Formation of *cisoid*-η^4(5e)-Butadienylrhenium Complexes by Coupling of Alkene and Alkyne Ligands

Stephen J. Dossett, Michael Green,* Mary F. Mahon and Jacqueline M. McInnes

School of Chemistry, University of Bath, Claverton Down, Bath, UK BA2 7AY

The reaction of the η^2(4e)-bonded alkyne complexes [$ReBr_2(\eta^2$-$RC_2Ph)(\eta$-$C_5H_5)$] (R = Me or Ph) with *o*-diphenylphosphinostyrene and 2 equiv. $AgBF_4$ in THF surprisingly affords HBF_4, AgBr and excellent yields of the cationic η^4(5e)-butadienyl complexes [Re=C(Ph)-η^3-{C(R)CHCHC$_6H_4PPh_2$-*o*}(η-C_5H_5)][BF_4]; the methyl-substituted system being structurally characterised by a single-crystal X-ray diffraction study.

Earlier in our studies of the chemistry of η^2(4e)-bonded molybdenum alkyne complexes we observed[1] that when the cation [Mo{η^2(4e)-MeC_2Me}(dpps)(η-C_5H_5)][BF_4] (dpps = *o*-diphenylphosphinostyrene) was heated under reflux in acetonitrile solution, a carbon–carbon coupling reaction and 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=CHC$_6H_4PPh_2$-*o*}(η-C_5H_5)][BF_4]. Later in a related study it was reported[2] by Herrmann and coworkers that treatment of [$ReCl_2(\eta^2$-$RC_2R')(\eta$-$C_5Me_5)$] (R = Me, R′ = Ph, also R = R′ = Me, Et) with an alkene and a catalytic amount of HBF_4·Et_2O results in the formation of the 1,3-diene complexes [$ReCl_2(\eta^4$-1,3-diene)(η-C_5Me_5)]. In both of these reactions metallacyclopent-2-enes were implicated as intermediates, the overall result achieving a formal addition of an alkene carbon–hydrogen bond to an alkyne. In both systems it was suggested that the five-membered ring intermediates are formed by oxidative coupling[3] of coordinated alkyne and alkene ligands, but in order to transform these species into a 1,3-diene a 1,3-H-shift process is required, and this poses a major difficulty in that a suprafacial 1,3-shift is disallowed and a β-H elimination, with its strict requirement of a *cis*-coplanar transition state, followed by a reductive elimination is a most unlikely pathway. Thus, it is clear that if the synthetic organic potential of the coupling of alkenes and alkynes is to be exploited, an understanding of the hydrogen shift process is required.

We recently[4] found that the four-electron donor alkyne complexes [$ReBr_2(\eta^2$-$RC_2Ph)(\eta$-$C_5H_5)$] **1** (R = Me) and **2** (R = Ph) can be accessed readily in good yield by heating a toluene solution of *cis*/*trans*-[$ReBr_2(CO)_2(\eta$-$C_5H_5)$] and the corresponding alkynes RC_2Ph, and that on reaction of **1** and **2** with bis(diphenylphosphino)ethane (dppe) and 2 equiv. $AgBF_4$ in CH_2Cl_2 as solvent, the dications [Re(η^2-RC_2Ph)(dppe)(η-C_5H_5)][BF_4]$_2$ are formed. This suggested that in view of the earlier work it would be interesting to examine the reactions of **1** and **2** with *o*-diphenylphosphinostyrene in the presence of $AgBF_4$ in the expectation of forming reactive η^2(4e)-alkyne/η^2(2e)-alkene substituted dications. In the event an unexpected reaction occurred. Addition (room temp.) of $AgBF_4$ to a THF solution of **1** and dpps led to the rapid precipitation of AgBr (2 mol equiv.) and *formation of HBF_4*. When the solvent was removed and the residue dissolved in CH_2Cl_2, addition of diethyl ether afforded a green crystalline mono-cationic complex **3** in 90% yield. A similar reaction with **2** gave (90% yield) the corresponding green mono-cation **4**.

The formation of a mono-cation and the elimination of HBF_4 was particularly surprising, suggesting that a new type of reaction had occurred. This was confirmed by the ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra.† Especially interesting was the appearance in the $^{13}C\{^1H\}$ spectra of **3** and **4** of low field doublet signals at δ 257.7 [*J*(CP) 16.3 Hz] and 252.9 [*J*(CP) 14.9 Hz], respectively, characteristic of rhenium alkylidene α-carbons.

A single-crystal X-ray diffraction study‡ with the complex **3** resolved the structural problem showing (Fig. 1) that the cation contains a η^4(5e)-butadienyl ligand formed by the regioselective linking ($C_2 + C_2$) of alkyne MeC_2Ph and alkene (dpps)

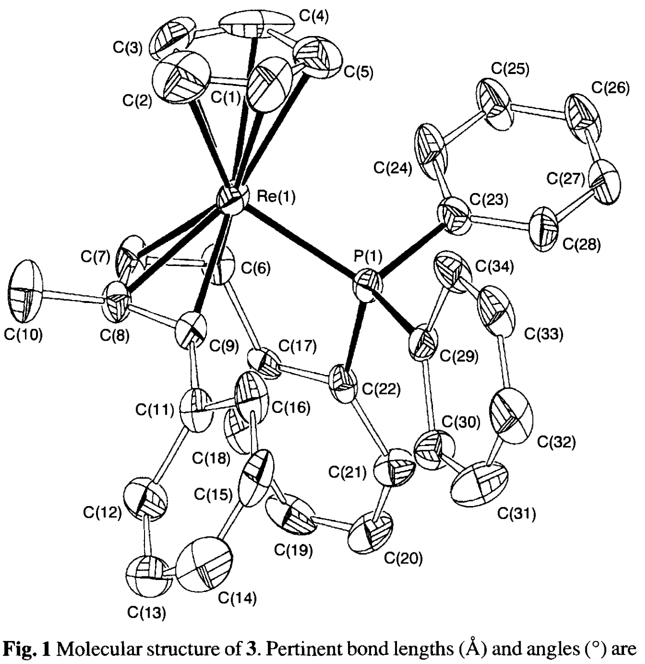
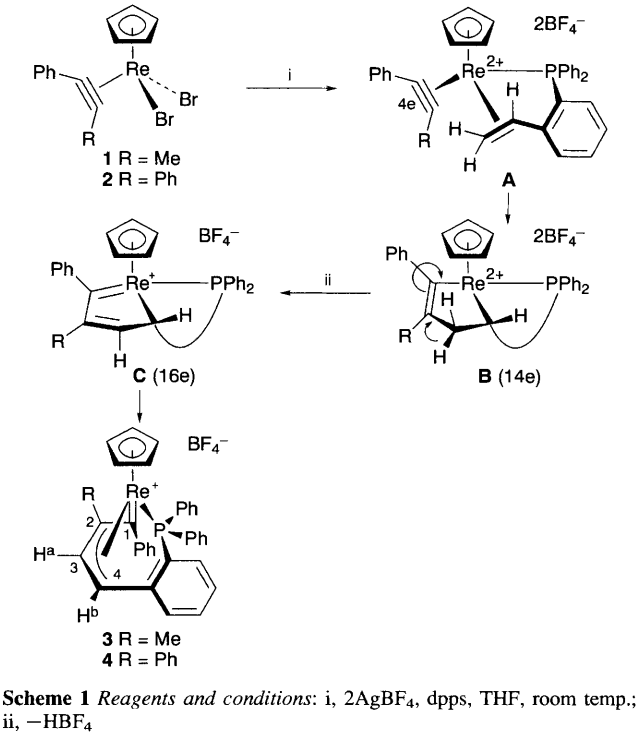


Fig. 1 Molecular structure of **3**. Pertinent bond lengths (Å) and angles (°) are as follows: Re–C(9) 1.936(12), Re–C(8) 2.222(13), Re–C(7) 2.216(13), Re–C(6) 2.172(14), Re–P(1) 2.375(5), Re–C(1) 2.244(20), Re–C(2) 2.230(19), Re–C(3) 2.248(26), Re–C(4) 2.299(24), Re–C(5) 2.256(22), Re–C(9)–C(8) 81.2(7), Re–C(6)–C(7) 72.5(8), C(7)–C(6)–C(17) 122.6(11), C(6)–C(7)–C(8) 122.0(11), C(7)–C(8)–C(9) 117.6(10).



Scheme 1 *Reagents and conditions*: i, 2AgBF$_4$, dpps, THF, room temp.; ii, $-HBF_4$

ligands, the C_4 chain adopting an essentially *cisoid*-coplanar geometry [torsion angle C(6)–C(7)–C(8)–C(9) = 11.27(1.61)°]. The Re–C(9) bond distance is significantly short [1.936(12) Å], suggesting that C(9) is an alkylidene carbon doubly bonded to the rhenium centre, whereas the remaining three carbons of the butadienyl chain have Re–C(6), Re–C(7) and Re–C(8) distances of 2.172(14), 2.216(13) and 2.222(13) Å, respectively, consistent with the illustrated (Scheme 1) η^3-allylic formulation. Previously, complexes containing *cisoid*-η^4(5e)-butadienyl ligands have been shown to be formed either by ring-opening of a η^3-cyclobutenylruthenium complex,[5] or by coupling (C_2 + C_2) of alkyne and η^2-vinyl ligands at molybdenum and tungsten centres,[6–11] and therefore the reaction which affords the complexes **3** and **4** represents a new approach to η^4(5e)-butadienyls or masked coordinatively unsaturated η^3(3e)-butadienyls, species of interest in relation to alkyne oligomerisation and cyclisation, and which contain a metal–carbon double bond.

The formation of **3** and **4** is also of importance in that it provides an insight into the previously mentioned Mo[1] and Re[2] mediated formation of 1,3-dienes by coupling of alkynes and alkenes. Thus, if it is assumed that reaction of **1** and **2** with $AgBF_4$ and dpps does indeed form the η^2(4e)-alkyne/η^2(2e)-alkene substituted dication **A** (Scheme 1), then oxidative [$Re^{III} \rightarrow Re^{V}$] carbon–carbon coupling can provide access to the dicationic rhenacyclopent-2-ene **B**. Loss of a proton from **B** assisted by the synchronous formation of a strong Re–C double bond, would then lead to the intermediate **C**, an obvious precursor of the isolated products **3** and **4**. Clearly, because these products carry a positive charge they are protected from attack by the HBF_4 present in solution. If, however, a similar proton loss occurred from the β-carbons of the metallacyclopent-2-enes implicated in the corresponding molybdenum chemistry[1] or in Herrmann's rhenium[2] system, then the resulting metallacyclopentadienes, *i.e.* analogues of **C** (Scheme 1), would be neutral and therefore liable to attack by a proton on the alkylidene α-carbon resulting in the formation of a 1,3-diene. Thus, it is suggested that the required suprafacial 1,3-H shift mentioned earlier is actually achieved by deprotonation followed by transfer of the resulting proton across the face of the five-membered ring to the electron-rich alkylidene carbon.

In summary, a new synthetic pathway to η^4(5e)-butadienyl ligands has been established, and a mechanistic insight gained into how 1,3-dienes can be formed from alkenes and alkynes.

We thank the SERC(EPSRC) for support, and for a studentship (J. M. M.).

Received, 16th January 1995; Com. 5/00262A

Footnotes

† *Selected spectroscopic data* for **3**: ^{1}H NMR (CD_2Cl_2) δ 7.65–6.46 (m, 15H, aryl), 6.60 and 6.55 [AB, 2H, H^a and H^b, $J(H^aH^b)$ = 8.4 Hz], 5.46 [d, 5H, C_5H_5, J(HP) 1.65 Hz], 2.17 (s, 3H, Me); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 257.7 [d, Re=C(1), J(CP) 16.3 Hz], 152.0–126.7 (aryl), 88.1 (C_5H_5), 78.3 [C(3) or C(4)], 69.2 [C(2)], 57.3 [C(3) or C(4)] 17.0 (Me); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 41.0. For **4**: ^{1}H NMR (CD_2Cl_2) δ 7.70–6.51 (m, 22H, aryl 6.81 and 6.9 [AB, 2H, H^a and H^b, $J(H^aH^b)$ = 8.3 Hz], 5.42 [d, 5H, C_5H_5, J(HP) 1.65 Hz]; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 252.9 [d, Re=C(1), J(CP) 14.9 Hz], 151.5–125.8 (aryl), 89.3 (C_5H_5) 73.5 [C(3) or C(4)], 71.3 [C(2)], 57.7 [C(3) or C(4)]; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 39.9.

‡ *Crystal data*: $C_{34}H_{29}BF_4PRe$, M = 741.6, monoclinic, a = 11.324(1), b = 15.033(2), c = 17.598(2) Å, β = 98.08(1)°, U = 2966.0 Å^3, space group $P2_1/c$, Z = 4, D_c = 1.66 g cm^{-3}, μ(Mo-Kα) = 40.3 cm^{-1}, F(000) = 1456. Data were measured at room temperature on a CAD 4 automatic four circle diffractometer in the range $2 \leqslant \theta \leqslant 24°$. 5099 reflections were collected of which 2741 were unique with $I \geqslant 2\sigma(I)$. Data were corrected for Lorentz and polarisation effects and also for absorption (max. and min. absorption corrections, 1.357, 0.898, 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 except for the boron, as disorder in the anion, which could not be successfully modelled, precluded a clean refinement in this region. Thus, in the latter stages of convergence, the tetrafluoroborate moiety was refined as a rigid group, in a block separate from the cation. Hydrogen atoms were included at calculated positions except for H(61) and H(71) [attached to C(6) and C(7), respectively], which were located in an advanced difference Fourier and refined at a distance of 0.96 Å from the relevant parent atoms. Final residues after 36 cycles of blocked-matrix least squares were R = 0.0466, R_w = 0.0406, for a weighting scheme of $w = 2.2345/[\sigma^2(F) + 0.000242\ (F)^2]$. Max. final shift/esd values in the two blocks were −0.010 [in the fractional z coordinate of H(61)] and −1.321 [in the isotropic thermal parameter of B(1)]. The max. and min. residual densities were 0.64 and −0.56 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.

References

1 S. R. Allen, M. Green, G. Moran, A. G. Orpen and G. E. Taylor, *J. Chem. Soc., Dalton Trans.*, 1984, 441.

2 W. A. Herrmann, R. A. Fischer and E. Herdtweck, *Organometallics*, 1989, **8**, 2821.

3 E.-I. Negishi and T. Takahashi, *Acc. Chem. Res.*, 1994, **27**, 124; and references cited therein.

4 C. Carfagna, R. J. Deeth, S. J. Dossett, M. Green, M. F. Mahon and C. Vaughan, *J. Chem. Soc., Dalton Trans.*, to be submitted.

5 M. Crocker, M. Green, A. G. Orpen, H.-P. Neumann and C. J. Schaverien, *J. Chem. Soc., Chem. Commun.*, 1984, 1351; M. Crocker, M. Green, K. R. Nagle, A. G. Orpen, H.-P. Neumann, C. E. Morton and C. J. Schaverien, *Organometallics*, 1990, **9**, 1422.

6 J. R. Morrow, T. L. Tonker and J. L. Templeton, *J. Am. Chem. Soc.*, 1985, **107**, 5004.

7 S. G. Feng, A. S. Gamble and J. L. Templeton, *Organometallics*, 1989, **8**, 2024.

8 L. Carlton, J. L. Davidson, P. Ewing, L. Manojlovic-Muir and K. W. Muir, *J. Chem. Soc., Chem. Commun.*, 1985, 1474.

9 N. M. Agh-Atabay, J. L. Davidson and K. W. Muir, *J. Chem. Soc., Chem. Commun.*, 1990, 1399.

10 N. M. Agh-Atabay, L. Carlton and J. L. Davidson, *J. Organomet. Chem.*, 1991, **413**, 205.

11 G. C. Conole, M. Green, M. McPartlin, C. Reeve and C. M. Woolhouse, *J. Chem. Soc., Chem. Commun.*, 1988, 1310.