



The syntheses and structures of mono- and di-bromovinylidenes

Neil J. Brown, Mark A. Fox, Mark E. Smith, Dmitry S. Yufit, Judith A.K. Howard, Paul J. Low*

Department of Chemistry, Durham University, South Rd., Durham DH1 3LE, UK

ARTICLE INFO

Article history:

Received 16 July 2009

Received in revised form 13 August 2009

Accepted 19 August 2009

Available online 23 August 2009

Keywords:

Ruthenium

Iron

Vinylidene

ABSTRACT

Reactions of metal acetylide complexes $M(C\equiv CAr)(PP)Cp'$ ($M = Fe, Ru$; $Ar = C_6H_5, C_6H_4Me-4$; $PP = (PPh_3)_2, dppe$; $Cp' = Cp, Cp^*$; not all combinations), or the analogous vinylidene, with cyanogen bromide yield monobromovinylidene complexes $[M\{C=C(Br)Ar\}(PP)Cp']^+$, isolated as PF_6^- salts. The trimethylsilyl-capped acetylides $M(C\equiv CSiMe_3)(PP)Cp'$ react with cyanogen bromide to give $[M(C\equiv CBr_2)(PP)Cp']^+$, the first examples of metal complexes containing a terminal dihalovinylidene ligand, which can be isolated as the BF_4^- salts. Molecular structures of representative mono- and di-bromovinylidene complexes are reported, together with those of $Ru(C\equiv CSiMe_3)(PPh_3)_2Cp$ and $Ru(C\equiv CSiMe_3)(dppe)Cp^*$.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The chemistry of terminal vinylidene complexes has been extensively developed since the first reports of such species in the early 1970s [1], with studies of the synthesis, structure, bonding and stoichiometric reactions of vinylidenes [2] leading to the development of synthetically useful metal-catalysed reaction cycles based on the formation and reaction of a vinylidene species [3]. The development of convenient synthetic routes to vinylidene complexes from the re-arrangement of a terminal alkyne within the coordination sphere of an appropriate metal complex (Scheme 1), or from the addition of an electrophile to C_β of a metal acetylide (Scheme 2), has greatly assisted the development of the chemistry of this fascinating unsaturated carbene ligand.

Although 1-haloalkynes have found considerable application in synthetic organic chemistry, halovinylidenes remain relatively rare. The first halogenated vinylidene complexes were prepared by re-arrangement of 1-haloalkynes or dihaloalkynes upon a binuclear Co framework (Scheme 3) [4]. The difluorovinylidene ligand has also been stabilised on a bimetallic scaffold from reaction of $CF_2(COCl)_2$ with $[Fe_3(CO)_{11}]^-$ [5].

A more general route to halovinylidenes has been developed by Bruce and co-workers who have demonstrated electrophilic addition of halogens (Cl_2, Br_2, I_2) to half-sandwich ruthenium and osmium acetylide complexes to give a series of terminal mono-halovinylidenes (Scheme 4), although in the case of reaction between $Ru(C\equiv CPh)(PPh_3)_2Cp$ and Br_2 , bromination of the acetylide phenyl substituent *para* to the C_β carbon was also observed [6]. The related iron iodovinylidene complexes $[Fe\{C=C(I)R\}(dppm)Cp]$

($R = Ph, Bu^t$) are also known, having been formed from closely related reactions of I_2 or $[I(py)_2]BF_4$ with $Fe(C\equiv CR)(dppm)Cp$ [7]. The recent preparation of $[Ru\{C=Cl(H)\}(dppe)Cp^*]BF_4$ from $Ru(C\equiv CH)(dppe)Cp^*$ and $[I(py)_2]BF_4$, and subsequent deprotonation to afford the iodoacetylide complex $Ru(C\equiv Cl)(dppe)Cp^*$ is worthy of particular note [8]. However, aside from these few flurries of activity, the chemistry of halovinylidenes has remained largely undeveloped for much of the last 20 years.

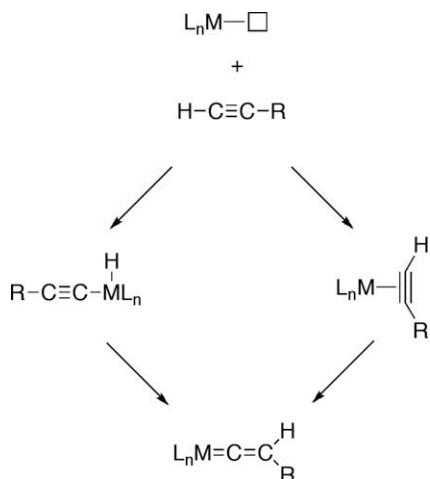
Iwasawa's demonstration of the synthetic utility of iodo-vinylidenes generated *in situ* from 1-iodoalkynes and $W(thf)(CO)_5$ [9] has generated something of a surge of interest in the chemistry of halovinylidene complexes [10]. In the course of surveying conditions for the cyanation of acetylide ligands [11] we investigated the reactions of cyanogen bromide ($BrCN$) with metal acetylides, and found this reagent suitable instead for the bromination of the acetylide ligand under mild conditions. In this short report we describe the use of cyanogen bromide in the preparation of mono- and di-bromovinylidene complexes.

2. Results and discussion

CARE: the likely evolution of cyanide ions and potentially HCN as by-products in the reactions described herein necessitates extreme care in their conduct.

The reaction of $Fe(C\equiv CAr)(dppe)Cp$ ($Ar = Ph$ **1a**, C_6H_4Me-4 **1b**) with an excess of cyanogen bromide, $BrCN$, in the presence of NH_4PF_6 in CH_2Cl_2 resulted in the ready formation of the dark green bromovinylidene complexes $[Fe\{C=CBr(Ar)\}(dppe)Cp]PF_6$ ($Ar = Ph$ **2a**] PF_6 , C_6H_4Me-4 **2b**] PF_6) in good (ca. 60%) yield (Scheme 5). The complexes were readily characterised on the basis of the solution spectroscopic data, which included a triplet at ca. 350 ppm ($J_{CP} = 33$ Hz) for the vinylidene C_α carbon, a clear bromine isotope

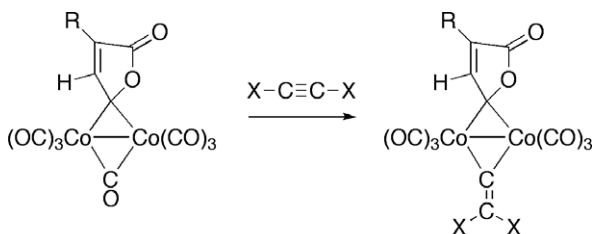
* Corresponding author. Tel.: +44 (0)191 334 2114; fax: +44 (0)191 384 4737.
E-mail address: p.j.low@durham.ac.uk (P.J. Low).



Scheme 1. The formation of vinylidene complexes by the re-arrangement of terminal alkynes within the coordination sphere of a metal centre.



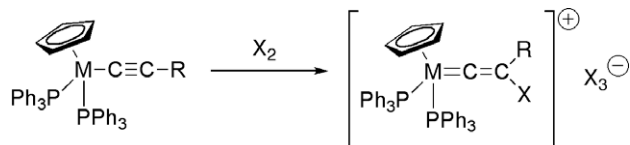
Scheme 2. The formation of a vinylidene from electrophilic addition to a metal acetylide.



R = H, *n*-Pr, *n*-Bu, *n*-Pe, Ph

X = I, Br

Scheme 3. The formation of a bimetallic complex featuring a dihalovinylidene ligand (not all combinations).

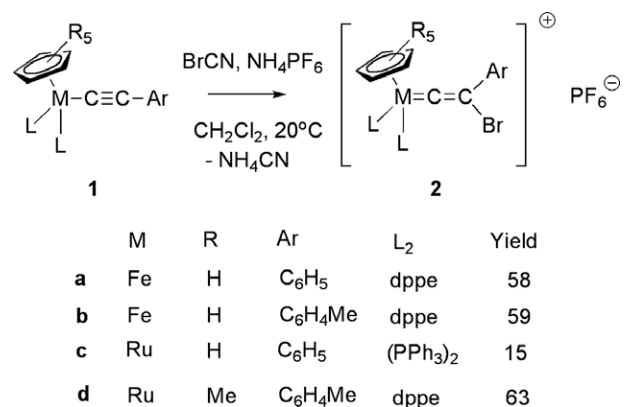


M = Ru, Os; R = Ph, Me, C₆F₅

X = Cl, Br, I

Scheme 4. Formation of terminal mono-halovinylidene complexes from reaction of halogens with metal acetylide complexes (not all combinations).

pattern in the molecular ion (ES-MS), and the observation of the vinylidene $\nu(\text{C}=\text{C})$ band ($[\mathbf{2a}]\text{PF}_6$ 1614 cm^{-1} , $[\mathbf{2b}]\text{PF}_6$ 1644 cm^{-1}) in the IR spectra. Whilst relatively stable as solids and in solution under an inert atmosphere, on standing in air solutions of the bromovinylidenes gradually oxidise to the carbonyl cation $[\text{Fe}(\text{CO})(\text{dppe})\text{Cp}]^+$ [12]. The presence of the carbonyl complex in solution is easily determined by the strong $\nu(\text{CO})$ band at 1979 cm^{-1} and the carbonyl ^{13}C resonance at 190 ppm.

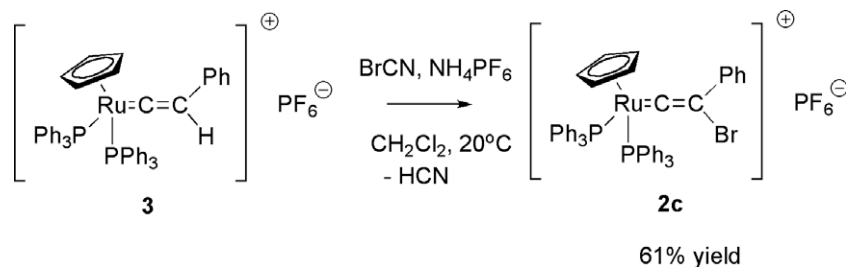


Scheme 5. The bromination of metal acetylides by cyanogen bromide.

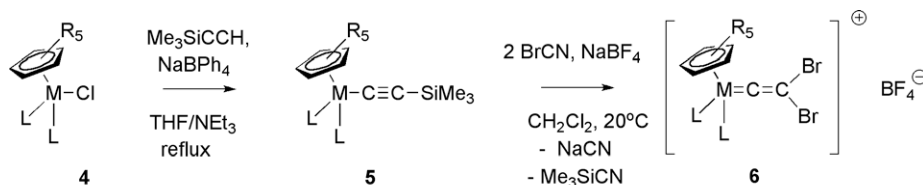
Reactions of BrCN with $\text{Ru}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2\text{Cp}$ (**1c**) and NH_4PF_6 in THF, CH_2Cl_2 or toluene solutions gave green solutions from which the bromovinylidene $[\text{Ru}\{\text{C}=\text{C}(\text{Br})\text{Ph}\}(\text{PPh}_3)_2\text{Cp}]\text{PF}_6$ ($[\mathbf{2c}]\text{PF}_6$) could be isolated in low yield, with traces of the cyanovinylidene $[\text{Ru}\{\text{C}=\text{C}(\text{CN})\text{Ph}\}(\text{PPh}_3)_2\text{Cp}]\text{PF}_6$ also being observed in the reaction mixture by ^1H NMR and IR spectroscopy [for a closely related compound see 11a]. After exploration of a range of reaction solvents, times and temperatures, $[\mathbf{2c}]\text{PF}_6$ was isolated in ca. 60% yield, free of the cyanovinylidene, simply from reaction of the vinylidene $[\text{Ru}\{\text{C}=\text{C}(\text{H})\text{Ph}\}(\text{PPh}_3)_2\text{Cp}]\text{PF}_6$ ($[\mathbf{3}]\text{PF}_6$) with excess BrCN and NH_4PF_6 in CH_2Cl_2 solution (Scheme 6). In contrast to the reaction of **1c** with Br_2 , there was no sign of bromination of the phenyl ring of the vinylidene ligand [6]. The relatively electron-rich acetylide complex $\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{dppe})\text{Cp}^*$ (**1d**) reacted with BrCN in the presence of NH_4PF_6 to give the monobromovinylidene $[\mathbf{2d}]\text{PF}_6$. Although the fine details of the mechanism leading to the formation of the bromovinylidene complexes $[\mathbf{2}]\text{PF}_6$ have not been investigated, the presence of NH_4PF_6 during the bromination step is important to these reactions, with significantly decreased yields being obtained in its absence.

With a view to exploring the scope of the reaction we considered the prospects of forming di-bromovinylidene complexes directly from a terminal metal acetylide or synthon, and two equivalents of BrCN. The metal acetylide complex $\text{Fe}(\text{C}\equiv\text{CH})(\text{dppe})\text{Cp}$ has been prepared from reactions of $[\text{Fe}(\text{dppe})\text{Cp}]\text{BF}_4$ with $\text{LiC}\equiv\text{CH}$ en [13], whilst related complexes featuring the $\text{C}\equiv\text{CH}$ ligand, such as, $\text{Fe}(\text{C}\equiv\text{CH})(\text{dppe})\text{Cp}^*$ [14], $\text{Ru}(\text{C}\equiv\text{CH})(\text{PPh}_3)_2\text{Cp}$ [15], and $\text{Ru}(\text{C}\equiv\text{CH})(\text{dppe})\text{Cp}^*$ [16] are prepared by deprotonation of the corresponding cationic vinylidenes $[\text{M}(\text{C}=\text{CH}_2)(\text{PP})\text{Cp}]^+$, obtained in turn from $\text{MCl}(\text{PP})\text{Cp}'$ (**4**) and $\text{HC}\equiv\text{CSiMe}_3$ [17] [18]. The trimethylsilyl-capped acetylide complex $\text{Fe}(\text{C}\equiv\text{CSiMe}_3)(\text{dppe})\text{Cp}$ (**5a**), which is a masked version of $\text{Fe}(\text{C}\equiv\text{CH})(\text{dppe})\text{Cp}$, is obtained rather more directly from $\text{FeCl}(\text{dppe})\text{Cp}$ (**4a**) and $\text{HC}\equiv\text{CSiMe}_3$ in THF/ NEt_3 solutions containing NaBF_4 [11c] and both $\text{Ru}(\text{C}\equiv\text{CSiMe}_3)(\text{PPh}_3)_2\text{Cp}$ (**5b**) and $\text{Ru}(\text{C}\equiv\text{CSiMe}_3)(\text{dppe})\text{Cp}^*$ (**5c**) can be obtained in entirely analogous fashion from $\text{RuCl}(\text{PPh}_3)_2\text{Cp}$ (**4b**) and $\text{RuCl}(\text{dppe})\text{Cp}^*$ (**4c**), respectively (Scheme 7). The route described in Scheme 7, which we find to be convenient, complements existing routes to similar half-sandwich ruthenium complexes based on trapping $\text{Ru}(\text{C}\equiv\text{CLi})(\text{PP})\text{Cp}'$ with SiClMe_3 [17,18], but without the complication of competing sites of lithiation reported by Kawata and Sato in the case of the preparation of **5b** [18].

Reaction of the trimethylsilyl-capped acetylide complexes **5a**, **5b**, and **5c** with excess BrCN were found to afford the di-bromovinylidene cations $[\text{Fe}(\text{C}=\text{CBr}_2)(\text{dppe})\text{Cp}]^+$ ($[\mathbf{6a}]^+$), $[\text{Ru}(\text{C}=\text{CBr}_2)(\text{PPh}_3)_2\text{Cp}]^+$ ($[\mathbf{6b}]^+$) and $[\text{Ru}(\text{C}=\text{CBr}_2)(\text{dppe})\text{Cp}^*]^+$ ($[\mathbf{6c}]^+$), which could be isolated as the BF_4^- salts. In each case, the reaction proceeded without NH_4PF_6 , and is apparently driven by the formation



Scheme 6. The formation of **2c** from the vinylidene complex **3**.



| | M | R | L ₂ | Yield 5 | Yield 6 |
|----------|----|----|----------------------------------|----------------|----------------|
| a | Fe | H | dppe | 79 | 73 |
| b | Ru | H | (PPh ₃) ₂ | 90 | 15 |
| c | Ru | Me | dppe | 45 | 94 |

Scheme 7. The formation of the trimethylsilyl-capped acetylide complexes **5** and the di-bromovinylidenes [**6**] BF₄.

of Me₃SiCN. Each of [**6a–c**]BF₄ exhibited the characteristically low field C_α resonance associated with the strongly deshielded carbene-like carbon, and a [M+H]⁺ or [M]⁺ ion in the ES-MS displaying the characteristic isotope pattern associated with the presence of two bromine atoms. The iron complex also featured the vinylidene ν(C=C) band at 1604 cm⁻¹. The ruthenium di-bromovinylidene complexes [**6b**]BF₄ and [**6c**]BF₄ proved to be rather sensitive in solution, possibly because of the significant ligand character in the frontier orbitals of ruthenium vinylidene complexes [11a], and the IR spectra of these species were always contaminated with the carbonyl cation. Although the sensitivity of the samples made accurate micro-analyses difficult to obtain, high resolution mass spectrometry data were consistent with the proposed structures (Supplementary material).

2.1. Molecular structures

The structures of [**2c**]PF₆ (Fig. 1) and [**2d**]PF₆ (Fig. 2) were determined from a crystal grown from acetone and hexane (Table 1), and, unsurprisingly, are similar to those of [Ru{C=C(X)C₆H₄R-4}(PPh₃)₂Cp][X₃] (X = Br, R = Br; X = I, R = H) determined in the earlier Bruce studies [6]. The Ru(PPh₃)₂Cp fragment exhibits the usual approximately octahedral geometry. The parameters associated with the Ru=C=C(Br)Ar fragment clearly establish the vinylidene character of the ligand, with the characteristically short Ru(1)–C(1) (1.835(6) Å) and C(1)–C(2) (1.303(7) Å) indicative of Ru=C and C=C double bonds. The average Ru(1)–C(cp) distance in the cation [**2c**]⁺ (2.360 Å) is similar to that found in [Ru{C=C(Br)C₆H₄Br-4}(PPh₃)₂Cp]⁺ (2.366(5) Å), with the longest distance associated with the carbon approximately *trans* to the vinylidene ligand. The Ru(1)–P(1, 2) bond lengths in the cation [**2c**]⁺ [Ru(1)–P(1, 2) 2.3461(13), 2.3729(13) Å] are arguably longer than those in [Ru{C=C(Br)C₆H₄Br-4}(PPh₃)₂Cp]⁺ (2.337(2), 2.356(2) Å). The non-equivalence of the Ru–P bond lengths in both [**2c**]⁺ and [**2d**]⁺ seems to be related to the orientation of the

electron-withdrawing vinylidene ligand: the longer Ru(1)–P(2) bond in [**2c**]⁺ is eclipsed relative to the C(2)–Br(1) bond (torsion angle Br(1)C(2)Ru(1)P(2) 9.0°) whilst in [**2d**] the longer Ru(1)–

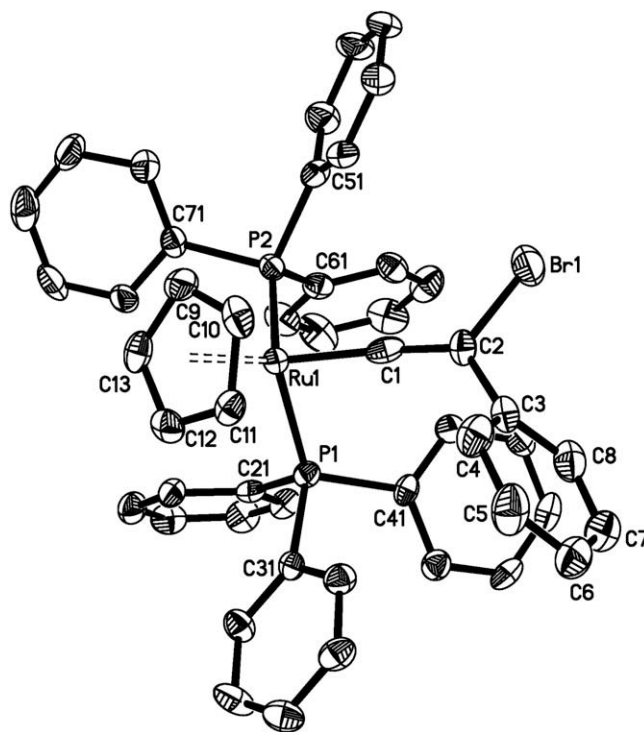


Fig. 1. The cation [**2c**]⁺ in [Ru{C=C(Br)C₆H₅}(PPh₃)₂Cp]PF₆. In this and subsequent figures hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–P(1,2) 2.3461(13), 2.3729(13); Ru(1)–C(1) 1.835(6); C(1)–C(2) 1.303(7); C(2)–C(3) 1.492(7); C(2)–Br(1) 1.909(5); P(1)–Ru(1)–P(2) 101.34(4); P(1)–Ru(1)–C(1) 87.76(15); P(2)–Ru(1)–C(1) 95.91(15); Ru(1)–C(1)–C(2) 173.3(4); C(1)–C(2)–C(3) 122.1(5); C(1)–C(2)–Br(1) 118.9(4).

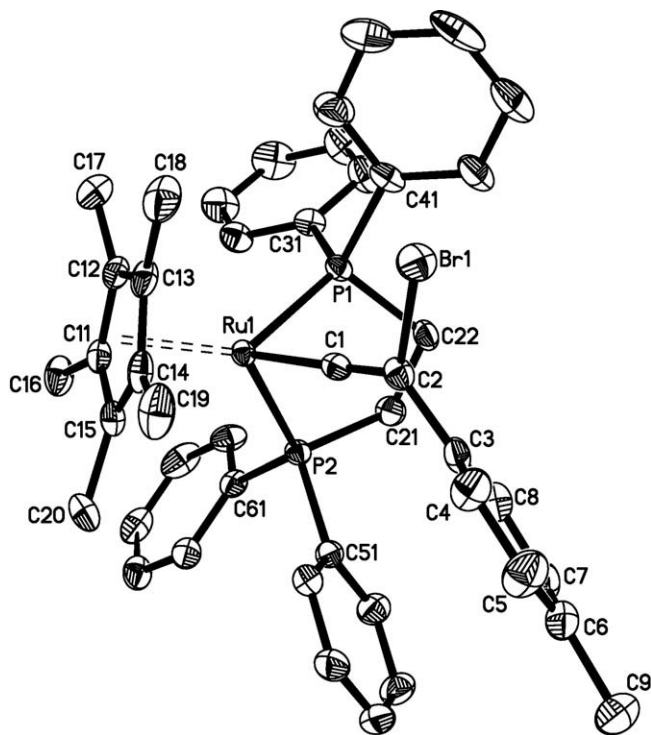


Fig. 2. The cation **[2d]⁺** in $[\text{Ru}(\text{C}=\text{C}(\text{Br})\text{C}_6\text{H}_4\text{Me}-4)(\text{dppe})\text{Cp}^*]\text{PF}_6$. Selected bond lengths (Å) and angles ($^\circ$): Ru(1)–P(1,2) 2.3049(2), 2.3176(5); Ru(1)–C(1) 1.851(2); C(1)–C(2) 1.303(3); C(2)–C(3) 1.484(3); C(2)–Br(1) 1.937(2); P(1)–Ru(1)–P(2) 82.244(19); P(1)–Ru(1)–C(1) 83.13(6); P(2)–Ru(1)–C(1) 92.92(6); Ru(1)–C(1)–C(2) 173.31(16); C(1)–C(2)–C(3) 128.64(19); C(1)–C(2)–Br(1) 114.74(15).

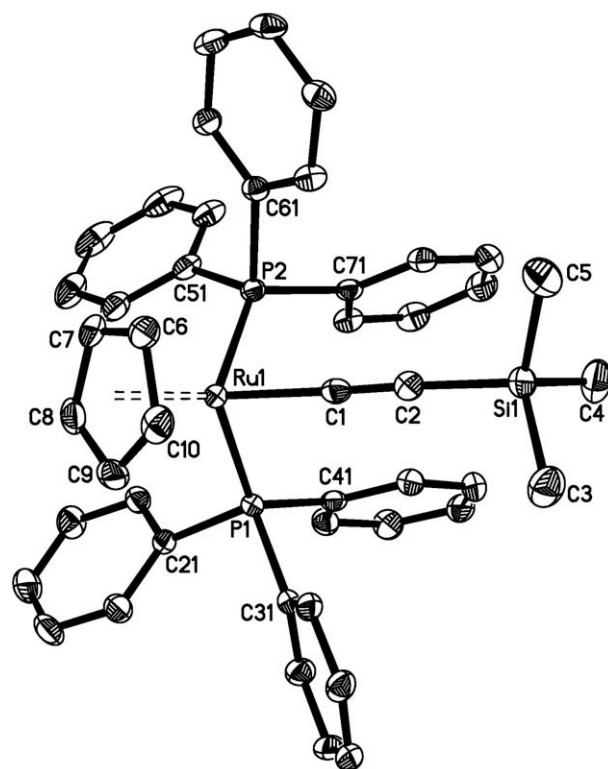


Fig. 3. The molecular structure of **5b** showing the atom labelling scheme. Selected bond lengths (Å) and angles ($^\circ$): Ru(1)–P(1,2) 2.2841(5), 2.2811(6); Ru(1)–C(1) 2.004(2); C(1)–C(2) 1.218(3); C(2)–Si(1) 1.806(2); P(1)–Ru(1)–P(2) 100.205(19); P(1)–Ru(1)–C(1) 90.20(6); P(2)–Ru(1)–C(1) 87.01(6); Ru(1)–C(1)–C(2) 174.39(19); C(1)–C(2)–Si(1) 176.9(2).

P(2) bond is almost eclipsed relative to the C(2)–C(3) bond of the vinylidene ligand (corresponding torsion angle C(3)C(2)Ru(1)P(2) -30.6°).

The trimethylsilyl-capped precursors **5b** and **5c** crystallised readily from THF/ CDCl_3 and slow evaporation of NCMe/hexane solutions, respectively. Aside from the differences imposed by the different supporting phosphine and cyclopentadienyl ligands, the key metric parameters of **5b** and **5c** are broadly similar. Thus, compound **5c** has somewhat shorter Ru–P bonds due to the enhanced metal to phosphine back-bonding brought about by the more electron-rich pentamethylcyclopentadienyl ligand. In the case of **5b**

which features the $\text{Ru}(\text{PPh}_3)_2\text{Cp}$ fragment, the longer Ru–P distances are likely due to steric effects between the bulky PPh_3 and Cp fragments, and is comparable with other examples of this type [19]. The small differences in bond lengths along the linear $\text{Ru}-\text{C}(1)\equiv\text{C}(2)-\text{Si}$ chain are not statistically significant, and the bonding parameters are largely indistinguishable from those associated with the phenylacetylide analogues [19b,20].

The iron di-bromovinylidene **[6a]** BF_4 was sufficiently stable to permit recrystallisation, which afforded yellow–orange coloured

Table 1
Crystal data and refinement details.

| Complex | [2c] PF_6 | [2d] PF_6 | 5b | 5c | [6a] BF_4 |
|--|--|--|---|---|---|
| Empirical formula | $\text{C}_{49}\text{H}_{40}\text{BrP}_2\text{Ru} \times \text{PF}_6 \times \text{C}_3\text{H}_6\text{O}$ | $\text{C}_{45}\text{H}_{46}\text{P}_2\text{BrRu} \times \text{PF}_6$ | $\text{C}_{46}\text{H}_{44}\text{RuP}_2\text{Si} \times 0.5 \text{C}_4\text{H}_8\text{O}$ | $\text{C}_{41}\text{H}_{48}\text{SiP}_2\text{Ru}$ | $\text{C}_{34}\text{H}_{31}\text{Br}_2\text{FeCl}_2\text{P}_2 \times \text{BF}_4 \times \text{CH}_2\text{Cl}_2$ |
| Formula weight | 1074.78 | 974.71 | 823.96 | 731.89 | 874.91 |
| T (K) | 120(2) | 120(2) | 120(2) | 120(2) | 120(2) |
| Crystal system | Orthorhombic | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | P bca | $\text{P}2_1/\text{n}$ | $\text{P}2_1/\text{n}$ | $\text{P}2_1/\text{c}$ | $\text{P}2_1/\text{n}$ |
| a (Å) | 18.0476(2) | 10.4118(3) | 10.4778(9) | 17.6283(4) | 11.7249(4) |
| b (Å) | 14.2539(2) | 20.8537(7) | 22.480(2) | 12.9530(3) | 23.3677(7) |
| c (Å) | 35.9566(4) | 19.5593(6) | 17.3638(15) | 16.1175(3) | 13.4513(4) |
| α ($^\circ$) | 90 | 90 | 90 | 90 | 90 |
| β ($^\circ$) | 90 | 90.966(10) | 98.786(2) | 92.80(2) | 104.984(10) |
| γ ($^\circ$) | 90 | 90 | 90 | 90 | 90 |
| V (Å ³) | 9249.79(19) | 4246.2(2) | 4041.9(6) | 3675.86(14) | 3560.13(19) |
| ρ_c (g cm ⁻³) | 1.544 | 1.525 | 1.354 | 1.323 | 1.632 |
| Z | 8 | 4 | 4 | 4 | 4 |
| μ (Mo K α) (mm ⁻¹) | 5.270 | 1.481 | 0.531 | 0.574 | 2.954 |
| N_{tot} | 36641 | 44754 | 54624 | 45758 | 52890 |
| N (R_{int}) | 6558 [0.0823] | 11,829 [0.0469] | 10,746 [0.0548] | 10,244 [0.0249] | 9457 [0.0747] |
| R_1 | 0.0553 | 0.0480 | 0.0518 | 0.0345 | 0.0634 |
| wR_2 | 0.1534 | 0.0695 | 0.0795 | 0.0785 | 0.1858 |
| GOOF | 1.110 | 0.962 | 1.061 | 1.027 | 1.019 |

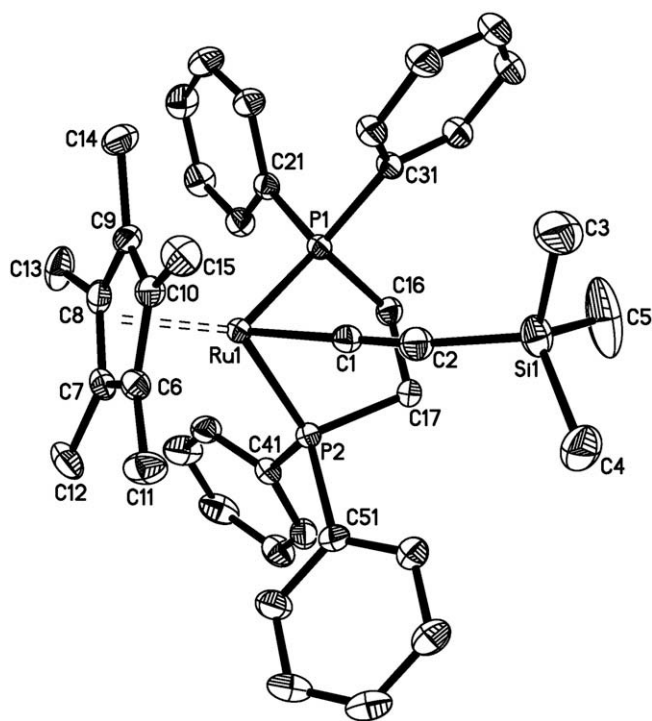


Fig. 4. The molecular structure of **5c** showing the atom labelling scheme. Selected bond lengths (Å) and angles (°): Ru(1)–P(1, 2) 2.2745(4), 2.2539(4); Ru(1)–C(1) 2.0104(16); C(1)–C(2) 1.224(2); C(2)–Si(1) 1.8184(18); P(1)–Ru(1)–P(2) 83.38(2); P(1)–Ru(1)–C(1) 86.17(4); P(2)–Ru(1)–C(1) 81.15(4); Ru(1)–C(1)–C(2) 179.65(15); C(1)–C(2)–Si(1) 164.15(15).

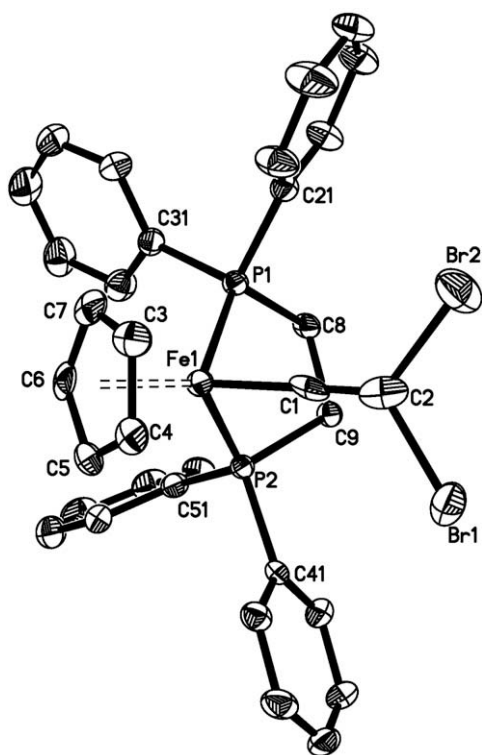


Fig. 5. The molecular structure of the cation **[6a]⁺** from $[\text{Fe}(\text{C}=\text{CBr}_2)(\text{dppe})\text{Cp}]\text{BF}_4$. Selected bond lengths (Å) and angles (°): Fe(1)–P(1, 2) 2.2229(14), 2.2164(14); Fe(1)–C(1) 1.823(6); C(1)–C(2) 1.192(8); C(2)–Br(1, 2) 1.923(6), 1.927(6); P(1)–Fe(1)–P(2) 84.30(5); P(1)–Fe(1)–C(1) 92.97(15); P(2)–Fe(1)–C(1) 89.12(15); Fe(1)–C(1)–C(2) 179.1(5); C(1)–C(2)–Br(1, 2) 122.9(5), 125.3(5).

single crystals suitable for X-ray diffraction. The crystallographically determined structure of **[6a]BF₄** (Fig. 5) reveals the usual approximately octahedral coordination geometry around the iron centre. The Fe(1)–C(1) is relatively long (1.823(6) Å), and the C(1)–C(2) bond is notably short (1.192(8) Å) in comparison with related bond lengths in other vinylidene complexes containing the Fe(dppe)Cp moiety in which these bonds fall in the range 1.74–1.76 Å [Fe–C(1)] and 1.31–1.33 Å [C(1)–C(2)] [21]; similar ranges are also associated with vinylidenes derived supported by the more electron-rich Fe(dppe)Cp* fragment [22]. The inductively electron-withdrawing bromine substituents on the vinylidene C_α likely cause these bond length variations by polarising the C=C bond, hence introducing a larger electrostatic component to the C=C bond.

3. Conclusion

This work has described the preparation and crystallographic characterisation of mono- and di-bromo vinylidenes from the reactions of cyanogen bromide with metal acetylides, or vinylidenes. The use of cyanogen bromide in the presence of NH₄PF₆ as a mild brominating agent avoids side reactions such as electrophilic aromatic halogenation reactions encountered when bromine is used as the halogenating agent. The complexes **[6a–c]BF₄** are the first examples of complexes bearing terminal dihalovinylidene ligands, and have been obtained under mild conditions from double halogenation of readily synthesised precursors bearing trimethylsilyl acetylide ligands, and thereby avoiding the use of dihaloacetylenes. With these synthetic routes in hand, the chemistry of the dihalovinylidene ligand may now be explored with greater convenience.

4. Experimental

All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques as a matter of routine, although no special precautions were taken to exclude air or moisture during work-up. Dichloromethane was purified and dried using an Innovative Technology SPS-400, and degassed before use. Diethyl ether, hexane and acetone were the best available commercial grade, and used without further purification. The compounds Fe(C≡CPh)(dppe)Cp [23], [Fe(C≡CC₆H₄Me-4)(dppe)Cp] [23], [Fe(C≡CSiMe₃)(dppe)Cp] [11c], Ru(C≡CC₆H₄Me-4)(dppe)Cp* [23], [Ru(C≡CHPh)(PPh₃)₂Cp]PF₆ [24], FeCl(dppe)Cp [25], RuCl(PPh₃)₂Cp [26] and RuCl(dppe)Cp* [16] were prepared by the literature methods. Cyanogen bromide was purchased (Aldrich) and sublimed at atmospheric pressure under nitrogen immediately prior to use. Other reagents were purchased and used as received.

NMR spectra were recorded on a Bruker Avance (¹H 400.13 MHz, ¹³C 100.61 MHz, ³¹P 161.98 MHz) spectrometer from CDCl₃ solutions unless otherwise indicated, and referenced against solvent resonances (CDCl₃ ¹H 7.26, ¹³C 77.0; d₆-acetone ¹H 2.05, ¹³C 29.8 ppm; CD₂Cl₂ ¹H 5.31, ¹³C 53.8) or external H₃PO₄ (³¹P). See Figs. 1–5 for the atom labelling schemes used in the NMR assignments. IR spectra (CH₂Cl₂) were recorded using a Nicolet Avatar spectrometer from cells fitted with CaF₂ windows. Electrospray ionisation mass spectra were recorded using Thermo Quest Finnigan Trace MS-Trace GC or WATERS Micromass LCT spectrometers. Samples in dichloromethane (1 mg/mL) were 100 times diluted in either methanol or acetonitrile, and analysed with source and desolvation temperatures of 120 °C, with cone voltage of 30 V. Elemental analyses were carried out within the Department of Chemistry at Durham University.

Single crystal X-ray data for all structures were collected on a Bruker SMART CCD 6000 (compounds **[2c]PF₆·Me₂CO**, **[2d]PF₆** and **5c**) or 1 K (**5b**·0.5THF and **[6a]BF₄·CH₂Cl₂**) diffractometers

equipped with a Cryostream (Oxford Cryosystems) cooling devices at 120 K using λ Mo K α or λ Cu K α ($[2c]PF_6 \cdot Me_2CO$) radiation. All the structures were solved by direct methods and refined by full-matrix least squares on F^2 for all data using SHELXTL software. All ordered non-hydrogen atoms were refined with anisotropic displacement parameters, H-atoms were placed into calculated positions and refined in a “riding” mode. The crystallographic data and parameters of refinement are given in Table 1.

4.1. Preparation of $[Fe\{C\equiv CBr(Ph)\}(dppe)Cp]PF_6$ ($[2a]PF_6$)

To a solution of $Fe(C\equiv CPh)(dppe)Cp$ (0.100 g, 0.161 mmol) and NH_4PF_6 (0.060 g, 0.40 mmol) in CH_2Cl_2 (15 cm³), cyanogen bromide (0.043 g, 0.40 mmol) was added and the reaction mixture allowed to stir overnight. The resulting solution was concentrated, filtered and purified by preparative TLC (80:20, acetone/hexane). The major green band afforded the title compound (0.065 g, 58%) as a deep green solid after precipitation (CH_2Cl_2/Et_2O). IR (cm⁻¹): $\nu(C\equiv C)$ 1614. ¹H NMR: δ 3.10 (m, 2H, dppe); 3.15 (m, 2H, dppe); 5.30 (s, 5H, Cp); 6.75–7.45 (m, 25H, Ph). ¹³C NMR: 28.6 (m, dppe); 90.7 (s, Cp); 127.2 (C4), 128.1 (C3), 128.2 (C6), 128.8 (C5); 128.9, 129.4 (dd, ³J_{CP}, ⁵J_{CP} ~ 5 Hz, C_{m,m'}); 131.5, 131.5 (C_{p,p'}); 131.3, 132.3 (dd, ²J_{CP}, ⁴J_{CP} ~ 5 Hz, C_{o,o'}); 132.9, 134.9 (m, C_{i,i'}); 137.8 (s, C2); 348.4 (t, ²J_{CP} = 33 Hz, C1). ³¹P NMR: 93.6 (s, dppe); -143.1 (septet, PF₆). ES(+)-MS (*m/z*): 699.06761, [M]⁺; calculated 699.06631 amu.

4.2. Preparation of $[Fe\{C\equiv CBr(C_6H_4Me-4)\}(dppe)Cp]PF_6$ ($[2b]PF_6$)

A solution of $Fe(C\equiv CC_6H_4Me-4)(dppe)Cp$ (0.100 g, 0.158 mmol) and NH_4PF_6 (0.064 g, 0.39 mmol) in CH_2Cl_2 (15 cm³) was treated with cyanogen bromide (0.041 g, 0.39 mmol) and stirred overnight. Concentration of the solution, filtration, and purification by preparative TLC (45:55, acetone/hexane) gave a green band, which upon isolation by precipitation from CH_2Cl_2/Et_2O , gave the title compound as a deep green solid (0.067 g, 59%). IR (cm⁻¹): $\nu(C\equiv C)$ 1609. ¹H NMR: δ 2.26 (s, 3H, CH₃); 3.10 (m, 4H, dppe); 5.29 (s, 5H, Cp); 6.66 (d, *J*_{HH} = 7 Hz, C₆H₄), 6.80 (d, *J*_{HH} = 7 Hz, C₆H₄); 7.04–7.63 (m, 20H, Ph). ¹³C NMR: 21.1 (s, CH₃), 28.5 (m, dppe); 90.6 (s, Cp); 124.8 (C3), 127.4 (C4), 129.4 (C5 overlap with multiplet at 129.4), 138.3 (C6); 128.9, 129.4 (dd, ³J_{CP}, ⁵J_{CP} ~ 5 Hz, C_{m,m'}); 131.5, 131.5 (C_{p,p'}); 131.2, 132.4 (dd, ²J_{CP}, ⁴J_{CP} ~ 5 Hz, C_{o,o'}); 133.0, 135.1 (m, C_{i,i'}); 137.6 (s, C2); 349.2 (t, ²J_{CP} = 33 Hz, C1). ³¹P NMR: 94.0 (s, dppe); -143.1 (septet, PF₆). ES(+)-MS (*m/z*): 713.08313, [M]⁺; calculated 713.08196 amu.

4.3. Preparation of $[Ru\{C\equiv CBr(Ph)\}(PPh_3)_2Cp]PF_6$ ($[2c]PF_6$)

A solution of $[Ru\{C\equiv C(H)Ph\}(PPh_3)_2Cp]PF_6$ (0.100 g, 0.107 mmol), NH_4PF_6 (0.0383 g, 0.235 mmol) and cyanogen bromide (0.310 g, 0.293 mmol) in CH_2Cl_2 (10 cm³) was stirred for 14 h. The resulting dark green solution was concentrated, and filtered into rapidly stirred Et₂O, causing precipitation of the product as a dark green solid, which was recrystallised from acetone and hexane (0.066 g, 61%). IR (cm⁻¹): $\nu(C\equiv C)$ 1652. ¹H NMR (d₆-acetone): δ 5.62 (s, 5H, Cp), 7.12–7.52 (m, 35H, Ph). ¹³C NMR (d₆-acetone): δ 96.3 (s, Cp), 123.9 (s, C2), 128.4 (s, C4), 129.4 (overlapped C3, C5), 129.7 (s, C6); 128.9 (dd, ³J_{CP}, ⁵J_{CP} ~ 5 Hz, C_{m,m'}); 131.4 (C_{p,p'}); 131.3, 133.8 (m, C_{i,i'}); 134.0 (dd, ²J_{CP}, ⁴J_{CP} ~ 5 Hz, C_{o,o'}); 340.7 (t, *J*_{CP} = 16 Hz, C1). ³¹P NMR (d₆-acetone) δ 40.9 (s, PPh₃), -143.1 (septet, PF₆). ES(+)-MS (*m/z*): 872.9, [M+H]⁺; 918.2 [M+2Na]⁺. Elemental Anal. Calc. for RuC₄₉H₃₆F₆P₃Br: C, 57.87; H, 3.97. Found: C, 58.10; H, 4.29%.

4.4. Preparation $[Ru\{C\equiv CBr(C_6H_4Me-4)\}(dppe)Cp^*]PF_6$ ($[2d]PF_6$)

A solution of $Ru(C\equiv CC_6H_4Me-4)(dppe)Cp^*$ (0.068 g, 0.090 mmol), NH_4PF_6 (0.037 g, 0.23 mmol) and cyanogen bromide (0.037 g, 0.23 mmol) in CH_2Cl_2 (20 cm³) was stirred for 2 h, after which time the solvent was removed. The residue was redissolved in the minimum volume of CH_2Cl_2 and filtered through a small plug of celite or cotton-wool into Et₂O. The solution was then taken to dryness to yield the product (0.055 g, 63%). IR (cm⁻¹): $\nu(C\equiv C)$ 1649. ¹H NMR: δ 1.68 (s, 15H, C₅Me₅), 2.24 (s, 3H, Me), 2.74 (m, 2H, dppe), 3.08 (m, 2H, dppe), 6.60 (d, *J*_{HH} = 6 Hz, 2H, C₆H₄), 6.73 (d, *J*_{HH} = 6 Hz, 2H, C₆H₄), 7.02–7.54 (m, 20H, Ph). ¹³C NMR: δ 10.4 (s, C₅Me₅), 21.4 (s, Me), 28.8 (m, dppe), 104.7 (s, C₅Me₅), 122.4 (s, C2); 125.3 (C3), 129.1 (C4 overlap with 129.1 multiplet), 129.6 (C5), 138.6 (C6); 129.1 (dd, ²J_{CP}, ⁴J_{CP} ~ 5 Hz, C_{m,m'}), 130.9, 133.2 (m, C_{i,i'}), 131.5, 132.2 (C_{p,p'}), 132.8, 133.3 (dd, ²J_{CP}, ⁴J_{CP} ~ 5 Hz, C_{o,o'}), 332.4 (t, *J*_{CP} = 17 Hz, C1). ³¹P NMR: δ 74.5 (s, dppe), 165.6 (septet, PF₆). ES(+)-MS (*m/z*): 829.13041 [M]⁺; calculated 829.12961 amu.

4.5. Preparation of $Ru(C\equiv CSiMe_3)(PPh_3)_2Cp$ (**5b**)

A solution of $RuCl(PPh_3)_2Cp$ (1.00 g, 1.38 mmol), NaBPh₄ (0.567 g, 1.66 mmol) and $HC\equiv CSiMe_3$ (1.66 g, 16.9 mmol) in a 50:50 THF/NEt₃ solution (75 cm³ total volume) was heated at reflux for 3 h. After this time, the solution was filtered and the solvent removed. The residue was extracted with hot hexane to give a yellow solution, from which the product was isolated by removal of the solvent (0.98 g, 90%). IR (cm⁻¹): $\nu(C\equiv C)$ 1994 cm⁻¹. ¹H NMR: δ -0.03 (s, 9H, SiMe₃), 4.19 (s, 5H, C₅H₅), 7.02 (apparent-t, 24H, H_m), 7.14 (apparent-t, 12H, H_p), 7.53 (m, 24H, H_o). ¹³C NMR: δ 1.7 (SiMe₃); 85.4 (s, Cp); 118.7 (s, C2); 127.5 (dd, ³J_{CP}, ⁵J_{CP} ~ 5 Hz, C_m); 128.3 (C_p); 133.9 (dd, ²J_{CP}, ⁴J_{CP} ~ 5 Hz, C_o); 138.9 (m, C_i); 139.6 (t, *J*_{CP} = 24 Hz, C1). ³¹P NMR: δ 51.2.

Found: ES(+)-MS (*m/z*) 789.18110 [M]⁺; calculated for RuSiP₂C₄₆H₄₄: 789.18362.

4.6. Preparation of $Ru(C\equiv CSiMe_3)(dppe)Cp^*$ (**5c**)

A solution of $RuCl(dppe)Cp^*$ (0.100 g, 0.149 mmol), NaBPh₄ (0.061 g, 0.18 mmol) and $HC\equiv CSiMe_3$ (0.181 g, 1.84 mmol) in a 50:50 THF/NEt₃ (20 cm³ total volume) solution was heated under reflux for 2 h, after which time the solution is filtered and the solvent removed. The residue was extracted with hot hexane to give a yellow solution, from which the product could be isolated by removal of the solvent (0.049 g, 45%). Although the resulting yellow solid turns green upon prolonged exposure to air, NMR analysis reveals little change and the discoloured samples are suitable for further reaction. IR (cm⁻¹): $\nu(C\equiv C)$ 1996. ¹H NMR: δ -0.18 (s, 9H, SiMe₃), 1.52 (s, 15H, C₅Me₅), 2.05 (m, 2H, dppe), 2.75 (m, 2H, dppe), 7.12 (m, 4H, Ph), 7.22 (m, 4H, Ph), 7.30 (m, 8H, Ph), 7.78 (m, 4H, Ph). ¹³C NMR: δ 1.4 (s, SiMe₃); 9.9 (s, C₅Me₅); 29.1 (m, dppe); 92.4 (s, C₅Me₅); 112.1 (s, C2); 126.9, 127.3 (dd, ²J_{CP}, ⁴J_{CP} ~ 5 Hz, C_{m,m'}); 128.7, 128.7 (C_{p,p'}); 133.2, 133.9 (dd, ²J_{CP}, ⁴J_{CP} ~ 5 Hz, C_{o,o'}); 136.9, 138.8 (m, C_{i,i'}); 152.5 (t, *J*_{CP} = 23 Hz, C1). ³¹P NMR: δ 81.6. ES(+)-MS (*m/z*) 733.1 [M+H]⁺.

4.7. Preparation of $[Fe\{C\equiv CBr_2\}(dppe)Cp]BF_4$ ($[6a]BF_4$)

A stirred solution of $Fe(C\equiv CSiMe_3)(dppe)Cp$ (0.060 g, 0.097 mmol) in CH_2Cl_2 (6 cm³) was treated with cyanogen bromide (0.07 mg, 0.66 mmol) to immediately give a dark purple solution, which was stirred for 5 min before the solvent was removed *in vacuo*. The residue dissolved in acetone (5 cm³) and treated with NaBF₄ (0.05 g, 0.455 mmol). After stirring for 2 h, the crude product was treated with diethyl ether to afford a brown precipitate, which was purified by preparative TLC (3:7 acetone/hexane). A dark col-

oured band was collected and recrystallised by slow diffusion of hexane into a dichloromethane solution to give yellow–orange crystals of the product suitable for X-ray crystallography (0.056 g, 73%). IR (cm⁻¹): $\nu(\text{C}=\text{C})$ 1609. ¹H NMR: δ 2.98 (m, 2H, dppe); 3.26 (m, 2H, dppe); 5.32 (s, 5H, Cp); 7.10 (m, 4H, dppe), 7.41 (m, 16H, dppe). ¹³C NMR: δ 29.0 (m, dppe); 91.8 (s, Cp); 111.2 (s, C2); 129.4, 129.7 (dd, ³J_{CP}, ⁵J_{CP} ~ 5 Hz, C_{m,m'}); 131.6, 131.8 (C_{p,p'}); 131.4, 132.9 (dd, ²J_{CP}, ⁴J_{CP} ~ 5 Hz, C_{o,o'}); 132.9, 134.3 (m, C_{i,i'}); 341.6 (t, J_{CP} = 34 Hz, C1). ³¹P NMR: δ 91.1 (s, dppe). ES(+)-MS 703.0, [M]⁺.

4.8. Preparation of [Ru(C≡CBr₂)(PPh₃)₂Cp]BF₄ (**6b**)BF₄

A solution of Ru(C≡CSiMe₃)(PPh₃)₂Cp (0.100 g, 0.151 mmol), cyanogen bromide (0.048 g, 0.45 mmol) and NaBF₄ (0.033 g, 0.30 mmol) in CH₂Cl₂ (15 cm³) was stirred for 4 h, after which time the solvent removed and the product extracted into the minimum amount of CH₂Cl₂. The deep purple product was precipitated into rapidly stirring hexane, collected by filtration and dried (0.020 g, 15%). ¹H NMR (CD₂Cl₂): δ 4.35 (s, 5H, Cp), 7.05–7.80 (m, 30H, Ph). ¹³C NMR (CD₂Cl₂): 96.5 (s, Cp), 109.9 (s, C2), 129.1 (dd, ³J_{CP}, ⁵J_{CP} ~ 5 Hz, Ph_m), 131.7 (s, Ph_p), 133.0 (m, Ph_i), 133.8 (dd, ²J_{CP}, ⁴J_{CP} ~ 5 Hz, Ph_o), 337.9 (t, J_{CP} = 15 Hz, C1). ³¹P NMR (CD₂Cl₂) δ 38.5 (s, PPh₃). ES(+)-MS (*m/z*): 874.95885, [M]⁺; calculated: 874.95983 amu.

4.9. Preparation of [Ru(C≡CBr₂)(dppe)Cp*]BF₄ (**6c**)BF₄

A solution of Ru(C≡CSiMe₃)(dppe)(C₅Me₅) (0.100 g, 0.137 mmol), cyanogen bromide (0.043 g, 0.41 mmol) and NaBF₄ (0.030 g, 0.27 mmol) in CH₂Cl₂ (15 cm³) was stirred for 4 h, after which the solvent removed and the product extracted into the minimum amount of CH₂Cl₂. The deep purple product was precipitated into rapidly stirring hexane and collected by filtration (0.105 g, 94%). ¹H NMR (CD₂Cl₂) δ 1.75 (s, 15H, C₅Me₅); 2.72 (m, 2H, dppe); 2.86 (m, 2H, dppe); 7.09–7.63 (m, 20H, Ph). ¹³C NMR (CD₂Cl₂) δ 10.3 (s, C₅Me₅); 28.9 (m, dppe); 80.2 (s, C₅Me₅); 105.7 (s, C2); 129.2, 128.6 (dd, ²J_{CP}, ⁴J_{CP} ~ 5 Hz, C_{m,m'}); 130.5 (m, C_{i,i'}); 132.1, 132.4 (s, C_{p,p'}); 133.1 (m, C_{o,o'}), 329.3 (t, J_{CP} = 17 Hz, C1). ³¹P NMR (CD₂Cl₂) δ 73.0 (s, dppe). ES(+)-MS (*m/z*): 818.99261, [M]⁺; calculated 818.99113 amu.

Acknowledgements

We thank the EPSRC and the University of Durham for financial support.

Appendix A. Supplementary material

CCDC 740208, 740209, 7402010, 7402011 and 7402012 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.jorganchem.2009.08.027.

References

- [1] (a) R.B. King, M.S. Saran, J. Chem. Soc., Chem. Commun. (1972) 1053; (b) R.B. King, Coord. Chem. Rev. 248 (2004) 1533.
- [2] (a) M.I. Bruce, Chem. Rev. 91 (1991) 197; (b) M.I. Bruce, Chem. Rev. 98 (1998) 2797; (c) M.I. Bruce, in: C. Bruneau, P.H. Dixneuf (Eds.), Metal Vinylidenes and Allenylidenes in Catalysis, Wiley-VCH, Weinham, Germany, 2008, pp. 1–60; (d) M.C. Puerta, P. Valerga, Coord. Chem. Rev. 193–195 (1999) 977.
- [3] (a) B.M. Trost, A. McClory, Chem. Asian J. 3 (2008) 164; (b) C. Bruneau, P.H. Dixneuf, Angew. Chem., Int. Ed. 45 (2006) 2176.
- [4] (a) I.T. Horváth, G. Pályi, L. Markó, J. Chem. Soc., Chem. Commun. (1979) 1054; (b) I.T. Horváth, G. Pályi, L. Markó, G.D. Andreotti, Inorg. Chem. 22 (1983) 1049.
- [5] W. Schulze, K. Seppelt, Inorg. Chem. 27 (1988) 3872.
- [6] (a) M.I. Bruce, M.G. Humphrey, G.A. Koutsantonis, B.K. Nicholson, J. Organomet. Chem. 296 (1985) C47; (b) M.I. Bruce, M.G. Humphrey, G.A. Koutsantonis, B.K. Nicholson, J. Organomet. Chem. 320 (1987) 217.
- [7] M.P. Gamasa, J. Gimeno, E. Lastra, B.M. Martin, A. Anillo, A. Tiripicchio, Organometallics 11 (1992) 1373.
- [8] M.I. Bruce, M. Jevric, C.R. Parker, W. Patalinghug, B.W. Skelton, A.H. White, N.N. Zaitseva, J. Organomet. Chem. 693 (2008) 2915.
- [9] (a) T. Miura, N. Iwasawa, J. Am. Chem. Soc. 124 (2002) 518; (b) T. Miura, H. Murata, K. Kiyota, H. Kusama, N. Iwasawa, J. Mol. Catal. A: Chem. 213 (2004) 59.
- [10] (a) A. Allen, K. Villeneuve, N. Cockburn, E. Fatila, N. Riddell, W. Tam, Eur. J. Org. Chem. (2008) 4178; (b) M.-Y. Lin, S.J. Maddirala, R.-S. Liu, Org. Lett. 7 (2005) 1745; (c) A.W. Sromek, M. Rubina, V. Gevorgyan, J. Am. Chem. Soc. 127 (2005) 10500; (d) V. Mamane, P. Hannen, A. Fürstner, Chem. Eur. J. 10 (2004) 4556.
- [11] (a) N.J. Brown, P.K. Eckert, M.A. Fox, D.S. Yufit, J.A.K. Howard, P.J. Low, Dalton Trans. (2008) 433; (b) R.L. Cordiner, M.E. Smith, A.S. Batsanov, D. Albesa-Jove, F. Hartl, J.A.K. Howard, P.J. Low, Inorg. Chim. Acta 359 (2006) 946; (c) M.E. Smith, R.L. Cordiner, D. Albesa-Jove, D.S. Yufit, F. Hartl, J.A.K. Howard, P.J. Low, Can. J. Chem. 84 (2006) 154; (d) R.L. Cordiner, D. Corcoran, D.S. Yufit, A.E. Goeta, J.A.K. Howard, P.J. Low, Dalton Trans. (2003) 3541.
- [12] S.G. Davies, J. Hibberd, S.J. Simpson, S.E. Thomas, O. Watts, J. Chem. Soc., Dalton Trans. (1984) 701.
- [13] A. Davison, J. Selegue, J. Am. Chem. Soc. 100 (1978) 7763.
- [14] N. Le Narvor, L. Toupet, C. Lapinte, J. Am. Chem. Soc. 117 (1995) 7129.
- [15] M.I. Bruce, G.A. Koutsantonis, Aust. J. Chem. 44 (1991) 207.
- [16] M.I. Bruce, B.G. Ellis, P.J. Low, B.W. Skelton, A.H. White, Organometallics 22 (2003) 3184.
- [17] L. Dahlenburg, A. Weiß, M. Moll, J. Organomet. Chem. 535 (1997) 195.
- [18] Y. Kawata, M. Sato, Organometallics 16 (1997) 1093.
- [19] (a) M. Sato, Y. Kawata, H. Shintate, Y. Habata, S. Akabori, K. Unoura, Organometallics 16 (1997) 1693; (b) M.I. Bruce, B.C. Hall, N.N. Zaitseva, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans. (1998) 1793.
- [20] (a) M.I. Bruce, M.G. Humphrey, M.R. Snow, E.R.T. Tiekink, J. Organomet. Chem. 314 (1986) 213; (b) J.M. Wisner, T.J. Bartczak, J.A. Ibers, Inorg. Chim. Acta 100 (1985) 115; (c) F. Paul, B.G. Ellis, M.I. Bruce, L. Toupet, T. Roisnel, K. Costuas, J.-F. Halet, C. Lapinte, Organometallics 25 (2006) 649.
- [21] (a) J.P. Selegue, J. Am. Chem. Soc. 104 (1982) 119; (b) R.S. Iyer, J.P. Selegue, J. Am. Chem. Soc. 109 (1987) 910; (c) Y.-S. Yen, Y.-C. Lin, Y.-H. Liu, Y. Wang, Organometallics 26 (2007) 1250.
- [22] (a) M.I. Bruce, P.A. Humphrey, M. Jevric, G.J. Perkins, B.W. Skelton, A.H. White, J. Organomet. Chem. 692 (2007) 1748; (b) M. Akita, Y. Tanaka, M. Takeshita, A. Inagaki, M.-C. Chung, Organometallics 25 (2006) 5261; (c) G. Argouarch, P. Thomiot, F. Paul, L. Toupet, C. Lapinte, C.R. Chim. 6 (2003) 209.
- [23] W.M. Khairul, M.A. Fox, N.N. Zaitseva, M. Gaudio, D.S. Yufit, B.W. Skelton, A.H. White, J.A.K. Howard, M.I. Bruce, P.J. Low, Dalton Trans. (2009) 610.
- [24] M.I. Bruce, C. Hameister, A.G. Swincer, R.C. Wallis, Inorg. Synth. 21 (1982) 78.
- [25] M.J. Mays, P.L. Sears, J. Chem. Soc., Dalton Trans. (1973) 1873.
- [26] M.I. Bruce, C. Hameister, A.G. Swincer, R.C. Wallis, Inorg. Synth. 28 (1990) 270.