The Formation and Structural Characterisation of the *transoid*-η^4(5e)-Butadienyl Ligand; Evidence for a 'Bent' Rhenium–Carbon Bond

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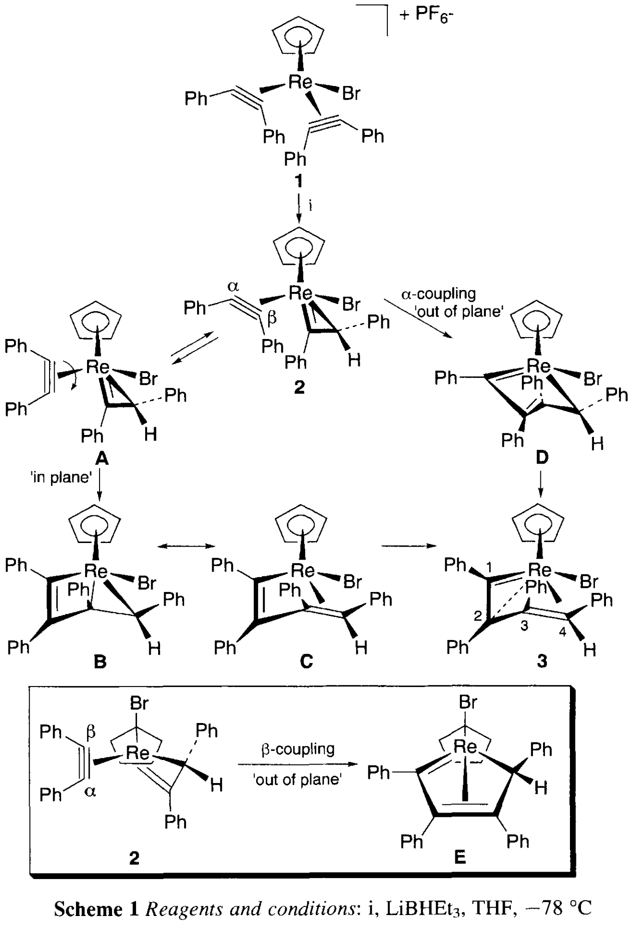
Treatment of $[ReBr(\eta^2\text{-}PhC_2Ph)_2(\eta\text{-}C_5H_5)][PF_6]$ with $Li[BHEt_3]$ in THF affords the η^2(3e)-vinyl/η^2(2e)-alkyne complex $[BrRe\{=C(Ph)C(H)Ph\}(\eta^2\text{-}PhC_2Ph)(\eta\text{-}C_5H_5)]$ and the *transoid*-η^4(5e)-butadienyl complex $[BrRe\{=C(Ph)\text{-}\eta^3\text{-}C(Ph)C(Ph)C(H)Ph\}(\eta\text{-}C_5H_5)]$, the latter containing a metal to carbon double bond and a novel 'bent' rhenium to carbon bond.

The availability of a vacant coordination site is recognised as an essential requirement for both the stoichiometric and catalytic molecular transformation of organic molecules at a transition metal centre. One of the interesting developments of recent years has been the realisation that vinyl,[1] prop-2-ynyl[2] and butadienyl[3–9] ligands are able to undergo reversible changes in their bonding modes [vinyl: η^1(1e) $\rightleftharpoons$ η^2(3e); prop-2-ynyl: η^1(1e) $\rightleftharpoons$ σ, η^2(3e); butadienyl: η^2(3e) $\rightleftharpoons$ η^4(5e)] thus providing the potential for the temporary masking of a vacant coordination site, and hence stabilisation of reactive metal centres. In the case of the η^4(5e)-butadienyl system a *cisoid* bonding arrangement for the C_4 ligand is now well established,[3,5,7,9] however, in developing the chemistry of η^2(4e)-bonded alkyne d^4-rhenium complexes we have discovered that this ligand can also adopt an unusual *transoid* bonding mode, which incorporates a'bent' rhenium to carbon bond.

We have recently shown[10] that the η^2(4e)-donor alkyne complex $[ReBr_2(\eta^2\text{-}PhC_2Ph)(\eta\text{-}C_5H_5)]$ can be readily prepared by refluxing a solution of *cis/trans*- $[ReBr_2(CO)_2(\eta\text{-}C_5H_5)]$ and *diphenylacetylene* in toluene. We have now found that treatment (room temp. 48 h) of this compound with $TlPF_6$ and an excess of PhC_2Ph in dichloromethane affords (75% yield) the bis-alkyne substituted monocation $[ReBr(\eta^2\text{-}PhC_2Ph)_2(\eta\text{-}C_5H_5)][PF_6]$ **1**.† The availability of this potentially reactive molecule suggested that we should examine its reactivity towards a hydride anion donor source in the expectation of forming either a η^2(3e)-vinyl/η^2(2e)-alkyne complex or a η^4(5e)-butadienyl complex; the C_4 chain being assembled by linking[9] of the η^2-vinyl and alkyne ligands.



Scheme 1 *Reagents and conditions*: i, $LiBHEt_3$, THF, −78 °C

Addition (−78 → +25 °C) of 1 equiv. of $Li[BHEt_3]$ to a stirred solution of **1** in THF led to a change in colour from red to green. After 5 h at room temperature, column chromatography (silica) of the reaction mixture afforded two isomeric complexes, which were isolated as orange **2** (5% yield) and green **3** (60% yield) crystalline materials. The NMR spectrum† of **2** showed resonances [δ 215.5 (Re=C), 21.8 (CHPh)] consistent with the η^2(3e)-vinyl/η^2(2e)-alkyne substituted structure illustrated in Scheme 1, but attempts to obtain crystals suitable for X-ray crystallography resulted in isomerisation to the green isomer **3** and decomposition. The ^{13}C NMR spectrum† of the major product **3** also showed a low field resonance (δ 234.9) characteristic of a rhenium alkylidene carbon, however, in this case crystals suitable for a single crystal X-ray diffraction study‡ were obtained.

As is shown in Fig. 1, the green complex **3** contains a $ReBr(\eta\text{-}C_5H_5)$ fragment bonded to a C_4 butadienyl ligand [C(6)–C(7)–C(8)–C(9)], but instead of the familiar *cisoid*- arrangement, this molecule adopts a twisted *transoid*-form [torsion angle C(6)–C(7)–C(8)–C(9) 110.8(5)°] such that C(6) is doubly bonded to the rhenium centre [Re(1)–C(6) 1.931(7) Å] and C(8)–C(9)

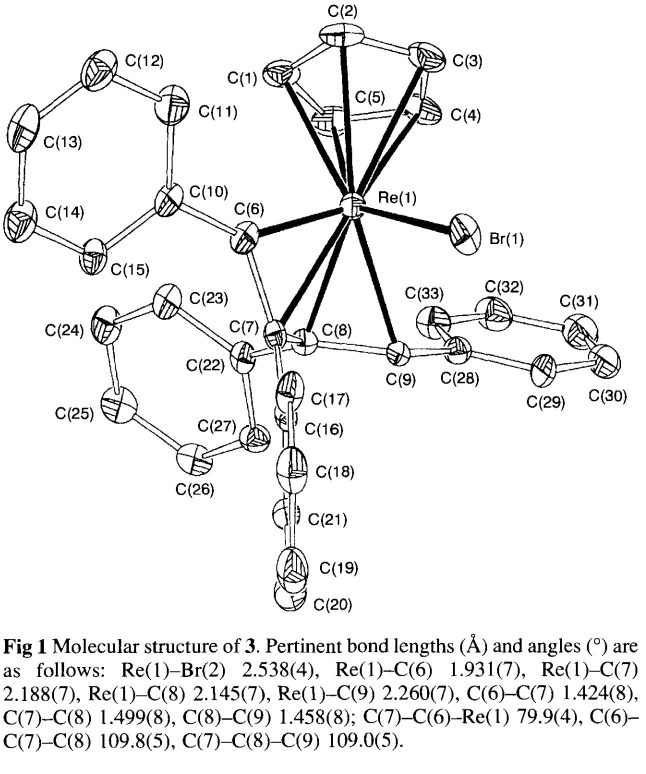


Fig 1 Molecular structure of **3**. Pertinent bond lengths (Å) and angles (°) are as follows: Re(1)–Br(2) 2.538(4), Re(1)–C(6) 1.931(7), Re(1)–C(7) 2.188(7), Re(1)–C(8) 2.145(7), Re(1)–C(9) 2.260(7), C(6)–C(7) 1.424(8), C(7)–C(8) 1.499(8), C(8)–C(9) 1.458(8); C(7)–C(6)–Re(1) 79.9(4), C(6)–C(7)–C(8) 109.8(5), C(7)–C(8)–C(9) 109.0(5).

functions as an η^2(2e)-bonded alkene. Especially interesting is the C(7) centre, which is within bonding distance of the rhenium [Re(1)–C(7) 2.188(7) Å], but is in an essentially planar environment§ [deviation of C(7) from the least squares plane subtended by C(6), C(7), C(8), and C(16) is 0.038 Å]. An insight into the nature of the bonding between the Re centre and the C_4 fragment present in **3** was provided by an EHMO study[12] based on the crystallographic coordinates and the simplification of hydrogen atoms in place of the phenyl substituents on C(6), C(7), C(8) and C(9) with all C–H distances fixed at the idealised value of 1.10 Å. This confirmed that there are a variety of interactions leading to both σ and π symmetry bonding between C(6) and Re(1) *d* orbitals, as well as a strong interaction between the C(8)–C(9) π-bond and metal based *d* functions. However, in addition, and of special interest, a *p* orbital on C(7) is involved in a non-linear σ overlap with the Re *d* function. This is illustrated in Fig. 2, where it can be seen that the geometric constraints imposed by the twisted conformation of the C_4 ligand and the essentially planar geometry at C(7) leads to a 'bent' rhenium to carbon σ-bond. This picture is supported by the overlap populations. The metal carbon overlaps are 0.68, 0.10, 0.22 and 0.28 for C(6), C(7), C(8) and C(9), respectively. Taking C(8) and C(9) as a π-bonded pair, this leads to large overlaps of 0.68 and 0.50 at each end of the C_4 chain, and a smaller overlap for the middle, *i.e.* C(7), carbon atom. It is interesting to note that this smaller overlap does not translate into a radically different atomic charge, on the contrary, the largest charge is on C(9) (−0.19), whilst the remaining carbon atoms all have small positive charges of about 0.02.

It is suggested that the novel bonding mode adopted by the butadienyl ligand present in **3**, arises from the geometrical requirements of an alkyne/alkylidene coupling reaction of the type thought to be involved in the Dötz reaction.[13] If it is assumed, as is shown in Scheme 1, that H^- is delivered to the inside of the alkyne carbon atom adjacent (*cis*) to the Re–Br bond, then a η^2(3e)vinyl/η^2(2e)-alkyne substituted species **2** is accessed with the geometry illustrated. Since the η^2(2e)-bonded diphenylacetylene ligand present in **2** has a low barrier to rotation, as evidenced by the $^{13}C\{^1H\}$ NMR spectrum, there are two possible pathways from **2** to **3**. One involves 'in-plane' coupling [**A** → (**B**, **C**) → **3**], and the second the direct formation of the vinylcarbene **D** *via* an 'out of plane' coupling of the alkyne α-carbon to the rhenium centre, *i.e.* **2** → **D** → **3**. Because the alkyne in **2** is in an unsymmetrical environment there is also the possibility of an 'out of plane' β-coupling reaction (see box in Scheme 1), which leads interestingly to a *cisoid*-η^4(5e)-butadienyl of the type observed[5,7,9] on coupling of cationic η^2-vinyl/alkyne substituted molybdenum and tungsten complexes. Although a detailed theoretical study of the rhenium system is needed, it is interesting that calculations[14,15] on the model chromium system ($OC_4Cr{=}CH_2$ + HC_2H → vinylcarbene), show that 'out of plane' coupling is preferred.

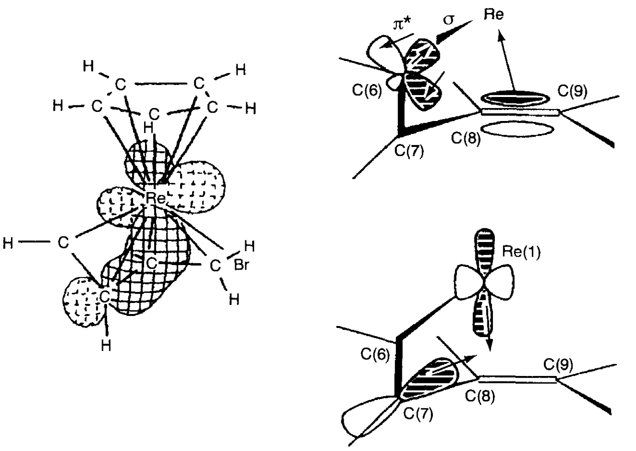


Fig. 2 Orbital interactions for the 'bent' rhenium–carbon bond and a simplified picture of the bonding in complex **3**. (For clarity, only the Re(1)–C(7) contributions to the MO plot are shown)

In summary this investigation has shown for the first time that the η^4(5e)-butadienyl ligand can adopt a *transoid* or twisted bonding mode involving a 'bent' rhenium to carbon bond. It will be interesting to see how this is reflected in the reaction chemistry of **3**.

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Footnotes

† Selected spectroscopic data for compound **1**: ^1H NMR (CD_2Cl_2) δ 7.6–7.5 (m, 20H, Ph), 6.50 (s, 5H, C_5H_5); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 168.0 (PhC_2Ph), 133.4–129.5 (Ph), 105.0 (C_5H_5) (The illustrated structure has been confirmed by single-crystal X-ray crystallography). Compound **2**: ^1H NMR (C_6D_6) δ 7.7–6.9 (m, 20H, Ph), 4.80 (s, 5H, C_5H_5), 3.20 (s, 1H, CHPh); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 215.5 (Re=C), 173.3 (PhC_2Ph), 135.0–125.1 (Ph), 85.1 (C_5H_5), 21.8 (CHPh) [^1H coupled ^{13}C, d, *J*(CH) 129.4 Hz].

Compound **3**: ^1H NMR (CD_2Cl_2) δ 7.9–6.9 (m, 20H, Ph), 5.40 (s, 1H, CHPh), 5.30 (s, 5H, C_5H_5); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 234.9 (Re=C), 151.5–143.7 (*ipso*-Ph), 134.6–125.6 (Ph), 94.3 (C_5H_5), 77.5 (C_2), 64.8 (C_3), 59.0 (C_4) [^1H coupled ^{13}C, d, CHPh, *J*(CH) 161.77 Hz].

‡ *Crystal data* for $C_{33}H_{26}ReBr$, $M = 688.7$, monoclinic, $a = 10.2440(8)$, $b = 16.084(2)$, $c = 15.790(1)$ Å, $\beta = 94.60(1)°$, $U = 2593.3$ Å^3, space group $P2_1/n$, $Z = 4$, $D_c = 1.76$ g cm^{-3}, μ(Mo-Kα) = 60.4 cm^{-1}, $F(000) = 1336$. Data were measured on a CAD4 automatic four-circle diffractometer at room temperature in the range $2 \leqslant \theta \leqslant 24°$. 4481 reflections were collected of which 2916 were unique with $I \geqslant 2\sigma(I)$. Data were corrected for Lorentz and polarisation and also for absorption (max. and min. absorption corrections, 1.438, 0.909 respectively). The structure was solved by Patterson methods and refined using the SHELX suite of programs. In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions except for H(91) [attached to C(9)] which was located in the penultimate difference Fourier map and refined at a fixed distance of 0.96 Å from the parent atom. Final residuals after 10 cycles of least squares were $R = 0.0266$, $R_w = 0.0225$, for a weighting scheme of $w = 2.0672/[\sigma^2(F) + 0.000134(F)^2]$. Max final shift/esd was 0.002. The max and min residual densities were 0.31 and −0.24 e Å^{-3} respectively.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ There has recently been considerable interest in planar tetra coordinate carbon centres, see ref. 11, and refs. therein.

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