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Preliminary communication

REACTIONS OF TRANSITION METAL ACETYLIDE COMPLEXES

IV*. SYNTHESIS AND X-RAY STRUCTURE OF A BROMOVINYLIDENE COMPLEX, $[Ru\{C{=}CBr(C_6H_4Br\text{-}4)\}(PPh_3)_2(\eta\text{-}C_5H_5)][Br_3]\cdot CHCl_3$

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Summary

Halogens react with ruthenium acetylide complexes to give dark green halovinylidene derivatives. In one case, bromination of the phenyl ring of the parent phenylacetylide complex occurs, as shown by the X-ray structure of $[Ru\{C{=}CBr(C_6H_4Br\text{-}4)\}(PPh_3)_2(\eta\text{-}C_5H_5)][Br_3]\cdot CHCl_3$. The Ru—C and C=C distances are 1.85(1) and 1.31(2) Å, respectively.

Both experimental [1] and theoretical studies [2] have shown that in transition metal acetylide complexes, the β-carbon is electron-rich, and behaves as a nucleophile towards reagents such as H^+, Me^+ and Et^+ (as the trialkyloxonium salts), alkyl halides [3], $C_7H_7^+$ and arenediazonium salts [4]. The resulting complexes contain vinylidene ligands, and there is considerable current interest in the chemistry of these metallocumulene complexes [5].

We have found that this characteristic reactivity extends to the halogens Cl_2, Br_2 and I_2. For example, excess liquid bromine reacted with $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (1) in tetrahydrofuran solution to give an essentially quantitative yield of a dark green crystalline complex 2. Its relative insolubility, and salt-like nature, precluded full characterisation by conventional spectroscopic methods; a single crystal X-ray study was therefore carried out.

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*For Part 3, see ref. 4.

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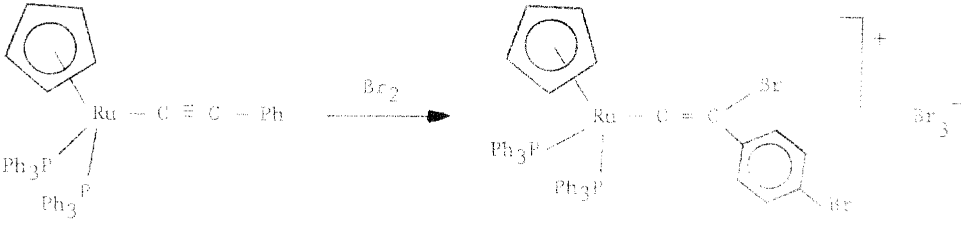

(1) (2)

A suitable crystal was obtained from a chloroform/light petroleum mixture, and was mounted on an Enraf—Nonius CAD4 four-circle diffractometer, equipped with a graphite monochromator. The lattice parameters were determined and refined from 23 high-angle reflections by a least-squares routine.

Crystal data. $C_{40}H_{39}Br_2P_2Ru^+ \cdot Br_3^- \cdot CHCl_3$, M.Wt. 1309.8, monoclinic, space group $P2_1/c$, a 19.390(7), b 14.472(4), c 19.861(5) Å, β 116.52(3)°, U 4987 Å^3, D_c ($Z = 4$) 1.74 g cm^{-3}, $F(000)$ 2560 electrons, λ(Mo-K_α) 0.7107 Å, μ(Mo-K_α) 44.56 cm^{-1}. Crystal size 0.45 × 0.20 × 0.38 mm^3. T 293 K.

A total of 6021 data in the range $1.3 < \theta < 21°$ were collected, of which 4391 were unique; the 2411 data with $I > 2.5\sigma(I)$ were used in the structure solution [6]. A combination of direct methods and Patterson maps revealed the Ru and Br atoms; all other non-hydrogen atoms were routinely located in subsequent difference maps. For the final cycles of least squares refinement, the Ru, Br and Cl atoms, and the C of $CHCl_3$, were assigned anisotropic temperature factors; all other atoms were treated isotropically. The cyclopentadienyl and phenyl rings were included as rigid groups (d(C—C) 1.42 and 1.395 Å, respectively) with all hydrogens in calculated positions (d(C—H) 1.08 Å). The C_5H_5, C_6H_5 and C_6H_4Br hydrogens had a common thermal parameter. Final convergence at $R = 0.0547$, $R_w = 0.0566$ was obtained using the weightinh scheme $w = 1.523/[\sigma^2(F_0) + 0.001139(F_0)^2]$. The largest residual in the final difference map was 0.6 eÅ^{-3}, associated with the Br_3^- ion[*].

The crystal structure determination revealed that the reaction product is the tribromide salt of a bromovinylideneruthenium cation. A plot of the cation is given in Fig. 1, which also includes selected bond distances and angles. In addition, a fifth bromine atom is substituted in the *para* position of the vinylidene phenyl group. The ruthenium stereochemistry is nearly octahedral, with the PPh_3 ligands and a C_5H_5 group completing the coordination. The Ru—C bond (1.85(1) Å) indicates a considerable degree of backbonding from the metal to the α-carbon, while the C(1)—C(2) bond (1.31(2) Å) is rather shorter than those found in earlier examples of vinylidene complexes [7]; the Ru—C(1)—C(2) moiety is slightly bent (169.4(14)°). The 4-bromophenyl ring is twisted out of conjugation with the vinylidene group. The Br_3^- anion is linear (angle Br(3)—Br(4)—Br(5) 179.2(1)°), with Br—Br separations of 2.530(4) and 2.561(4) Å.

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[*] Atomic coordinates for this work can be obtained from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (England). The full literature citation for this communication should accompany any request.

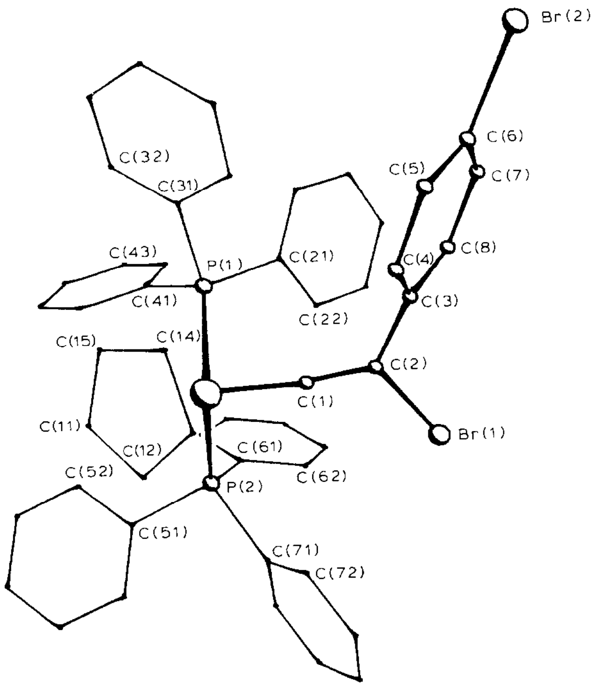

Fig. 1. PLUTO plot of cation in $[Ru\{C{=}CBr(C_6H_4Br\text{-}4)\}(PPh_3)_2(\eta\text{-}C_5H_5)][Br_3]\cdot CHCl_3$ (2), showing atom numbering system. Bond lengths: Ru—C(cp) (av.) 2.26, Ru—P(1) 2.366(5), Ru—P(2) 2.366(5), Ru—C(1) 1.85(1), C(1)—C(2) 1.31(2), C(2)—Br(1) 1.93(2), C(2)—C(3) 1.49(2) Å. Bond angles: P(1)—Ru—P(2) 103.3(2), P(1)—Ru—C(1) 88.2(5), P(2)—Ru—C(1) 93.6(5), Ru—C(1)——C(2) 169.4(14), C(1)—C(2)—Br(1) 116.8(13), C(1)—C(2)—C(3) 126.8(15)°.

There are two points of interest in this reaction. One is the remarkable resistance of the Ru—C bond in the parent acetylide to cleavage by the halogen, a reaction commonly found in alkylmetal chemistry [8]. The reaction is consistent, however, with previous experience of the highly nucleophilic character of the β-carbon atom. Secondly, the facile bromination of the phenyl ring is consistent with the highly electron-releasing substituent *para* to the substitution position. Whether addition to the β-carbon or ring substitution occurs first has not been determined; even with a deficiency of bromine, the characteristic dark green colour of 2 is observed.

Full details of the chemistry of this and related complexes obtained in similar reactions with other halogens will be described elsewhere.

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