate itself parallel to one of the rhenium–phosphorus vectors rather than parallel to the plane of the cyclopentadienyl ring so as to maximise back bonding to the alkene.

This is the first reported study of the reaction of a nucleophile with an η^2(3e)-vinyl complex, and it is interesting that a search of the Cambridge Crystallographic Data File suggests that **13** is the first member of the family of complexes [Re(η^2-alkene)L_2(η-C_5H_5)] to be structurally characterised.

Table 7 Fractional atomic coordinates (× 10^4) with e.s.d.s in parentheses for [Re(η^2-*Z*-PhCH=CHPh)(dppe)(η-C_5H_5)] **13**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re	1036.0(4)	701.6(3)	2042.5(2)	C(25)	712(6)	2948(5)	635(2)
P(1)	1591(3)	1550(2)	1360(1)	C(26)	3235(7)	1756(4)	1425(3)
P(2)	160(3)	−99(2)	1287(1)	C(27)	3950(7)	1088(4)	1275(3)
C(1)	2881(10)	86(8)	2263(4)	C(28)	5183(7)	1207(4)	1345(3)
C(2)	2823(9)	834(8)	2612(4)	C(29)	5701(7)	1993(4)	1565(3)
C(3)	1980(9)	668(8)	2932(4)	C(30)	4986(7)	2661(4)	1715(3)
C(4)	1486(10)	−173(8)	2809(4)	C(31)	3754(7)	2542(4)	1645(3)
C(5)	2025(9)	−524(7)	2407(4)	C(32)	1270(10)	990(6)	683(4)
C(6)	−201(9)	1740(7)	2215(4)	C(33)	1070(9)	3(7)	757(4)
C(7)	−848(9)	913(7)	2166(5)	C(34)	−22(7)	−1301(6)	1351(3)
C(8)	−1353(7)	442(6)	2605(3)	C(35)	336(7)	−1895(6)	988(3)
C(9)	−2371(7)	−69(6)	2428(3)	C(36)	175(7)	−2799(6)	1049(3)
C(10)	−2914(7)	−508(6)	2806(3)	C(37)	−343(7)	−3111(6)	1473(3)
C(11)	−2439(7)	−436(6)	3360(3)	C(38)	−701(7)	−2518(6)	1836(3)
C(12)	−1421(7)	76(6)	3537(3)	C(39)	−540(7)	−1613(6)	1775(3)
C(13)	−878(7)	514(6)	3159(3)	C(40)	−1330(8)	195(4)	880(3)
C(14)	−54(6)	2327(5)	2718(3)	C(41)	−2122(8)	−435(4)	611(3)
C(15)	−1082(6)	2545(5)	2913(3)	C(42)	−3160(8)	−167(4)	258(3)
C(16)	−1007(6)	3108(5)	3359(3)	C(43)	−3406(8)	730(4)	174(3)
C(17)	97(6)	3452(5)	3609(3)	C(44)	−2614(8)	1360(4)	444(3)
C(18)	1125(6)	3234(5)	3414(3)	C(45)	−1576(8)	1092(4)	796(3)
C(19)	1049(6)	2671(5)	2968(3)	C(46)	1952(21)	1494(17)	4602(9)
C(20)	1028(6)	2684(5)	1176(2)	C(47)	1959(22)	567(19)	4488(10)
C(21)	939(6)	3277(5)	1592(2)	C(48)	1430(25)	−1091(19)	4744(11)
C(22)	534(6)	4135(5)	1466(2)	C(49)	1913(28)	−62(25)	4879(14)
C(23)	218(6)	4400(5)	925(2)	C(50)	1674(35)	−1801(27)	5231(16)
C(24)	307(6)	3807(5)	509(2)	C(51)	1093(27)	−2327(20)	5013(13)



Scheme 7 L_2 = dppe. (*i*) K[$BHBu^s_3$], thf, −78 to +25 °C; (*ii*) K[$BHBu^s_3$], thf, +25 °C

Interestingly, the most convenient published[18] synthesis of the complexes [Re(η^2-alkene)$(CO)_2$(η-C_5H_5)] involves the reaction of alkynes with the heterobimetallic dihydride [$(Ph_3P)_2$HPtRe$(CO)_2$(η-C_5H_5)].

In order to understand the formation of complex **13** an EHMO study[14] was carried out on the precursor **12** using the molecular parameters established in the X-ray crystallographic study. If we make the reasonable assumption that the η^2(3e)-vinyl does not undergo an $\eta^2(3e) \longrightarrow \eta^1(1e)$ switch in its

Table 8 Selected bond distances (Å) and angles (°) for complex **13**

P(1)–Re	2.322(5)	P(2)–Re	2.309(5)
C(1)–Re	2.27(1)	C(2)–Re	2.26(1)
C(3)–Re	2.28(1)	C(4)–Re	2.31(1)
C(5)–Re	2.27(1)	C(6)–Re	2.21(1)
C(7)–Re	2.25(1)	C(20)–P(1)	1.860(9)
C(26)–P(1)	1.88(1)	C(32)–P(1)	1.87(1)
C(33)–P(2)	1.84(1)	C(34)–P(2)	1.84(1)
C(40)–P(2)	1.86(1)	C(7)–C(6)	1.45(2)
C(14)–C(6)	1.53(2)	C(8)–C(7)	1.52(2)
C(33)–C(32)	1.530(16)		
P(2)–Re–P(1)	79.8(2)	C(6)–Re–P(1)	91.4(4)
C(6)–Re–P(2)	110.0(4)	C(7)–Re–P(1)	115.2(4)
C(7)–Re–P(2)	85.1(4)	C(7)–Re–C(6)	37.8(4)
C(7)–C(6)–Re	72.7(7)	C(14)–C(6)–Re	127.1(7)
C(14)–C(6)–C(7)	123(1)	C(6)–C(7)–Re	69.5(7)
C(8)–C(7)–Re	122.6(7)	C(8)–C(7)–C(6)	127(1)

bonding mode in order to accommodate an incoming hydride anion donor, the reaction **12** ⟶ **13** can be interpreted in terms of an FMO-controlled interaction between the incoming nucleophile on the LUMO acceptor function of the η^2(3e)-vinyl ligand. Two views of this LUMO are given in Fig. 6(*a*) and 6(*b*). The first can be characterised as describing the Re=C_α π*-antibonding component with an additional contribution located on the adjacent phenyl ring, whereas the rhenium–vinyl component is emphasised in Fig. 6(*b*). It is clear that the main LUMO component is located on C_α, which would therefore be expected to be the site of nucleophilic attack. Although at first sight the presence in the LUMO of contributions on the adjacent phenyl might suggest a competitive reaction, this effect is probably overridden by the occurrence of a positive charge on the η^2(3e)-vinyl α-carbon some seven times larger than that on the adjacent phenyl ring carbons (0.23 on C_α *vs.* 0.03 on the aryl-ring carbons) [see Fig. 6(*c*)]. Thus, the overall conclusion is that 'H^-' is delivered directly to C_α. This analysis does not, however, explain why the reaction leads to selective formation of a *cis*-stilbene ligand, which is particularly interesting because examination of a space-filling model of **12** shows that there is

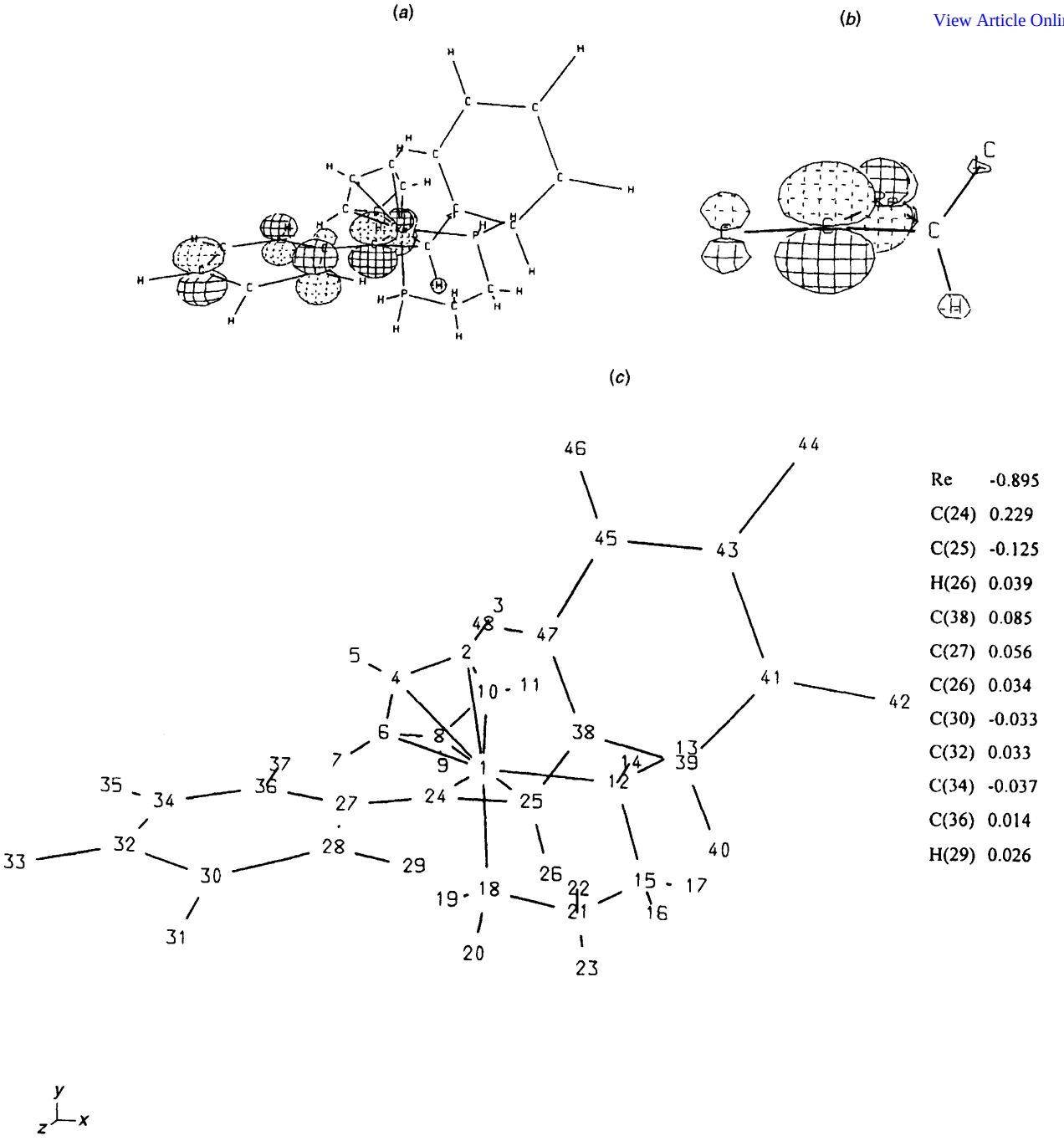


Fig. 6 The LUMO associated with the complex [Re(η^2-*Z*-PhCH=CHPh)(dppe)(η-C_5H_5)] **13** illustrating (*a*) the Re=C_α π^*-antibonding component and the contribution from the adjacent phenyl group, (*b*) the rhenium–vinyl component. The calculated relative charge distribution in the complex is shown in (*c*)

relatively free access to C_α from both faces of the rhena-η^2(3e)-vinyl. This is a similar situation to the problem discussed earlier of the selective formation of **10a** and **11a**, and it is possible that the *cis*-stilbene ligand is formed because of a 'push-pull' effect arising from the interaction of BBu^s_3 with the dppe phenyl group C(28)–C(33) depicted in Fig. 4.

An attempt to extend this study to the corresponding unsymmetrically substituted dication **9** led to the discovery of a new reaction. Treatment (−78 to +25 °C) of a thf solution of **9** with 1 equivalent of K[$BHBu^s_3$] afforded (45% yield) the expected monocationic η^2(3e)-vinyl-substituted complex **14** characterised by elemental analysis and NMR spectroscopy. The ^{13}C-{^1H} spectrum showed doublets at δ 258.1 [Re=C, *J*(CP) 19.0] and 33.3 [Re=CPh*C*HPh, *J*(CP) 12.0 Hz] similar to the corresponding signals and couplings exhibited by the monocation **12** suggesting a similar stereochemistry for **14** (Scheme 8) to that established by X-ray crystallography for **12**. However, in contrast with the reaction **12** ⟶ **13**, addition at *room temperature* of a further molecule of K[$BHBu^s_3$] did not lead to the expected delivery of 'H^-' to the α-carbon of the η^2(3e)-vinyl fragment, but to an elimination reaction, *i.e.* deprotonation and formation (70% yield) of the yellow crystalline η^2-allene-substituted rhenium d^6 complex **15** (Scheme 8) isolated by crystallisation from dichloromethane–hexane and characterised by elemental analysis, ^1H, ^{13}C-{^1H}, and ^{31}P-{^1H} NMR spectroscopy. Comparison of the NMR data with those reported by Gladysz and co-workers[19] for the cations [Re(η^2-allene)(NO)(PPh_3)(η-C_5H_5)][BF_4] showed that the rhenium in complex **15** is co-ordinated onto the substituted double bond of the η^2-allene. This is particularly significant because in all other studies of substituted mononuclear η^2-allene complexes the metal is always bonded to the

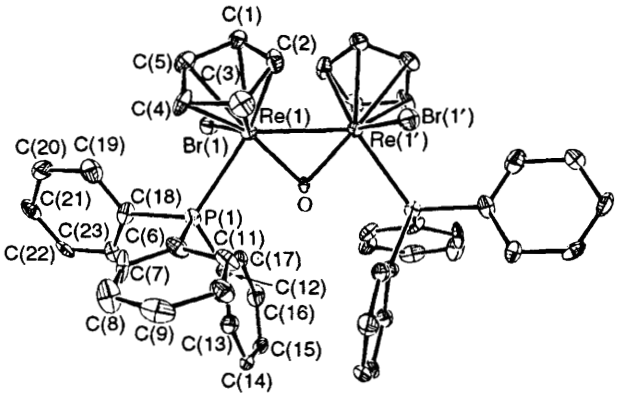
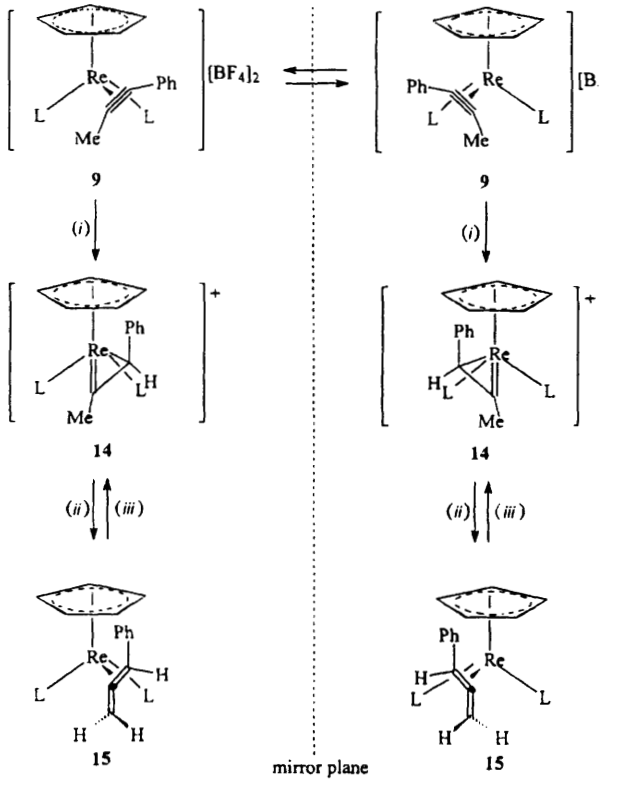


Fig. 7 Molecular structure of the dication associated with the complex $[Re_2Br_2(PPh_3)_2(\mu\text{-}O)(\eta\text{-}C_5H_5)_2][BF_4]_2$ **16**

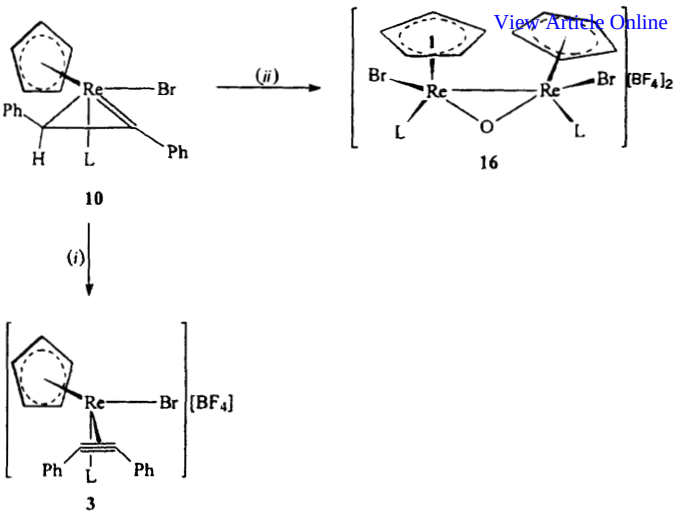


Scheme 8 L_2 = dppe. (*i*) K[BHBu$^s_3$], thf, −78 to +25 °C; (*ii*) K[BHBu$^s_3$], thf, +25 °C; (*iii*) HBF_4·Et_2O, CH_2Cl_2, −78 to +25 °C

unsubstituted double bond. The reason for this difference must be that the allene ligand present in **15** is formed within the co-ordination sphere.

As was mentioned earlier Pombeiro *et al.*[13] have reported that protonation (HBF_4·Et_2O) of the η^2-allene complex $[Re(\eta^2\text{-}CH_2{=}C{=}CHPh)Cl(dppe)_2]$ affords the cationic complex $[Re\{{=}C(CH_2Ph)CH_2\}Cl(dppe)_2][BF_4]$, and therefore it was obviously interesting to examine the protonation of **15**. Indeed, treatment (−78 °C) of the η^2-allene complex **15** with 1 equivalent of HBF_4·Et_2O led to quantitative reformation of **14** in a reaction involving the selective delivery of a proton to the end carbon of the unco-ordinated double bond of the phenylallene, *i.e.* the unsubstituted double bond.

The η^2(3e)-vinyl complexes **10** and **11** were also of interest in the context of protonation reactions, since it has been reported[20] that addition of HBF_4·Et_2O to $[W\{{=}C(Ph)CHMe\}(CO)_2\{HB(dmpz)_3\}]$ (dmpz = 3,5-dimethylpyrazolyl) resulted in delivery of a proton to C_β of the η^2(3e)-vinyl ligand and formation of the carbene complex $[W\{{=}C(Ph)CH_2Me\}(CO)_2\{HB(dmpz)_3\}][BF_4]$, stabilised by a β-C(μ-H)W agostic interaction. An EHMO study of the model system $[Re(=CHCH_2)Br(PH_3)(\eta\text{-}C_5H_5)]$ using the molecular parameters found for complex **11** and setting the hydrogens at a distance of 1.10 Å from their parent atoms gave the charge distribution Re (−0.465), C_α (0.010) and C_β (−0.22), suggesting that a charge-controlled reaction between the η^2(3e)-vinyl complex **10** and HBF_4·Et_2O might lead to initial formation of a rhenium hydride, thus providing an interesting contrast with Templeton's tungsten system.



Scheme 9 L = PPh_3. (*i*) HBF_4·Et_2O, CH_2Cl_2, +PhC_2Ph, −78 to +25 °C; (*ii*) HBF_4·Et_2O, CH_2Cl_2, −78 to +25 °C

Addition (0 to 25 °C) of HBF_4·Et_2O to a stirred solution of complex **10** afforded a green precipitate, which on crystallisation by slow diffusion of diethyl ether into a dichloromethane solution afforded a good yield (68%) of deep purple prisms of complex **16**. Elemental analysis and NMR spectroscopy (see Experimental section) suggested that the η^2-vinyl moiety CPhCHPh was not present, and therefore a single-crystal X-ray diffraction study was undertaken.

The molecular structure of complex **16** is shown in Fig. 7, the fractional coordinates and selected bond lengths and angles being listed in Tables 9 and 10, respectively. The dication is the *trans* isomer of a dinuclear species containing two rhenium centres, each of which carries a η^5-cyclopentadienyl, a bromo and a triphenylphosphine ligand. In addition there is a bridging oxygen atom. The rhenium–rhenium separation is 2.731(5) Å, which on comparison with published data for single (2.817–2.946 Å),[21] double (2.650 Å)[22] and triple [2.411(1) Å][23] rhenium–rhenium bond lengths suggests the presence within the dication **16** of a single metal–metal bond. This has the interesting consequence that in terms of simple electron-counting rules the molecule contains adjacent 16e rhenium centres.

An insight into the mode of formation of complex **16** was provided by the observation that protonation of **10** with HBF_4·Et_2O in dichloromethane solution in the presence of an excess of diphenylacetylene gave a good yield of a green powder. Examination of the NMR spectra of this material showed it to be a mixture (11:2) of **16** and the cationic alkyne complex **3** (Scheme 9). This suggested, along with the EHMO calculation discussed earlier, that the protonation of **10** involves an initial charge-controlled attack by a proton on the electron-rich rhenium centre, the resulting cationic hydrido η^2(3e)-vinyl-substituted rhenium complex then undergoing a hydrido migratory insertion reaction to form the labile alkene complex $[Re(\eta^2\text{-}E\text{-}PhCH{=}CHPh)Br(PPh_3)(\eta\text{-}C_5H_5)][BF_4]$. This could then react with diphenylacetylene to form **3**, or alternatively react with a source of O to form the sixteen-electron species $[ReO(Br)(PPh_3)(\eta\text{-}C_5H_5)][BF_4]$, which is captured by a further molecule of the *trans*-stilbene-substituted cation

Table 9 Fractional atomic coordinates ($\times 10^4$) with e.s.d.s in parentheses for $[Re_2Br_2(PPh_3)_2(\mu\text{-}O)(\eta\text{-}C_5H_5)_2][BF_4]_2$ **16**

Atom	*x*	*y*	*z*
Re(1)	4212(1)	5372(1)	1831(1)
Br(1)	4263(1)	5491(1)	238(2)
O	5000	4604(11)	2500
P(1)	3439(3)	4187(3)	1017(4)
C(1)	3975(12)	6645(13)	1919(17)
C(2)	4181(13)	6304(13)	2816(16)
C(3)	3584(14)	5739(14)	2633(18)
C(4)	2995(13)	5781(14)	1576(16)
C(5)	3262(13)	6348(13)	1192(16)
C(6)	2849(14)	3865(12)	1552(15)
C(7)	2076(12)	3663(15)	1023(15)
C(8)	1656(15)	3385(16)	1466(16)
C(9)	2022(15)	3261(13)	2462(20)
C(10)	2849(13)	3443(12)	3072(16)
C(11)	3235(14)	3735(12)	2598(16)
C(12)	4050(13)	3378(12)	1112(14)
C(13)	3940(13)	2639(12)	1405(14)
C(14)	4350(12)	1998(12)	1336(14)
C(15)	4882(12)	2096(12)	999(14)
C(16)	4988(13)	2809(13)	697(16)
C(17)	4593(11)	3440(12)	765(15)
C(18)	2735(12)	4232(13)	−327(14)
C(19)	2253(14)	4867(15)	−718(17)
C(20)	1715(16)	4888(14)	−1759(17)
C(21)	1691(15)	4274(14)	−2367(16)
C(22)	2171(12)	3653(12)	−1960(16)
C(23)	2704(12)	3628(13)	−942(14)
B(1)	866(11)	6438(11)	−629(13)
F(1)	322(14)	7020(16)	−1028(20)
F(2)	1421(14)	6532(18)	−917(20)
F(3)	1219(19)	6462(25)	394(13)
F(4)	500(21)	5737(14)	−964(33)

Table 10 Selected bond distances (Å) and angles (°) for complex **16**

Re(1)–Re(1′)	2.731(5)	Re(1)–Br(1)	2.500(5)
Re(1)–P(1)	2.478(7)	Re(1)–O	1.90(2)
Re(1)–C(1)	2.26(2)	Re(1)–C(2)	2.22(2)
Re(1)–C(3)	2.21(2)	Re(1)–C(4)	2.32(2)
Re(1)–C(5)	2.33(2)	P(1)–C(6)	1.80(2)
P(1)–C(12)	1.79(2)	P(1)–C(18)	1.82(2)
Re(1)–O–Re(1′)	91.9(9)	O–Re(1)–Re(1′)	44.0(3)
Br(1)–Re(1)–Re(1′)	99.22(7)	P(1)–Re(1)–Re(1′)	124.0(2)
Br(1)–Re(1)–O	99.9(2)	Br(1)–Re(1)–P(1)	83.3(2)
P(1)–Re(1)–O	80.2(5)		

resulting in the formation of the dirhenium μ-O complex **16**. The exact source of the oxygen is at present unknown, however the most likely origin would be the diethyl ether present or traces of water.

Experimental

All reactions were carried out under an atmosphere of dry, oxygen-free dinitrogen, using standard Schlenk techniques. Solvents were freshly distilled over an appropriate drying agent and futher degassed before use where necessary. Column chromatography was performed using BDH alumina, Brockmann activity II. The ^1H, $^{13}C\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$ NMR spectra were recorded on JEOL GX 270 and EX 400 spectrometers. Data are given for room-temperature measurements unless otherwise stated. Chemical shifts are referenced relative to tetramethylsilane and external H_3PO_4. The IR spectra were recorded on a Nicolet 510 P FT-IR spectrometer.

Preparations

$[ReBr_2(\eta^2\text{-}PhC_2Ph)(\eta\text{-}C_5H_5)]$ 1. A solution of a mixture of *cis*- and *trans*-$[ReBr_2(CO)_2(\eta\text{-}C_5H_5)]$ (1.00 g, 2.14 mmol) and diphenylacetylene (1.91 g, 10.7 mmol) in toluene (90 cm^3) was heated under reflux. To monitor the progress of the reaction aliquots of the mixture were examined by IR spectroscopy at 30 min intervals. When the terminal carbonyl absorption bands corresponding to the *trans* isomer were no longer visible (8 h) the reaction mixture was allowed to cool to room temperature. The volatile material was removed *in vacuo* and the residue washed with hexane (10 × 30 cm^3). Recrystallisation from CH_2Cl_2–hexane afforded red *crystals* of complex **1** (0.98 g, 78%) (Found: C, 38.8; H, 2.3. $C_{19}H_{15}Br_2Re$ requires C, 38.7; H, 2.6%). NMR ($CDCl_3$): ^1H, δ 8.10–7.5 (m, 10 H, Ph) and 5.91 (s, 5 H, C_5H_5); $^{13}C\text{-}\{^1H\}$, δ 219.2 (Ph*C*≡CPh), 137.7, 132.6, 131.1, 129.9 (Ph), and 95.7 (C_5H_5).

$[ReBr_2(\eta^2\text{-}MeC_2Ph)(\eta\text{-}C_5H_5)]$ 2. In a similar way, reaction of *cis*- and *trans*-$[ReBr_2(CO)_2(\eta\text{-}C_5H_5)]$ (1.00 g, 2.14 mmol) and 1-phenylprop-1-yne (0.50 g, 4.3 mmol) in toluene (90 cm^3) afforded on recrystallisation from CH_2Cl_2–hexane brown *crystals* of complex **2** (0.85 g, 75%) (Found: C, 31.8; H, 2.4. $C_{14}H_{13}Br_2Re$ requires C, 31.9; H. 2.5%). NMR (CD_2Cl_2); ^1H, δ 7.91–7.65 (m, 5 H, Ph), 5.90 (s, 5 H, C_5H_5) and 4.13 (s, 3 H, Me); $^{13}C\text{-}\{^1H\}$, δ 229.8 (*C*≡C), 209.2 (*C*≡C), 137.2, 133.2, 131.6, 130.0 (Ph), 96.5 (C_5H_5), and 22.9 (Me).

$[ReBr(\eta^2\text{-}PhC_2Ph)(PPh_3)(\eta\text{-}C_5H_5)][BF_4]$ 3. Triphenylphosphine (0.10 g, 0.36 mmol) was added to a stirred (room temperature) solution of complex **1** (0.18 g, 0.31 mmol) in dichloromethane (20 cm^3). There was an immediate change from red to green. The addition of $AgBF_4$ (0.06 g, 0.30 mmol) to the green solution followed by stirring for 1 h resulted in the precipitation of AgBr and a gradual lightening in colour. The reaction mixture was filtered through Celite and the volume of the solvent reduced (5 cm^3) *in vacuo*. Addition of diethyl ether (40 cm^3) gave a fine green solid, which was washed with hexane (5 × 20 cm^3) and recrystallised from CH_2Cl_2–diethyl ether to give pale green *crystals* of complex **3** (0.2 g, 77%) (Found: C, 51.5; H, 3.4. $C_{37}H_{30}BBrF_4PRe$ requires C, 51.8; H, 3.5%). NMR ($CDCl_3$): ^1H, δ 7.64–7.23 (m, 10 H, Ph) and 5.98 (s, 5 H, C_5H_5); $^{13}C\text{-}\{^1H\}$, δ 224.4 (Ph*C*≡C), 136.6–129.1 (Ph) and 97.4 (C_5H_5); $^{31}P\text{-}\{^1H\}$, δ 0.15 (PPh_3).

$[ReBr(\eta^2\text{-}PhC_2Ph)(PMePh_2)(\eta\text{-}C_5H_5)][PF_6]$ 4. A similar reaction with complex **1** (0.18 g, 0.31 mmol), methyldiphenylphosphine (0.06 g, 0.31 mmol) and $TlPF_6$ (0.11 g, 0.31 mmol) in dichloromethane (20 cm^3) afforded on recrystallisation from CH_2Cl_2–diethyl ether bright green *crystals* of complex **4** (0.25 g, 80%) (Found: C, 44.3; H, 3.1. $C_{32}H_{28}BrF_6PRe$ requires C, 45.0; H, 3.3%). NMR: ^1H (CD_2Cl_2), δ 7.66–7.15 (m, 20 H, Ph), 5.88 (s, 5 H, C_5H_5) and 2.37 [d, 3 H, MeP, *J*(HP) 11.0]; $^{13}C\text{-}\{^1H\}$ (CD_2Cl_2), δ 223.9 [d, Ph*C*≡C, *J*(CP) 3.0], 136.7–129.3 (Ph), 97.3 (C_5H_5) and 18.5 [d, MeP, *J*(CP) 43.0 Hz]; $^{31}P\text{-}\{^1H\}$ [$(CD_3)_2CO$], δ −15.86 ($PMePh_2$).

$[ReBr(\eta^2\text{-}PhC_2Ph)\{P(OMe)_3\}(\eta\text{-}C_5H_5)][PF_6]$ 5. Similarly, reaction of complex **1** (0.18 g, 0.31 mmol), $P(OMe)_3$ (0.04 g, 0.31 mmol) and $TlPF_6$ (0.11 g, 0.31 mmol) in dichloromethane (20 cm^3) afforded on recrystallisation from CH_2Cl_2–diethyl ether dark green *crystals* of complex **5** (0.23 g, 77%) (Found: C, 33.4; H, 2.5. $C_{22}H_{24}BrF_6O_3P_2Re$ requires C 33.9; H, 3.0%). NMR: ^1H (CD_2Cl_2), δ 8.10–7.05 (m, 10 H, Ph), 6.01 (s, 5 H, C_5H_5) and 3.80 [d, 9 H, POMe, *J*(HP) 11.0]; $^{13}C\text{-}\{^1H\}$ (CD_2Cl_2), δ 214.9 [d, Ph*C*≡CPh, *J*(CP) 10.0], 137.5–127.0 (Ph), 95.9 (C_5H_5) and 56.7 [d, POMe, *J*(CP) 9.0 Hz]; $^{31}P\text{-}\{^1H\}$ [$(CD_3)_2CO$], δ 85.9 (POMe).

$[ReBr(\eta^2\text{-}MeC_2Ph)(PPh_3)(\eta\text{-}C_5H_5)][PF_6]$ 6. Reaction of complex **2** (0.15 g, 0.43 mmol), PPh_3 (0.12 g, 0.46 mmol) and $TlPF_6$ (0.16 g, 0.46 mmol) in dichloromethane (20 cm^3) gave on recrystallisation from CH_2Cl_2–diethyl ether dark green *crystals* of complex **6** (0.25 g, 68%) (Found: C, 44.9; H, 3.3.

$C_{32}H_{28}BrF_6P_2Re$ requires C, 45.0; H, 3.3%). NMR (CD_2Cl_2): ^1H, δ 7.97–7.4 (m, 20 H, Ph), 5.68 (s, 5 H, C_5H_5) and 3.20 (s, 3 H, Me); ^{13}C-{^1H}, δ 218.1 (*C*≡C), 214.4 [d, C≡*C*, *J*(CP) 6.6], 135.1–129.6 (Ph), 96.8 (C_5H_5) and 24.7 [d, Me, *J*(CP) 4.4 Hz]; ^{31}P-{^1H}, δ 9.87 (PPh_3).

[ReBr(NCMe)(η²-PhC₂Ph)(η-C₅H₅)][BF₄] 7. A solution of $AgBF_4$ (0.05 g, 0.27 mmol) in MeCN (10 cm^3) was added dropwise with stirring to a solution of complex **1** (0.16 g, 0.27 mmol) in MeCN (10 cm^3). After 1 h the precipitated AgBr was filtered off through Celite. Addition of diethyl ether (10 cm^3) afforded a green powder which on recrystallisation from MeCN–Et_2O (1:1) gave green *crystals* of complex **7** (0.04 g, 25%) (Found: C, 39.0; H, 2.4. $C_{21}H_{18}BBrF_4NRe$ requires C, 39.6; H, 2.8%), ν(NCMe) 2339 cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 7.78–7.71 (m, 10 H, Ph), 6.2 (s, 5 H, C_5H_5) and 3.14 (s, 3 H, Me); ^{13}C-{^1H} δ 218.0 (Ph*C*≡CPh), 136.5 (N*C*Me), 133.1–129.5 (Ph), 96.9 (C_5H_5) and 5.18 (NC*Me*).

[Re(η²-PhC₂Ph)(dppe)(η-C₅H₅)][BF₄]₂ 8. A solution of complex **1** (0.16 g, 0.27 mmol) and 1,2-bis(diphenylphosphino)ethane (dppe) (0.11 g, 0.27 mmol) in dichloromethane (30 cm^3) was added to 2 equivalents of $AgBF_4$ (0.11 g, 0.54 mmol). The reaction mixture was stirred for 1 h at room temperature and the resulting deep red solution was filtered through Celite to remove the precipitated AgBr. Reduction (2 cm^3) of the volume of the solvent *in vacuo* followed by addition of diethyl ether gave a red-brown solid. This was washed with hexane (5 × 20 cm^3) and then recrystallised from CH_2Cl_2–diethyl ether to give dark red *crystals* of complex **8** (0.17 g, 62%) (Found: C, 53.8; H, 3.6. $C_{45}H_{39}B_2F_8P_2Re$ requires C, 54.0; H, 3.9%). NMR (CD_2Cl_2): ^1H, δ 7.64–7.14 (m, 30 H, Ph), 5.86 (s, 5 H, C_5H_5) and 3.78–3.47 (m, 4 H, PCH_2CH_2P); ^{13}C-{^1H}, δ 218.8 [t, Ph*C*≡C, *J*(CP) 5.0], 137.5–129.7 (Ph), 99.4 (C_5H_5) and 29.8 [d, PCH_2CH_2P, *J*(CP) 5.0 Hz]; ^{31}P-{^1H}, δ 30.3 (PCH_2CH_2P).

[Re(η²-MeC₂Ph)(dppe)(η-C₅H₅)][BF₄]₂ 9. A similar reaction between complex **2** (0.15 g, 0.43 mmol), dppe (0.18 g, 0.45 mmol) and $AgBF_4$ (0.17 g, 0.87 mmol) in dichloromethane (30 cm^3) gave on recrystallisation from CH_2Cl_2–diethyl ether red *crystals* of complex **9** (0.29 g, 71%) (Found: C, 51.3; H, 3.8. $C_{40}H_{37}B_2F_8P_2Re$ requires C, 51.1; H, 4.0%). NMR (CD_3CN): ^1H, δ 8.08 7.35 (m, 25 H, Ph), 5.93 (s, 5 H, C_5H_5), 3.81–3.68 (m, 4 H, PCH_2CH_2P) and 1.73 (s, 3 H, Me); ^{13}C-{^1H}, δ 222.5 [t, *C*≡C, *J*(CP) 11.0], 212.9 (*C*≡C), 136.8–130.4 (Ph), 99.7 (C_5H_5), 29.3 [d, P*C*H_2*C*H_2P, *J*(CP) 37.0 Hz] and 24.7 (Me); ^{31}P-{^1H}, δ 26.6 (PCH_2CH_2P).

[Re{≡C(Ph)CHPh}Br(PPh₃)(η-C₅H₅)] 10. A solution of K[BHBu$^s_3$] (140 μl, 0.14 mmol, 1.0 mol dm^{-3} in thf) was added dropwise to a stirred solution of complex **3** (0.10 g, 0.14 mmol) in dichloromethane (20 cm^3) at −78 °C. A complete change from light green through dark red to dark green occurred over 7 min. There was no further change in colour on warming to room temperature. After 1 h the solvent was removed *in vacuo* and the residue extracted with hexane. Column chromatography of the extract gave on elution with hexane one green band, which was collected and recrystallised from thf–hexane to give dark green *crystals* of complex **10** (0.08 g, 70%) (Found: C, 57.1; H, 4.2. $C_{37}H_{31}BrPRe$ requires C, 57.5; H, 4.1%). NMR (CD_2Cl_2): ^1H, δ 8.18–6.87 (m, 25 H, Ph), 4.67 (s, 5 H, C_5H_5), and 3.48 [d, 1 H, ReC*H*(Ph), *J*(HP) 15.4]; ^{13}C-{^1H}, δ 258.3 [Re=*C*(Ph)], 152.4–123.5 (Ph), 90.8 (C_5H_5) and 15.5 [d, ReCH(Ph), *J*(CP) 2.0 Hz]; ^{31}P-{^1H}, δ 19.4 (PPh_3).

[Re{≡C(Ph)CHPh}Br(PMePh₂)(η-C₅H₅)] 11. A similar reaction between K[BHBu$^s_3$] (140 μl, 0.14 mmol, 1.0 mol dm^{-3} in thf) and complex **4** (0.11 g, 0.14 mmol) in CH_2Cl_2 (20 cm^3) gave on work-up and recrystallisation from thf–hexane green *crystals* of complex **11** (0.07 g, 68%) (Found: C, 54.5; H, 4.7. $C_{32}H_{29}BrPRe$ requires C, 54.2; H, 4.2%). NMR: ^1H (CD_2Cl_2), δ 8.182–6.60 (m, 20 H, Ph), 4.71 (s, 5 H, C_5H_5), 3.43 [d, 1 H, ReC*H*(Ph), *J*(HP) 14.0] and 2.04 [d, 3 H, PMe, *J*(HP) 10.0]; ^{13}C-{^1H} (CD_2Cl_2), δ 253.6 (Re=C), 152.6–121.0 (Ph), 90.9 (C_5H_5), 17.7 [d, PMe, *J*(CP) 36.0 Hz] and 16.7 [ReCH(Ph)]; ^{31}P-{^1H} ($CDCl_3$), δ 17.5 ($PMePh_2$).

[Re{≡C(Ph)CHPh}(dppe)(η-C₅H₅)][BF₄] 12. A suspension of complex **8** (0.08 g, 0.08 mmol) in vigorously dried and degassed thf (20 cm^3) was cooled to −78 °C. Addition of K[BHBu$^s_3$] (80 μl, 0.08 mmol, 1.0 mol dm^{-3} in thf) resulted in a gradual change from red to green. The reaction mixture was allowed to warm to room temperature and stirred for 40 min, after which it was filtered through Celite and the volume of solvent then reduced *in vacuo* to 5 cm^3. Addition of hexane precipitated a green solid which was washed with pentane (5 × 20 cm^3) and then recrystallised (0 °C) from thf–hexane to give dark green *crystals* of complex **12** (0.04 g, 57%) (Found: C, 58.7; H, 4.0. $C_{45}H_{40}BF_4P_2Re$ requires C, 59.0; H, 4.4%). NMR (CD_2Cl_2): ^1H, δ 7.66–6.05 (m, 30 H, Ph), 5.54 (s, 5 H, C_5H_5), 3.16 [d, 1 H, ReC*H*(Ph), *J*(HP) 11.0] and 3.10–2.85 (m, 4 H, PCH_2CH_2P); ^{13}C-{^1H}, δ 260.9 [d, Re=*C*(Ph), *J*(CP) 10.0], 146.6–125.0 (Ph), 90.9 (C_5H_5), 32.2 [dd, P*C*H_2*C*H_2P, *J*(CP) 37.1], 29.0 [dd, PCH_2*C*H_2P, *J*(CP) 34.1] and 25.2 [d, ReCH(Ph), *J*(CP) 12.0, *J*(CH) 164.0 Hz]; ^{31}P-{^1H}, δ 47.65 (*P*CH_2CH_2P) and 36.55 (PCH_2CH_2*P*).

[Re(η²-*Z*-PhCH=CHPh)(dppe)(η-C₅H₅)] 13. A solution of K[BHBu$^s_3$] (109 μl, 0.10 mmol, 1.0 mol dm^{-3} in thf) was added dropwise to a stirred solution of complex **12** (0.10 g, 0.10 mmol) in thf (10 cm^3). The mixture changed from green to yellow-brown. After 30 min the solvent was removed *in vacuo* and the residue dissolved in CH_2Cl_2–hexane (1:4, 5 cm^3). Chromatography on an alumina-packed column using the same solvent mixture as eluent afforded a single yellow band which was collected. Removal of the solvent *in vacuo* followed by recrystallisation (−30 °C) from CH_2Cl_2–hexane (1:4) gave yellow *crystals* of complex **13** (0.04 g, 40%) (Found: C, 65.0; H, 5.1. $C_{45}H_{41}P_2Re$ requires C, 65.1; H, 5.0%). NMR (CD_2Cl_2): ^1H, δ 7.53–6.69 (m, 30 H, Ph), 4.02 (s, 5 H, C_5H_5), 3.00 [br d, 2 H, *CH*PhC*H*Ph, *J*(HP) 14.0] and 2.36 [br d, 4 H, PCH_2CH_2P, *J*(HP) 16.0 Hz]; ^{13}C-{^1H}, δ 151.0–122.7 (Ph), 84.1 (C_5H_5), 33.2 (*C*HPh*C*HPh) and 32.8–32.1 (m, PCH_2CH_2P); ^{31}P-{^1H}, δ 52.9 (*P*CH_2CH_2*P*).

[Re{≡C(Me)CHPh}(dppe)(η-C₅H₅)][BF₄] 14. The reaction was carried out by the procedure described for complex **11**. Treatment of a thf (20 cm^3) suspension of **9** (0.20 g, 0.21 mmol) with K[BHBu$^s_3$] (211 μl, 0.21 mmol, 1.0 mol dm^{-3} in thf) at −78 °C yielded a bright green solution. On warming to room temperature the solution became dark yellow. Work-up afforded yellow-brown *crystals* of complex **14** (0.08 g, 45%) (Found: C, 56.5; H, 4.5. $C_{40}H_{38}BF_4P_2Re$ requires C, 56.3; H, 4.5%). NMR (CD_2Cl_2): ^1H, δ 7.05–6.55 (m, 25 H, Ph), 4.75 [d, 5 H, C_5H_5, *J*(HP) 1.0], 3.35–3.30 [m, 1 H, ReC*H*(Ph)], 2.99–2.85 (m, 4 H, PCH_2CH_2P), 1.47 [t, 3 H, MeC, *J*(HP) 1.0]; ^{13}C-{^1H}, δ 258.1 [d, Re=C, *J*(CP) 19.0]. 149.2–122.4 (Ph), 90.3 (C_5H_5), 39.9 [dd, P*C*H_2CH$_2$P, *J*(CP) 38.8], 33.3 [d, ReCH(Ph), *J*(CP) 12.0], 29.3 [dd, PCH_2*C*H_2P, *J*(CP) 34.7] and 20.4 (Me); ^{31}P-{^1H}, δ 50.6 [d, *P*CH_2CH_2P, *J*(PP) 18.0] and 39.4 [d, PCH_2CH_2*P*, *J*(PP) 18.0 Hz].

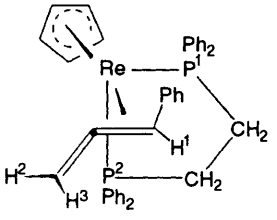
[Re{η²-CH(Ph)=C=CH₂}(dppe)(η-C₅H₅)] 15. Addition (room temperature) of K[BHBu$^s_3$] (180 μl, 0.18 mmol. 1.0 mol dm^{-3} in thf) to a stirred suspension of complex **14** (0.15 g, 0.18 mmol) in thf (20 cm^3) afforded a yellow-brown solution. The mixture was stirred overnight and then the solvent was removed *in vacuo*. The residue was extracted into CH_2Cl_2–hexane (1:4) and filtered through Celite. Removal of the solvent *in vacuo*

Table 11 Crystallographic data for compounds **4**, **11**–**13** and **16***

Complex	**4**	**11**	**12**	**13**	**16**
Empirical formula	$C_{32}H_{28}BrF_6PRe$	$C_{32}H_{29}BrPRe$	$C_{45}H_{40}BF_4P_2Re$	$C_{45}H_{41}P_2Re{\cdot}C_6H_{14}$	$C_{46}H_{40}B_2Br_2F_8OP_2Re_2$
M	854.62	710.7	915.8	916.1	1376.6
Crystal dimensions/mm	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.15	0.20 × 0.20 × 0.15	0.30 × 0.30 × 0.10	0.20 × 0.20 × 0.20
Space group	$P2_1/n$ (no.14)	$P2_1/a$ (no.14)	$P2_1/n$ (no.14)	$P2_1/n$ (no.14)	$C2/c$ (no.15)
a/Å	13.179(2)	17.469(3)	11.032(3)	11.048(1)	19.528(5)
b/Å	16.547(3)	17.473(2)	31.027(7)	15.145(2)	17.211(3)
c/Å	14.745(2)	11.065(1)	12.381(3)	25.068(8)	15.323(3)
β/°	107.97(2)	(γ) 112.84(1)	116.56(2)	101.09(1)	119.52(2)
U/Å^3	3058.6	3112.3	3790.7	4250.2	4481.5
D_c/g cm^{-3}	1.85	1.51	1.61	1.43	2.04
F(000)	1656	1384	1824	1864	2624
μ(Mo-Kα)/cm^{-1}	52.1	50.8	31.70	28.5	70.8
2θ range/°	4–44	4–44	4–48	4–48	4–48
No. data collected	4123	4194	6410	7318	3767
No. unique data and n in $I \geqslant n\sigma(I)$	2397, 3	2298, 3	3290, 2	3418, 2	2177, 2
R	0.0729	0.0658	0.0398	0.0491	0.0628
R'	0.0729	0.0638	0.0324	0.0352	0.0581
Maximum, minimum absorption corrections	1.352, 0.798	1.417, 0.809	1.113, 0.867	1.072, 0.852	1.079, 0.633
Maximum, minimum residual electron density/e Å^{-3}	1.00, −2.28	0.51, −0.58	0.31, −0.22	0.34, −0.38	1.43, −0.71

* Details in common: λ(Mo-Kα) 0.710 69 Å; monoclinic; $Z = 4$; $R = \Sigma|\Delta|/\Sigma|F_o|$; $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$, $\Delta = F_o - F_c$.

afforded yellow *crystals* of complex **15** (0.10 g, 70%) (Found: C, 62.5; H, 4.7. $C_{40}H_{37}P_2Re$ requires C, 62.7; H. 4.9%). NMR (CD_2Cl_2): ^1H, δ 5.52 [ddd, 1 H, H^3, $J(H^3P^1)$ 2.0, $J(H^2H^3)$ 2.0, $J(H^1H^3)$ 2.0], 4.48 (s, 5 H, C_5H_5), 4.15 [ddd, 1 H, H^2, $J(H^2P^2)$ 2.0, $J(H^2H^3)$ 2.0, $J(H^1H^2)$ 2.0], 2.29–2.62 (m, 4 H, PCH_2CH_2P) and 1.86 [dddd, 1 H, H^1, $J(H^1P^1)$ 14.0, $J(H^1P^2)$ 2.0, $J(H^2H^1)$ 2.0, $J(H^1H^3)$ 2.0]; ^{13}C-{^1H}, δ 162.0 [d, =C=, J(CP) 16.0], 152.0–121.0 (Ph), 104.2 [d, C=CH_2, J(CP) 8.0 Hz], 83.3 (C_5H_5), 29.9, 29.5 (m, PCH_2PCH_2) and 9.3 (C=*C*HPh); ^{31}P-{^1H}, δ 61.7 (br s) and 57.8 (br s).



Protonations

[Re{η²-CH(Ph)=C=CH₂}(dppe)(η-C₅H₅)] 15. Addition of HBF_4·Et_2O (17 μl, 0.10 mmol) to a stirred and cooled solution of complex **15** (0.08 g, 0.10 mmol) in CH_2Cl_2 (5 cm^3) resulted in a darkening of the reaction mixture. Warming to room temperature and addition of diethyl ether (5 cm^3) afforded a quantitative yield of **14** as identified by NMR spectroscopy.

[Re{=C(Ph)CHPh}Br(PPh₃)(η-C₅H₅)] 10. Compound **10** (0.10 g, 0.13 mmol) was disolved in Et_2O (20 cm^3) and the resulting green solution was cooled to 0 °C. The acid HBF_4·Et_2O (34 μl, 0.196 mmol) was added and the solution was rapidly stirred while warming to room temperature and then for 20 h. The resulting pale green supernatant was removed *via* cannula and the residue washed with diethyl ether (2 × 10 cm^3) and dried *in vacuo* to give green *microcrystals* of $[Re_2Br_2(PPh_3)_2(\mu\text{-}O)(\eta\text{-}C_5H_5)_2][BF_4]_2$ **16** (0.06 g, 68%) (crystals suitable for X-ray diffraction study were grown as deep purple prisms by slow diffusion of diethyl ether into a CH_2Cl_2 solution of the complex at −20 °C) (Found: C, 40.2; H, 3.0. $C_{46}H_{40}B_2Br_2F_8OP_2Re_2$ requires C, 40.1; H, 2.9%). NMR (CD_2Cl_2): ^1H, δ 8.30–6.30 (m, 30 H, Ph) and 6.27 (s, 10 H, C_5H_5); ^{13}C-{^1H}, δ 137.3–123.8 (Ph) and 102.2 (C_5H_5); ^{31}P-{^1H}, δ −0.03 (PPh_3).

In the presence of diphenylacetylene. A solution of complex **10** (0.09 g, 0.12 mmol) in CH_2Cl_2 (10 cm^3) held at −78 °C was treated with PhC_2Ph (0.03 g, 0.17 mmol) followed immediately by HBF_4·Et_2O (25 μl, 0.14 mmol) and then allowed to warm to room temperature. The solution changed from green to brown immediately after addition of the acid and then gradually turned green. After warming to room temperature the reaction mixture was stirred for 2 h, after which the volume of the solvent was reduced *in vacuo* to *ca.* 5 cm^3 and Et_2O (20 cm^3) was added to give a green precipitate which was collected, washed with Et_2O (2 × 10 cm^3) and dried *in vacuo* to give a green powder (0.08 g). Examination of the NMR spectral data of this material showed it to be a mixture (11 : 2) of **3** and **16**.

Crystal structure determinations

Many of the details of the structure analyses carried out on compounds **4**, **11**–**13**, and **16** are listed in Table 11. Data collections were carried out on Hilger and Watts (**4** and **11**) and CAD4 (**12**, **13** and **16**) automated diffractometers at 293(2) K, except for **16** which was at 170(2) K. Corrections for Lorentz, polarisation and X-ray absorption effects were applied, the latter by an empirical method using DIFABS.[24] The structures were solved by Patterson methods and refined using the SHELX suite of programs.[25,26] Crystals of **4** were qualitatively deficient and consequently only the rhenium, bromine, phosphorus and fluorine atoms were allowed to refine anisotropically. All other atoms were treated isotropically with the phenyl groups constrained to regular hexagons. Refinement with unit weights gave satisfactory convergence. For **11** all non-hydrogen atoms were allowed to vibrate anisotropically with the phenyl groups constrained to regular hexagons. A weighting scheme $w = 2.185[\sigma^2(F) + 0.000\,823(F)^2]^{-1}$ gave satisfactory convergence. Similarly, all non-hydrogen atoms of **12** were refined anisotropically with $w = 2.8285[\sigma^2(F) + 0.000\,059(F)^2]^{-1}$. The hydrogen atom on C(7) was located in the penultimate Fourier-difference synthesis and refined at a fixed distance (0.96 Å) from the parent atom. With the exception of the carbon atoms of the hexane solvent of crystallisation, all non-hydrogen atoms of **13** were anisotropically refined, with $w = 2.2818[\sigma^2(F) + 0.000\,121(F)]^{-1}$. The hydrogen atoms associated with C(6) and C(7) were located in an advanced Fourier-difference synthesis and positionally refined. Very heavy smearing of the electron density in the solvent molecule, particularly in the region of C(49) and C(50), did not approximate to a model which could be readily refined and consequently hydrogen atoms were not included in the solvent molecule. For **16** the asymmetric unit consists of one half of a dimer molecule with the bridging oxygen atom situated on a two-fold axis. The remaining portion was generated by the operator $1 - x$, y, $0.5 - z$. All non-hydrogen atoms except boron and fluorine were refined anisotropically with $w = 3.0213[\sigma^2(F) + 0.000\,597(F)^2]^{-1}$. Severe disorder in the $[BF_4]^-$ anion, which could not be readily modelled, precluded a clean refinement in this region of the map and the most satisfactory results were obtained by fixing the B–F distances. For all the structures, hydrogen atoms were included at geometrically calculated positions and allowed to ride on the parent atom with fixed isotropic thermal parameters, unless otherwise stated.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Extended-Hückel molecular orbital calculations

Extended-Hückel MO calculations were performed using the CACAO2 program package of Mealli and Prosierpio.[14]

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