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REACTIONS OF TRANSITION METAL σ-ACETYLIDES

VII *. SYNTHESIS AND PROPERTIES OF COMPLEXES CONTAINING HALOVINYLIDENE LIGANDS. X-RAY STRUCTURE OF $[Ru(C{=}CIPh)(PPh_3)_2(\eta\text{-}C_5H_5)][I_3]$

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Summary

Addition of halogen (Cl_2, Br_2 or I_2) to ruthenium or osmium acetylide complexes has afforded cationic halovinylidene derivatives; in one case, halogenation of the phenyl group of a phenylacetylide ligand also occurred. The structure of $[Ru(C{=}CIPh)(PPh_3)_2(\eta\text{-}C_5H_5)][I_3]$ has been determined; crystals are monoclinic, space group $P2_1/c$, with a 18.693(5), b 15.460(5), c 15.679(5) Å, β 101.49(2)° and Z 4; 5180 data with $I > 2\sigma(I)$ were refined to R 0.045, R_w 0.051. Significant distances are Ru–C 1.839(7), C=C 1.31(1) Å; angle Ru–C=C is 171.0(7)°.

Introduction

The addition of electrophilic reagents to the β-carbon of transition metal σ-acetylide complexes has now been achieved with a wide range of reagents, including HBF_4 or HPF_6 [1,2], $[Me_3O]^+$ or $[Et_3O]^+$ [3], alkyl halides [4], arenediazonium cations [5] and tropylium cation [5]. The products are vinylidene complexes [6], and the reactions accord with theoretical expectations [7]. In the course of our studies of the reactivity of σ-acetylide complexes such as $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$, we have found that addition of halogens occurs rapidly and quantitatively to form novel halovinylidene complexes. Some of this work has been communicated briefly [8]. Binuclear halovinylidene complexes $Co_2(\mu\text{-}C{=}CR^1R^2)\{\mu\text{-}\overline{CCR^3{=}CR^4C(O)O}\}(CO)_6$

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* For Part VI, see ref. 23.

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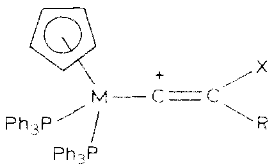
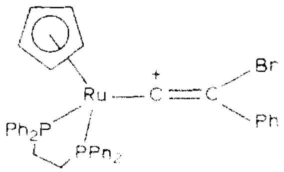
have been obtained from the corresponding μ-butenolido complexes in reactions with α-haloalkynes [9]. Their formation involves a 1,2-shift of the substituent of the haloalkyne and contrasts with previously reported isomerisations of alkynes to vinylidenes which proceed via a 1,2-shift of a hydrogen atom [6].

Results and discussion

Addition of iodine to a tetrahydrofuran (thf) solution of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ resulted in an immediate change in colour from bright yellow to dark green. From the resulting solution deep green microcrystals of the novel iodovinylidene complex $[Ru\{C{=}CIPh\}(PPh_3)_2(\eta\text{-}C_5H_5)][I_3]$ (**1**) were readily obtained. Tentative identification by elemental microanalysis and IR (ν(CC) at 1638 cm^{-1}) was followed by complete characterisation by a single-crystal X-ray study (see below); the compound was not soluble enough for a ^{13}C NMR spectrum to be obtained, but a similar derivative (**2**) prepared from $Ru(C_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)$ exhibited the low-field triplet at δ 325.9 ppm characteristic of the metal-bonded carbon of a vinylidene ligand. Iodine was also found to react similarly with $Ru(C_2\text{-}C_6F_5)(PPh_3)_2(\eta\text{-}C_5H_5)$ and $Os(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ to give the complexes **3** and **4**, respectively; all were obtained as the triiodide salts.

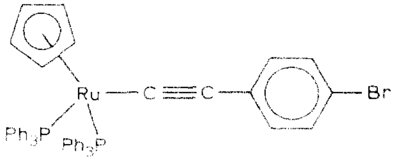
Reactions of bromine with selected acetylides have given bromovinylidene complexes. With $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$, the phenyl group originally present on the phenylacetylide ligand is also brominated, to give the complex $[Ru\{C{=}CBr(C_6H_4Br\text{-}4)\}(PPh_3)_2(\eta\text{-}C_5H_5)][Br_3]$ (**5**). The identity of this complex was confirmed by a single-crystal X-ray study, which also revealed the presence of the tribromide anion. A deficiency of bromine still results in the formation of the 4-bromophenyl complex, so that the ring substitution either precedes, or is concurrent with, the





(**6**)

	X	R	M
1	I	Ph	Ru
2	I	Me	Ru
3	I	C_6F_5	Ru
4	I	Ph	Os
5	Br	C_6H_4Br-4	Ru
7	Cl	Ph	Ru



(**8**)

addition of bromine to the β-carbon of the acetylide ligand. In contrast, bromination of $Ru(C_2Ph)(dppe)(\eta\text{-}C_5H_5)$ afforded the bromo(phenyl)vinylidene complex $[Ru(C{=}CBrPh)(dppe)(\eta\text{-}C_5H_5)]Br$ (**6**).

Chlorine reacts with $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ to give the chloro(4-chlorophenyl)vinylidene complex **7**, which was isolated as the hexafluorophosphate salt. A similar chloro(phenyl)vinylidene compound was first isolated, but not recognised as such, from the decomposition products of the unstable adduct of $[MeCO][SbCl_6]$ and $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$. Subsequently a fast-atom bombardment (FAB) mass spectrum confirmed the identities of these two complexes.

The surprising feature of all these reactions is the resistance to cleavage of the Ru–C bond in the parent acetylide; halogenation of M–C(sp^3) bonds results in rapid formation of M–X and C–X bonds, and similar observations have been reported for M–C(sp^2) bonds, e.g. in $Fe(CMe{=}CHMe)(CO)(PPh_3)(\eta\text{-}C_5H_5)$ [10]. However, we have previously noted the addition of HCl across the C≡C triple bond in *trans*-$Pt(C_2CF_3)_2(PEt_3)_2$ [11], and a similar reaction between *trans*-$Pt(C_2H)_2(PMe_2Ph)_2$ and HCl afforded the α-chlorovinyl complex *trans*-$Pt(CCl{=}CH_2)_2(PMe_2Ph)_2$ [12]. In this case, ready hydrolysis of the α-C–Cl bond was related to the unusual length of this bond and to the stability of the resulting vinylidene-platinum (metal-stabilised carbonium ion) system.

The recent structural determinations of the Ru–C bond length in $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ and related complexes [13,14] was interpreted as showing that the degree of back-bonding into the phenylacetylide ligand was minimal, since the observed value (2.016 Å) is close to that calculated by addition of normal covalent radii for Ru (1.33 Å) and C(sp) (0.66 Å). However, we feel that this observation, coupled with theoretical studies, indicates that while the bond order of the Ru–C bond is close to one, the HOMO of the Ru–C≡C system, which is centred on the β-carbon, nevertheless encompasses the metal as well, providing the observed resistance to cleavage by electrophilic agents. Certainly, the Ru–C bond order of the resulting halovinylidenes is considerably increased, as shown by the structural determinations carried out on complexes **1** and **5**.

Crystal structures of $[Ru\{C{=}C(I)Ph\}(PPh_3)_2(\eta\text{-}C_5H_5)][I_3]$ *(1) and* $[Ru\{C{=}C(Br)(C_6H_4Br\text{-}4)\}(PPh_3)_2(\eta\text{-}C_5H_5)][Br_3]$ *(5)*

Although a brief report describing the structure of the cation in **5** has been presented [8], it is convenient to compare the structures of the two cations in detail here. These are shown in Figs. 1 and 2, together with the numbering schemes used; Table 1 summarises pertinent bond parameters determined for each complex.

The cations in **1** and **5** contain the now-familiar ruthenium(II) atoms coordinated by the C_5H_5 group and two PPh_3 ligands; the nearly octahedral geometry is achieved by the halovinylidene ligand in the sixth position. The Ru–C(cp) distances lie within the ranges 2.250(5)–2.284(5) and 2.226(11)–2.306(11) Å (parameters given for **1** and **5**, respectively), with the longest Ru–C separation being approximately *trans* to the vinylidene ligand. The two Ru–P distances (2.337(2) and 2.356(2), and 2.366(5) Å, respectively) are normal for this type of complex.

The Ru–C(vinylidene) separations are 1.839(7) and 1.85(1) Å, providing evidence for considerable multiple bond-order and hence back-bonding into the unsaturated ligand (cf. Ru–CO 1.869(2) Å in $[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)][BPh_4]$ [12]). The C(1)–C(2) bonds have lengths of 1.31(1) and 1.31(2) Å, both of which are short for

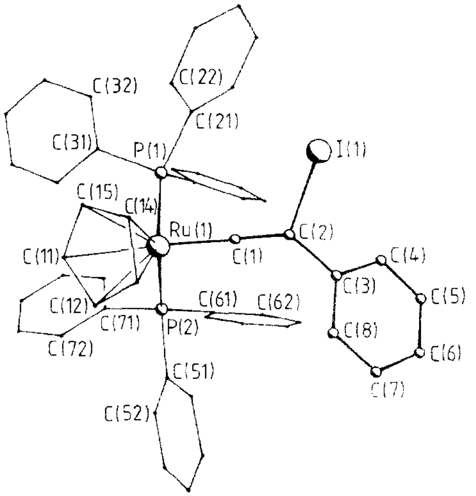


Fig. 1. Computer drawing of cation in [Ru{C=C(I)Ph}$(PPh_3)_2(\eta$-$C_5H_5)$][I_3] (1), showing atom numbering scheme.

C=C double bonds. The Ru–C=C moiety is slightly bent at the α-carbon (angles Ru–C(1)–C(2) 171.0(7) and 169.4(14)°), while angles about the β-carbon in **1** (C(1)–C(2)–I(1) 115.7(6), C(1)–C(2)–C(3) 129.4(7), I(1)–C(2)–C(3) 114.9(5)°) show bending of the C–I bond caused by the steric bulk of the Ph group. The C(2)–I(1) bond (2.124(7) Å) is similar to that in CH_2=CHI (2.092(5) Å) [15].

The geometry of the triiodide anion differs somewhat from those that have been found previously, with I–I separations of 2.896(1) ($\mathbf{d}^1$), 2.923(1) Å ($\mathbf{d}^2$), and angle

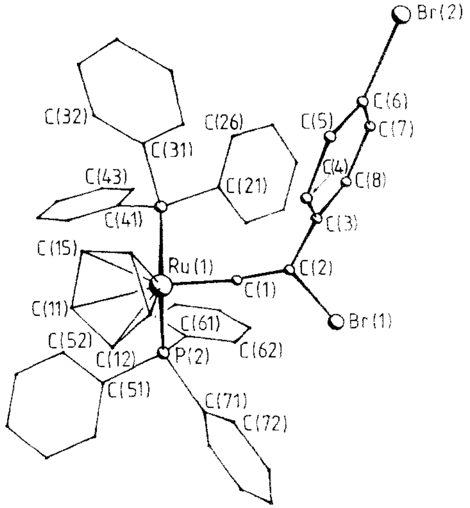
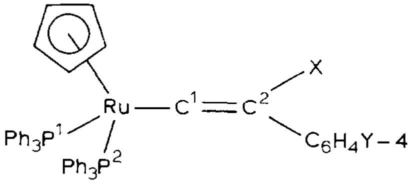


Fig. 2. Computer drawing of cation in [Ru{C=CBr(C_6H_4Br-4)}$(PPh_3)_2(\eta$-$C_5H_5)$][Br_3] (5), showing atom numbering scheme.

TABLE 1

SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR COMPLEXES 1 AND 5



	1	**5**
	X = I	X = Br
	Y = H	Y = Br
Ru-C(1)	1.839(7)	1.85(1)
C(1)-C(2)	1.31(1)	1.31(2)
C(2)-X	2.124(7)	1.93(2)
C(2)-C(Ar)	1.49(1)	1.49(2)
Ru-P(1)	2.337(2)	2.366(5)
Ru-P(2)	2.356(2)	2.366(5)
Ru-C(cp) (av)	2.26	2.26
P(1)-Ru-P(2)	97.0(1)	103.3(2)
P(1)-Ru-C(1)	89.6(2)	88.2(5)
P(2)-Ru-C(1)	97.4(2)	93.6(5)
Ru-C(1)-C(2)	171.0(7)	169.4(14)
C(1)-C(2)-X	115.7(6)	116.8(13)
C(1)-C(2)-C_6H_4Y	129.4(7)	126.8(15)

I(3)-I(2)-I(4) 174.7(1)°. A recent survey [16] quotes ranges of 2.794-2.850 (**d**^{1}) and 3.005-3.123 Å (**d**^{2}), with angles of 176.3-179.9°; in the present case, the smaller difference between **d**^{1} and **d**^{2} is no doubt the result of little or no interaction between the anion and the complex cation.

FAB mass spectra

The fast atom bombardment (FAB) technique of obtaining mass spectra is well suited to the study of ionic and high molecular weight compounds which cannot be volatilised in a conventional electron impact source. We have measured the FAB mass spectra of three typical halovinylidene complexes, **2**, **6** and **7**.

As found with other vinylidene complexes studied recently [17], the strong molecular cation readily loses the added electrophile (here X^+) to give an ion which corresponds to the molecular ion of the parent acetylide. In all spectra the major decomposition route of $[M^+]$ is loss of C_2Ph and PPh_3; in **7**, loss of C_5H_6 was found. The base peaks are either $[Ru(PPh_3)(C_5H_5)]^+$ or $[Ru(dppe)(C_5H_5)]^+$, depending on whether the tertiary phosphine ligand is monodentate or bidentate; further fragmentation involves loss of either Ph (from the former) or PPh_2 and C_2H_4 (from dppe), in both cases giving $[Ru(PPh_2)(C_5H_5)]^+$. Unusually, the σ-bonded acetylide fragment is preserved while Ph is lost from coordinated PPh_3, as shown by the formation of $[Ru(C_2R)(PPh_2)(C_5H_5)]^+$ (R = Me or Ph). Comparison with the EI mass spectra of $Ru(C_2R)(PPh_3)_2(\eta\text{-}C_5H_5)$ (R = Me, Ph) shows the formation of similar ions, except that the strong ion at *m/z* 429 ($[Ru(PPh_3)(C_5H_5)]^+$) in the spectra of the vinylidene complexes is replaced by one at

m/z 427, probably formed by linking of C_5H_4 and $C_6H_4PPh_2$ units as found in $Ru(C_6F_4N{=}NC_6F_5)\{PPh_2(C_6H_4\text{-}\eta\text{-}C_5H_5)\}$ [18].

Comparison of the FAB MS of complex **9** with that of the hexachloroantimonate salt showed the same molecular ions to be present in both complexes. The presence of carbonyl-containing ions in several spectra can be attributed to the formation of small amounts of the corresponding carbonyl cation by oxidation of the vinylidene ligand as previously observed [6].

Reactions of $[Ru\{C{=}C(Br)(C_6H_4Br\text{-}4)\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$

Attempted replacement of the vinylidene bromine by H or OMe resulted in formal displacement of Br^+ and formation of $Ru(C_2C_6H_4Br\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)$ (**8**), readily characterised by elemental microanalysis, and from its IR, NMR and mass spectra (see Experimental). These reactions are not altogether surprising, since the formation of the halovinylidene complexes occurs by formal addition of the electrophile X^+ to the β-carbon of the acetylide. In this behaviour, these complexes resemble the cycloheptatrienylvinylidene complexes [19].

Conclusion

Addition of halogens (Cl_2, Br_2, I_2) to substituted acetylide complexes of ruthenium or osmium results in the formation of cationic halovinylidene complexes. These are often isolated as polyhalide (Br_3^-, I_3^-) salts, and fully characterised by X-ray structures of examples of the bromo- and iodo-vinylidene complexes. Nucleophiles such as H^- or OMe^- displace X^+ to give the related acetylide complex.

Experimental

General conditions. Reactions were run under nitrogen and no special precautions were taken to exclude air during work-up, since most complexes proved to be stable in air as solids, and for short times in solution. Solvents were extensively dried and distilled (dme and thf from sodium/benzophenone) before use.

Instruments. Perkin–Elmer 683 double-beam spectrometer, NaCl optics (IR); Bruker WP80 spectrometer (^1H NMR at 80 MHz, ^{13}C NMR at 20.1 MHz); GEC-Kratos MS3074 mass spectrometer (mass spectra at 70 eV ionising energy, 4 kV accelerating potential).

FAB mass spectra were obtained on a VG ZAB 2HF instrument equipped with a FAB source. Argon was used as the exciting gas, with source pressures typically 10^{-6} mbar; the FAB gun voltage was 7.5 kV, current 1 mA, with ion accelerating potential 8 kV. Samples were dissolved in dichloromethane (ca. 0.5 *M*) and a drop of this solution was added to a drop of matrix (3-nitrobenzyl alcohol or dithioerythritol/dithiothreitol (1/6)), the volatile solvent evaporated and the resulting solution applied to the FAB probe tip.

Starting materials. The literature method was used to prepare ruthenium and osmium acetylide complexes [20].

Preparation of halovinylidenes

A. Reaction of iodine with η^1*-acetylides*

(a) With $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$. Addition of iodine (160 mg, 0.709 mmol) to a stirred solution of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (200 mg, 0.253 mmol) in thf (20

ml) resulted in an immediate colour change to dark green. After stirring for 20 min and removal of solvent, the residue was extracted with CH_2Cl_2 (2 ml) and the extract filtered into stirred diethyl ether (excess) to give green microcrystals of $[Ru\{C=C(I)Ph\}(PPh_3)_2(\eta\text{-}C_5H_5)][I_3]$ (**1**) (281 mg, 85%). An analytical sample was recrystallised (CH_2Cl_2/EtOH) m.p. 134–135°C (dec.) (Found: C, 44.85; H, 3.11; I, 36.56; $C_{49}H_{40}I_4P_2Ru$ calc: C, 45.29; H, 3.10; I, 39.06%). Infrared (Nujol): ν(C=C) 1638s; other bands at 1590w, 1518w, 1480(sh), 1438m, 1435m, 1412w, 1310w, 1187w, 1160w, 1092s, 1075w, 1040w, 1018w, 998w, 845s, 823m, 770w, 745s, 722w, 705w, 695vs, 613w cm^{-1}. ^1H NMR: δ $[(CD_3)_2CO]$ 5.46 (s, 5H, C_5H_5), 7.57 (m, 35H, Ph).

(b) With $Ru(C_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)$. As in (a) above, iodine (200 mg, 0.788 mmol) and $Ru(C_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)$ (200 mg, 0.274 mmol) afforded $[Ru\{C=C(I)Me\}(PPh_3)_2(\eta\text{-}C_5H_5)][I_3]$ (**2**) as dark olive-green crystals (293 mg, 86%) m.p. 140–142°C (dec.) (Found: C, 42.55; H, 3.10; I, 40.03; $C_{49}H_{40}I_4P_2Ru$ calc: C, 42.68; H, 3.15; I, 41.00%). Infrared: ν(C=C) 1690m; other bands at 1482m, 1438s, 1370w, 1185w, 1080m, 1035w, 1000m, 836w, 823w, 750m, 742m, 699s, 665w cm^{-1}. ^1H NMR: δ ($CDCl_3$) 2.22 (s, 3H, CH_3), 5.26 (s, 5H, C_5H_5), 7.03–7.39 (m, 30H, Ph). ^{13}C NMR: δ ($CDCl_3$) 18.57 (s, CH_3), 95.05 (s, C_5H_5), 128.7–133.9 (m, Ph), 325.91 (t, J(CP) 15 Hz, Ru=C).

(c) With $Ru(C_2C_6F_5)(PPh_3)_2(\eta\text{-}C_5H_5)$. As in (a) above, iodine (150 mg, 0.59 mmol) and $Ru(C_2C_6F_5)(PPh_3)(\eta\text{-}C_5H_5)$ (200 mg, 0.227 mmol) gave $[Ru\{C=C(I)C_6F_5\}(PPh_3)_2(\eta\text{-}C_5H_5)][I_3]$ (**3**) as dark green microcrystals (118 mg, 38%), m.p. 124–125°C (Found: C, 41.40; H, 2.55; I, 34.52. $C_{49}H_{35}F_5I_4P_2Ru$ calc: C, 42.36; H, 2.54; I, 36.53%). Infrared (Nujol): ν(C=C) 1652m, 1649m, 1630m; other bands at 1588w, 1519s, 1497vs, 1482m, 1439s, 1310w, 1188w, 1159w, 1131w, 1100m, 1091m, 1012w, 1000w, 934s, 857w, 835w, 828w, 752s, 745s, 739w, 705(sh), 697vs, 660m cm^{-1}. ^1H NMR: δ ($CDCl_3$) 5.40 (s, 5H, C_5H_5), 7.27–7.36 (m, 30H, Ph).

(d) With $Os(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$. As in (a) above, iodine (73 mg, 0.288 mmol) and $Os(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (80 mg, 0.091 mmol) afforded $[Os\{C=C(I)Ph\}(PPh_3)_2(\eta\text{-}C_5H_5)][I_3]$ (**4**) as dark green crystals (63 mg, 50%), m.p. 198–199°C (Found: C, 41.97; H, 2.93; I, 35.46; $C_{49}H_{40}I_4OsP_2$ calc: C, 42.38; H, 2.9; I, 36.56%). Infrared: ν(C=C) 1640m, other bands at 1360w, 1260m, 1100m, 1090s, 1000w, 842m, 825m, 742s, 722m, 696s, 660m cm^{-1}. ^1H NMR: δ ($CDCl_3$) 5.44 (s, 5H, C_5H_5), 6.9–7.4 (m, 35H, C_6H_5).

B. Reactions of bromine

(a) With $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$. Neat bromine (1 ml, excess) was added dropwise to a stirred solution of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (1000 mg, 1.26 mmol) in tetrahydrofuran (20 ml) to give immediately a dark green solution. After 15 min, evaporation to dryness, extraction of the residue with CH_2Cl_2 and filtration into excess Et_2O afforded green microcrystals of $[Ru\{C=CBr(C_6H_4Br\text{-}4)\}(PPh_3)_2(\eta\text{-}C_5H_5)][Br_3]\cdot Et_2O$ (**5**) (1401 mg, 88%) (Found: C, 47.01; H, 3.38; Br, 30.25; $C_{49}H_{39}Br_5P_2Ru\cdot C_4H_{10}O$ calc: C, 46.54; H, 3.11; Br, 31.60%). IR (KBr disc): ν(C=C) 1638s; other bands at 3060w, 2930w, 2860w, 1482s, 1435s, 1412w, 1392w, 1315w, 1272w, 1178w, 1160w, 1092s, 1072m, 1029w, 1009w, 1000m, 848m, 825m, 752(sh), 740s, 730m, 695vs, 685(sh), 660w, 538s, 523vs, 514w, 498m, 490m, 465w, 441w, 426w cm^{-1}. ^1H NMR: δ ($CDCl_3$) 1.21 (t, J(HH) 7 Hz, 6H, Me), 3.48 (q,

J(HH) 7 Hz, 4H, CH_2), 5.35 (s, 5H, C_5H_5), 6.6–7.5 (m, 34H, Ph + C_6H_4). ^{13}C NMR: δ ($CDCl_3$) 97.23 (s, C_5H_5), 128.0–135.0 (m, Ph + C_6H_4).

Metathesis of the tribromide counterion was achieved by stirring a solution of the vinylidene with a twofold excess of NH_4PF_6. (Found: C, 52.12; H, 3.77; Br, 15.06; $C_{49}H_{39}Br_2F_6P_3Ru$ calc: C, 53.72; H, 3.59; Br, 14.59%).

(b) With Ru(C_2Ph)(dppe)(η-C_5H_5). To a stirred solution of Ru(C_2Ph)(dppe)(η-C_5H_5) (200 mg, 0.30 mmol) in thf (15 ml) was added 20 ml of a bromine in CCl_4 solution (ca. 6 mg/ml) resulting in formation of a green precipitate of [Ru{C=C(Br)Ph}(dppe)(η-C_5H_5)]Br · 0.5Et_2O (**6**) (251 mg, 100%). Dark green crystals, m.p. 79–80°C (dec.) were obtained from addition of diethyl ether to a concentrated CH_2Cl_2/EtOH solution of **6**. (Found: C, 55.97; H, 4.60; Br, 18.73; $C_{39}H_{34}Br_2P_2Ru$ · 0.5Et_2O calc: C, 57.09; H, 4.56; Br, 18.53%). Infrared (Nujol): ν(C=C) 1640s; other bands at 1488(sh), 1445s, 1439vs, 1419m, 1358w, 1312w, 1100s, 1071w, 1045w, 1000w, 880w, 850m, 831m, 798w, 758m, 750m, 742m, 718s, 706s, 690s, 618m cm^{-1}. ^1H NMR: δ ($CDCl_3$) 1.20 (t, J(HH) 7 Hz, $(CH_3CH_2)_2O$), 2.5–3.8 (m, 6H, PCH_2 + $(CH_3CH_2)_2O$), 5.63 (s, 5H, C_5H_5), 7.34 (m, 25H, C_6H_5).

C. Reaction between chlorine and Ru(C_2Ph)(PPh_3)$_2$(η-C_5H_5)

A stirred solution of Ru(C_2Ph)(PPh_3)$_2$(η-C_5H_5) (200 mg, 0.25 mmol) in thf (20 ml) was treated with 6 ml of a solution of chlorine in diethyl ether (9.1 mg/ml) immediately giving a green solution. After 20 min the solution was filtered and evaporated to dryness. The residue was extracted with CH_2Cl_2 (20 ml) and NH_4PF_6 (300 mg, 1.84 mmol) was added to the solution. After 10 min, addition of EtOH and reduction in volume resulted in separation of emerald green needles of [Ru{C=C(Cl)Ph}(PPh_3)$_2$(η-C_5H_5)][PF_6] (**7**) (70 mg, 28%) m.p. 139–141°C (dec) (Found: C, 56.95; H, 4.07; Cl, 8.93; $C_{49}H_{40}ClF_6P_3Ru$ calc: C, 58.47; H, 3.90; Cl, 7.04%). Infrared (Nujol): ν(C=C) 1650s, ν(PF) 840vs(br); other bands at 1483s, 1430s, 1416m, 1312m, 1270m, 1220w, 1160m, 1092s, 1075(sh), 1030w, 1020w, 1000m, 880m, 860vs, 790m, 745(sh), 739s, 697vs, 640(sh), 635w, 620w cm^{-1}. ^1H NMR: δ ($CDCl_3$) 5.63 (s, 5H, C_5H_5), 7.10–7.73 (m, 34H, Ph).

Preparation of [Ru{C=C(Cl)Ph}(PPh_3)$_2$(η-C_5H_5)][$SbCl_6$]

A suspension of [MeCO][$SbCl_6$] (879 mg) in diethyl ether (10 ml) was added to Ru(C_2Ph)(PPh_3)$_2$(η-C_5H_5) (200 mg, 0.253 mmol) in the same solvent (10 ml). An immediate change from yellow suspension to red solution occurred. Evaporation afforded a red-orange solid which slowly changed to dark green overnight. The product was isolated by preparative TLC (silica gel, 1/1 acetone/light petroleum) from the largest of three green bands; crystallisation (benzene/ethanol) gave a green powder identified as [Ru{C=C(Cl)Ph}(PPh_3)$_2$(η-C_5H_5)][$SbCl_6$] (121 mg, 41%), m.p. 163–164°C (dec.) (Found: C, 50.69; H, 3.28; $C_{49}H_{40}Cl_7P_2RuSb$ calc: C, 50.66; H, 3.47%). Infrared (KBr disc): ν(C=C) 1655m; ν(SbCl) 346s; other bands at 3060w, 2922w, 2850w, 1481m, 1434s, 1418w, 1382w, 1361w, 1310w, 1188w, 1161w, 1089s, 1071w, 1025w, 999w, 832w, 821w, 781w, 740s, 693s, 614w, 551w, 532s, 520s, 512s, 500m, 461w, 422w cm^{-1}. ^1H NMR: δ ($CDCl_3$) 5.28 (s, 5H, C_5H_5), 7.26 (m, 35H, Ph).

Reactions of halovinylidene complexes

A. Reactions of [Ru{C=CBr(C_6H_4Br-4)}(PPh_3)$_2$(η-C_5H_5)][PF_6]

(i) With K[BH(CHMeEt)$_3$] (K-Selectride). Treatment of a green solution of **8**

(200 mg, 0.182 mmol) thf (10 ml) with *K*-Selectride (0.4 ml of 0.5 *M* solution in thf) gave a yellow solution. Addition of MeOH (10 ml) and reduction in volume gave a yellow precipitate of $Ru(C_2C_6H_4Br\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)$ (**9**) (101 mg, 64%) m.p. 192–197°C (dec) (Found: C, 67.40; H, 4.82; Br, 9.01%, *M* (mass spectrometry) 872; $C_{49}H_{39}BrP_2Ru$ calc: C, 67.59; H, 4.51; Br, 9.18%, *M* 872). Infrared (Nujol): $\nu(C{\equiv}C)$ 2076vs; other bands at 1587w, 1482s, 1436s, 1210w, 1185w, 1160w, 1095m, 1090m, 1068m, 1005m, 828m, 822w, 810w, 800w, 759m, 747m, 739m, 699vs cm^{-1}. ^1H NMR: δ ($CDCl_3$) 4.32 (s, 5H, C_5H_5), 7.14 (m, 34H, Ph).

(ii) With sodium methoxide. A solution of **8** (200 mg, 0.182 mmol) in CH_2Cl_2 (20 ml) was treated with NaOMe (0.5 ml of ca. 1 *M* solution in MeOH). After filtering, addition of MeOH and concentration of the solution a yellow powder of **9** was obtained (84 mg, 53%). The melting point infrared, NMR and mass spectra were identical with those obtained for the product from the reaction with *K*-Selectride.

FAB mass spectra

The following spectra were obtained (*m/z*, based on ^{35}Cl, ^{79}Br and ^{102}Ru, assignment and relative intensity).

Peaks marked ★ are centres of overlapping multiplets consisting of the designated ion and ions related to it by loss of one or two H atoms.

(i) $[Ru(C{=}ClMe)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ *(2).* 857, $[M]^+$, 57; 730★, $[M-I]^+$, 37; 691, $[Ru(PPh_3)_2(C_5H_5)]^+$, 23; 468★, $[M-I-PPh_3]^+$, 27; 429★, $[Ru(PPh_3)(C_5H_5)]^+$, 100; 391★, $[Ru(C_2Me)(PPh_2)(C_5H_5)]^+$, 36; 350★, $[Ru(PPh_2)(C_5H_5)-2H]^+$, 29.

(ii) $[RuC{=}CBrPh)(dppe)(\eta\text{-}C_5H_5)][Br_3]$ *(6).* 761, ?$[M+O]^+$, 5; 745, $[M]^+$, 56; 681, –, 5; 666★, $[M-Br]^+$, 49; 591, $[Ru(CO)(dppe)C_5H_5)]^+$, 32; 565, $[Ru(dppe)(C_5H_5)]^+$, 100; 380★, $[Ru(C_2H_4PPh_2)(C_5H_5)]^+$, 18; 352★, $[Ru(PPh_2)(C_5H_5]^+$, 30.

(iii) $[Ru(C{=}CClPh)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ *(7).* 843★, ?$[M+O]^+$, 1; 827, $[M]^+$, 53; 792★, $[M-Cl]^+$, 6; 719, $[Ru(CO)(PPh_3)_2(C_5H_5)]^+$, 4; 691, $[Ru(PPh_3)_2(C_5H_5)]^+$, 13; 624★, –, 2; 612★, $[Ru(PPh_2)(PPh_3)(C_5H_5)]^+$, 2; 565★, $[M-PPh_3]^+$, 3; 530, $[M-Cl-PPh_3]^+$, 33; 465★, $[Ru(C_2Ph)(PPh_3)]^+$, 70; 453, $[Ru(C_2Ph)(PPh_2)(C_5H_5)]^+$, 30; 429★, $[Ru(PPh_3)(C_5H_5)]^+$, 100; 352★, $[Ru(PPh_2)(C_5H_5)]^+$, 27; 287★, $[Ru(PPh_2)]^+$, 21; 244★, $[RuPh(C_5H_5)]^+$, 18.

(iv) $[Ru\{C{=}C(Cl)Ph\}(PPh_3)_2(\eta\text{-}C_5H_5)][SbCl_6]$. (Relative intensities not recorded). 827, $[M]^+$; 792, $[Ru(C_2Ph)(PPh_3)_2(C_5H_5)]^+$; 719, $[Ru(CO)(PPh_3)_2(C_5H_5)]^+$; 691, $[Ru(PPh_3)_2(C_5H_5)]^+$; 530, $[Ru(C_2Ph)(PPh_3)(C_5H_5)]^+$; 429, $[Ru(PPh_3)(C_5H_5)]^+$,

Crystallography

Suitable dark-green crystals of **1** were obtained from CH_2Cl_2/EtOH. Preliminary precession photography indicated a monoclinic unit cell. A crytal was mounted on a Nicolet XRD P3 four-circle diffractometer using monochromated Mo-K_α X-radiation for all measurements.

Crystal data. $C_{49}H_{40}I_4P_2Ru$, $M = 1299.5$, monoclinic, space group $P2_1/c$, *a* 18.693(5), *b* 15.460(5), *c* 15.679(5) Å, β 101.49(2)°, *U* 4440(2) $Å^3$ (from 25 high angle reflections), λ(Mo-K_α) 0.7107 Å. D_c 1.94 g cm^{-3}, D_m 1.92 g cm^{-3} for $Z = 4$, μ(Mo-K_α) 32.64 cm^{-1}, *T* 183 K.

TABLE 2

FINAL POSITIONAL PARAMETERS FOR $[\mathrm{Ru}\{\mathrm{C{=}C(I)(Ph)}\}(\mathrm{PPh_3})_2(\mathrm{C_5H_5})][\mathrm{I_3}]$

Atom	x	y	z	Atom	x	y	z
Ru(1)	0.2203(1)	0.5771(1)	0.2561(1)	C(36)	0.1378(2)	0.3539(2)	0.2277(3)
I(1)	0.4545(1)	0.6270(1)	0.2597(1)	C(41)	0.3006(2)	0.4045(3)	0.3956(2)
P(1)	0.2710(1)	0.4393(1)	0.2836(1)	C(42)	0.2818(2)	0.3234(3)	0.4232(2)
P(2)	0.1678(1)	0.5863(1)	0.3806(1)	C(43)	0.3100(2)	0.2958(3)	0.5080(2)
C(1)	0.3092(4)	0.6253(4)	0.3041(5)	C(44)	0.3570(2)	0.3494(3)	0.5651(2)
C(2)	0.3714(4)	0.6656(5)	0.3264(5)	C(45)	0.3757(2)	0.4306(3)	0.5375(2)
C(3)	0.3935(4)	0.7335(5)	0.3937(5)	C(46)	0.3476(2)	0.4581(3)	0.4527(2)
C(4)	0.4557(4)	0.7247(5)	0.4579(5)	C(51)	0.1271(2)	0.6917(2)	0.3934(3)
C(5)	0.4750(5)	0.7872(6)	0.5189(6)	C(52)	0.0778(2)	0.6986(2)	0.4491(3)
C(6)	0.4322(5)	0.8593(6)	0.5194(6)	C(53)	0.0533(2)	0.7798(2)	0.4694(3)
C(7)	0.3689(4)	0.8691(6)	0.4583(6)	C(54)	0.0782(2)	0.8542(2)	0.4341(3)
C(8)	0.3500(4)	0.8070(5)	0.3942(5)	C(55)	0.1275(2)	0.8473(2)	0.3784(3)
C(11)	0.1162(2)	0.5610(3)	0.1528(4)	C(56)	0.1520(2)	0.7661(2)	0.3581(3)
C(12)	0.1228(2)	0.6490(3)	0.1789(4)	C(61)	0.2212(2)	0.5825(3)	0.4922(3)
C(13)	0.1876(2)	0.6824(3)	0.1569(4)	C(62)	0.2814(2)	0.6377(3)	0.5091(3)
C(14)	0.2210(2)	0.6150(3)	0.1173(4)	C(63)	0.3210(2)	0.6472(3)	0.5939(3)
C(15)	0.1768(2)	0.5399(3)	0.1148(4)	C(64)	0.3004(2)	0.6015(3)	0.6618(3)
C(21)	0.3527(2)	0.4223(3)	0.2384(3)	C(65)	0.2401(2)	0.5464(3)	0.6450(3)
C(22)	0.3485(2)	0.4361(3)	0.1497(3)	C(66)	0.2006(2)	0.5368(3)	0.5602(3)
C(23)	0.4093(2)	0.4203(3)	0.1127(3)	C(71)	0.0920(2)	0.5112(3)	0.3764(3)
C(24)	0.4741(2)	0.3906(3)	0.1645(3)	C(72)	0.0232(2)	0.5346(3)	0.3297(3)
C(25)	0.4782(2)	0.3768(3)	0.2533(3)	C(73)	0.0341(2)	0.4753(3)	0.3185(3)
C(26)	0.4175(2)	0.3926(3)	0.2902(3)	C(74)	−0.0226(2)	0.3925(3)	0.3539(3)
C(31)	0.2130(2)	0.3508(2)	0.2322(3)	C(75)	0.0462(2)	0.3690(3)	0.4006(3)
C(32)	0.2444(2)	0.2784(2)	0.2011(3)	C(76)	0.1035(2)	0.4284(3)	0.4119(3)
C(33)	0.2005(2)	0.2093(2)	0.1655(3)	I(2)	0.2366(1)	0.0861(1)	0.3760(1)
C(34)	0.1252(2)	0.2124(2)	0.1611(3)	I(3)	0.6227(1)	0.5801(1)	0.1746(1)
C(35)	0.0939(2)	0.2848(2)	0.1922(3)	I(4)	0.0922(1)	0.1074(1)	0.4182(1)

A total of 6040 unique reflections was collected in the range $3 < 2\theta < 55°$ using a θ–2θ scan. These were corrected for Lorentz and polarisation effects, and for absorption based on a series of azimuthal scans (maximum and minimum transmission factors were 0.95 and 0.66 respectively). The 5180 reflections with $I > 2\sigma(I)$ were used in all subsequent calculations.

The structure was solved by a combination of direct methods and Patterson maps to reveal the Ru and I atoms: all other non-hydrogen atoms were routinely located in subsequent difference maps. In the final cycles of full-matrix least-squares refinement the Ru, I and P atoms were assigned anisotropic temperature factors while all other atoms were treated isotropically. The cyclopentadienyl and the phenyl rings of the triphenylphosphine ligands were included as rigid groups (d(C–C) 1.42 and 1.395 Å, respectively) with all hydrogen atoms in calculated positions (d(C–H) 0.98 Å). Convergence gave $R = 0.045$, $R_w = 0.051$, where $w = [\sigma^2(F_0) + 0.00075F_0^2]^{-1}$. A final difference map gave three peaks greater than 1 eÅ^{-3}, adjacent to the terminal iodine atoms of the anion. Neutral atom scattering factors were taken from ref. [21], while principal computing employed the SHELX programs [22].

Coordinates for non-hydrogen atoms are listed in Table 2. Supplementary material which includes thermal parameters for non-hydrogen atoms, atomic coordinates and thermal parameters for hydrogen atoms, complete bond lengths and bond angles, and structure factors, may be obtained from the authors.

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