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Journal of Organometallic Chemistry 522 (1996) 307–310

Journal of Organo metallic Chemistry

Preliminary communication

Some neutral ruthenium vinylidene complexes and a novel 1,3-elimination reaction: preparation of chiral ruthenium acetylides

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Received 24 November 1995

Abstract

Reactions of $RuCl(PPh_3)_2Cp^*$ with 1-alkynes in non-polar solvents afford the neutral vinylidene complexes $RuCl(C{=}CHR)(PPh_3)Cp^*$ [R = Ph (X-ray structure), Bu^t, $SiMe_3$, CO_2Me]; a novel 1,3 elimination of HCl induced by NaOMe in the presence of a variety of ligands gives the chiral-at-metal complexes $Ru(C{\equiv}CR)(L)(PPh_3)Cp^*$ [L = CO, C_2H_4 (X-ray structure), PR_3, $P(OR)_3$, O_2, S_2, CS_2 (for example)].

Keywords: Ruthenium; Chirality; Crystal structure; Vinylidene

The complexes $[M(C{=}CHR^1)L_2Cp]^+$ and the related acetylides $M(C{\equiv}CR)L_2Cp$ [M = Fe, Ru, Os; L = CO, PR_3, $P(OR)_3$] have played a seminal role in the development of the chemistry of the vinylidene ligand [1]. Their reactivity has been explored by many workers and they are beginning to feature in organic synthesis [2]. Vinylidene complexes of other transition metals have also been studied, particularly neutral complexes of Rh and Ir by Werner's group [3] and cationic derivatives of the $RuX(dppm)_2$ [4] and $RuCl(PR_3)(\eta$-arene) [5] systems which have been studied extensively by Dixneuf.

The introduction of the bulky Cp^* group has little effect seemingly on the synthesis of vinylidene complexes in the ruthenium system, the complexes $[Ru(C{=}CHR)(PMe_2Ph)_2Cp^*]^+$ (R = H, Ph, CH_2OH, CH_2OMe and CHMeOMe) being described recently [6]. More recently, it was found that the intermediate hydridoalkynyl complexes $RuH(C_2R)(dippe)Cp^*$ (R = Ph, CO_2Me or $SiMe_3$) could be obtained from $RuCl(dippe)Cp^*$ and 1-alkynes in MeOH in the presence of $NaBPh_4$ [7]. These complexes rearrange irreversibly to the corresponding vinylidene complexes.

However, in the case of the larger PPh_3 ligand, the reaction takes a different course. We now report that the well-established loss of a bulky PPh_3 ligand from $RuX(PPh_3)_2Cp$ complexes [8] can be applied to the synthesis of neutral vinylidene complexes. Thus, reactions between $RuCl(PPh_3)_2Cp^*$ and 1-alkynes in MeOH give a mixture of the cationic $[Ru(C{=}CHR)(PPh_3)_2Cp^*]^+$ (presumably as the chlorides, but isolated as PF_6^- salts) and the neutral complexes $RuCl(C{=}CHR)(PPh_3)Cp^*$ (**1**). Reasoning that these products are formed by displacement of Cl^- or PPh_3 respectively, from the precursor, as a result of the presence of the bulky Cp^* and PPh_3 ligands, we ran the reactions in a non-polar solvent (C_6H_6) to reduce the tendency of the Cl to ionise and thus obtained high yields of the neutral complexes (Scheme 1) [9].

These novel derivatives have been characterised by the usual methods: in particular, the $\nu(C{=}C)$ absorption occurs at ca. 1600 cm^{-1} and the ^{13}C NMR resonance for the metal-bound carbon is found as a doublet at δ ca. 340 [9]. Final confirmation of the structure was obtained from a single-crystal X-ray structure determination of **1**, R = Ph [10]. Fig. 1 shows a plot of a molecule of this complex, from which it can be seen that the complex adopts the usual piano-stool structure, with Cl, PPh_3 and C=CHPh ligands as the legs. The complex is chiral at ruthenium and crystallises as Pasteur pairs in the chiral space group $P2_12_12_1$. The Ru–C(1) distances in **1** (R = Ph) and the cationic ana-

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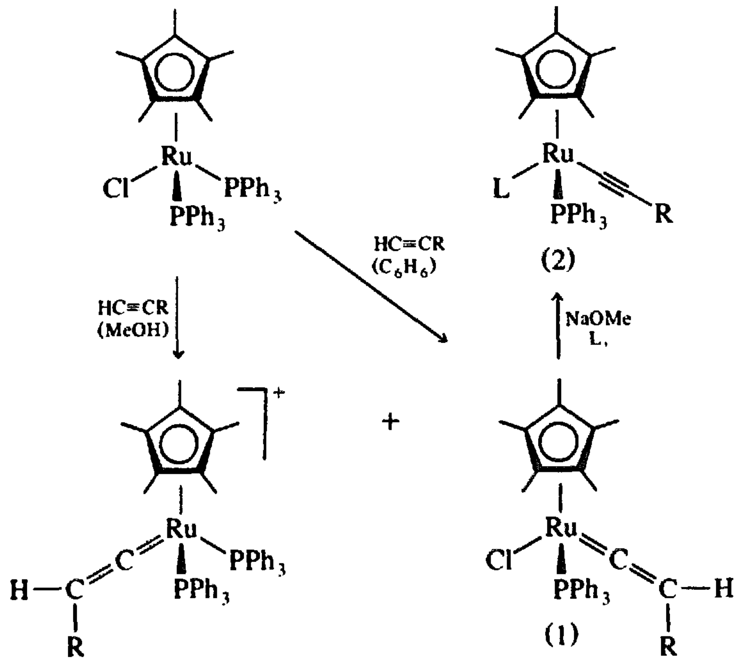
PII S0022-328X(96)06200-6



Scheme 1. R = Me, Bu^t, Ph, CO_2Me, $SiMe_3$; L = MeCN, CO, PR_3, $P(OR)_3$, O_2, S_2, CS_2 (not all combinations).

logue $[Ru(C=CMePh)(PPh_3)_2Cp]^+$ [12] are 1.86(1) and 1.80(1) Å, respectively. The major structural changes are found in the Ru–Cl [2.39(1) Å] and Ru–P [2.305(3) Å] distances which are somewhat shorter than those found for $RuCl(PPh_3)_2Cp$ [2.448(1) and 2.326(1) Å, respectively] [13]. Structurally related neutral ruthenium complexes were reported during the course of this work, and were made by utilising the hemi-labile property of the *O,P*-bound chelating phosphino-ether, PPh_2CH_2OMe, to generate a site for the vinylidene ligand [14].

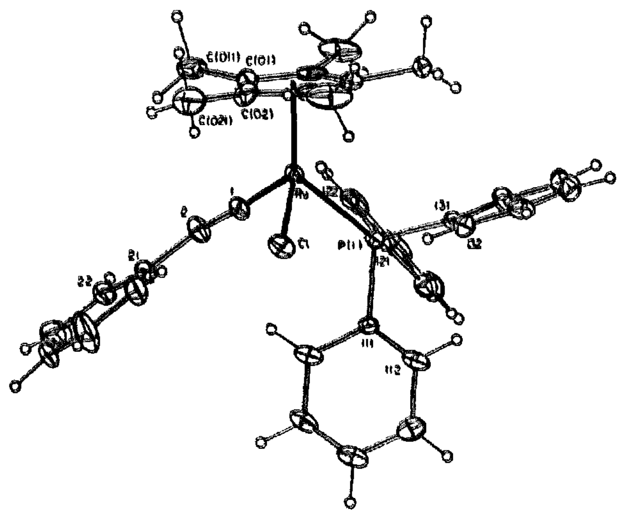


Fig. 1. Plot of a molecule of $RuCl(C=CHPh)(PPh_3)Cp^*$ (1) showing atom numbering scheme. Selected bond parameters: Ru–Cl 2.39(1), Ru–P(1) 2.305(3), Ru–C(1) 1.80(1), Ru–C(0) (centroid of Cp* ring) 1.930(6), C(1)–C(2) 1.40(2) Å; C(1)–Ru–Cl 128.2(4), Cl–Ru–P(1) 89.2(1), P(1)–Ru–C(1) 88.5(4), Ru–C(1)–C(2) 176(1)°.

The reactivity of the neutral complexes **1** is of interest. We have found that a novel 1,3 elimination of HCl occurs when **1** is treated with NaOMe in the presence of a 2e-donor ligand:

$$RuCl(C=CHR)(PPh_3)Cp^* + NaOMe + L \longrightarrow$$
$$Ru(C\equiv CR)(L)(PPh_3)Cp^* + MeOH + NaCl$$

This novel reaction allows the introduction of a wide variety of ligands, of which MeCN, CO, PR_3, $P(OR)_3$, C_2H_4, O_2, S_2, and CS_2 serve as examples [15]. The acetonitrile complex (L = MeCN; prepared in situ) can also be used as a precursor when L can react with NaOMe. The products are chiral at Ru (unless L = PPh_3) and they are obtained in high yield from reactions carried out in MeOH under mild conditions. Full details of these studies are deferred until the full paper, but the formation and molecular structure of the η-ethene complex (**2**; R = Bu^t, L = C_2H_4) are illustrative. Addition of NaOMe to a suspension of **1** (R = Bu^t) in MeOH while bubbling ethene through the mixture results in a rapid colour change to yellow; complex **2** (R = Bu^t, L = C_2H_4) was isolated in 55% yield. A plot of a molecule of this complex is shown in Fig. 2 [10]. The ^1H and ^{13}C NMR spectra indicate that the ethene ligand is fluxional, probably by rotation around the axis joining the mid-point of the C=C bond with the Ru atom. Again the familiar three-legged piano-stool structure is found, with the ethene C=C double bond being parallel to the Cp* ring plane [Ru–C(1,2) 2.186, 2.169(7) Å]. The Ru–C(3) distance [2.033(6) Å] is normal [cf. 2.016(3) Å in $Ru(C\equiv CPh)(PPh_3)_2Cp$] [16].

We have developed a significant amount of related chemistry which will be described elsewhere. However,

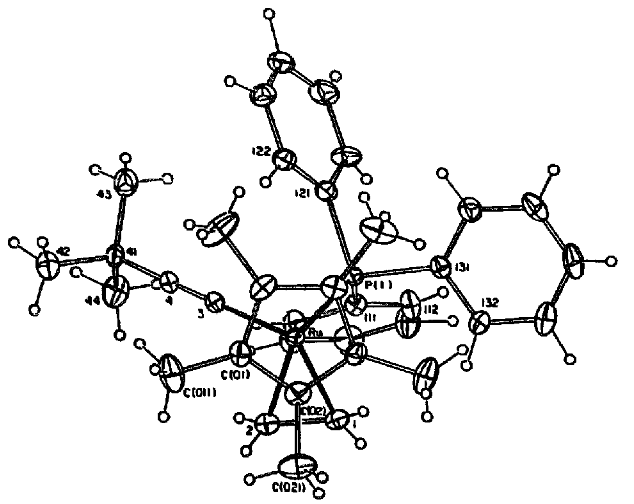


Fig. 2. Plot of a molecule of Ru(C≡CBu^t)(η-C_2H_4)(PPh_3)Cp* (2) showing atom numbering scheme. Selected bond parameters: Ru–P(1) 2.300(3), Ru–C(1) 2.186(7), Ru–C(2) 2.169(7), Ru–C(3) 2.033(6), Ru–C(0) (centroid of Cp* ring) 1.90$_2$, C(1)–C(2) 1.386(9), C(3)–C(4) 1.190(8) Å; C(3)–Ru–P(1) 83.3(2), C(1,2)–Ru–P(1) 93.8(2), C(1,2)–Ru–C(3) 95.6(2), Ru–C(3)–C(4) 179.0(5), C(3)–C(4)–C(41) 174.2(7)°.

it is pertinent to note here that the vinylidene ligand can be displaced by, for example, tertiary phosphites (which give complexes RuCl($P(OR)_3$)$_2$Cp*), which reaction is in marked contrast to the lack of substitutional reactivity found with the cationic analogues.

In conclusion, we have demonstrated the synthesis of simple neutral ruthenium-vinylidene complexes by displacement of PPh_3 from RuCl(PPh_3)$_2$Cp* and the facile elimination of HCl in the presence of a variety of 2e-donor ligands to give the related acetylide complexes Ru(C≡CR)(L)(PPh_3)Cp*. Both the vinylidene and acetylide complexes are chiral at ruthenium (unless L = PPh_3).

Acknowledgement

We thank the Australian Research Council for support of this work and Johnson Matthey Technology plc for a generous loan of $RuCl_3 \cdot nH_2O$.

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[9] Typical preparation: A mixture of RuCl(PPh_3)$_2$Cp* (100 mg, 0.13 mmol) and HC_2Bu^t (100 mg, 1.25 mmol) was heated in refluxing benzene (30 ml) for 30 min. Evaporation of solvent and preparative TLC of the residue (silica gel, acetone/hexane 3/7) gave a red band (R_f 0.70) which afforded air-stable red crystalline RuCl(C = CHBu^t)(PPh_3)Cp* (1, R = Bu^t) (60 mg, 78%), m.p. 158°C (dec.), soluble in benzene, CH_2Cl_2, acetone and similar solvents. Satisfactory C,H analyses were obtained for this and other complexes reported here.
Selected spectroscopic data for 1. R = Ph: IR (Nujol) ν(C=C) 1606, 1590 cm^{-1}. ^{1}H NMR: δ($CDCl_3$) 1.48 [d, J(HP) = 1.4 Hz), 15H, Cp*], 4.56 (s, 1H, C = CH), 6.93–7.59 (m, 20H, Ph). ^{13}C NMR: δ($CDCl_3$) 9.53 (s, Me), 102.34 (s, C=CH), 112.99 (s, C_5Me_5), 123.88–134.07 (m, Ph), 339.95 [d, J(CP) = 24.75 Hz, Ru=C]. FAB MS (m/z): 636, M$^+$; 601, [M–Cl]$^+$; 534, [M–CCHPh]$^+$; 499, [Ru(PPh_3)Cp*]$^+$; 237, [RuCp*]$^+$. R = Bu^t: IR (Nujol) ν(C=C) 1659, 1626 cm^{-1}. ^{1}H NMR: δ($CDCl_3$) 0.93 (s, 9H, CMe_3) 1.41 (s, 15H, C_5Me_5), 3.38 (s, 1H, C=CH), 7.25–7.68 (m, 15H, Ph). ^{13}C NMR: δ($CDCl_3$) 9.4 (s, C_5Me_5), 32.05 (s, CMe_3), 100.93 (s, C=CH), 120.49 (s, C_5Me_5), 127.16–134.44 (m, Ph), 336.38 [d, J(CP) = 24.37, Ru=C]. FAB MS (m/z): 615, M$^+$; 534, [M-CCHBu^t]$^+$, 499, [Ru(PPh_3)Cp*]$^+$.

[10] Crystal data. For 1 (R = Ph): red crystal (0.08×0.17×0.25 mm^3), orthorhombic, $P2_12_12_1$, a = 20.473(8), b = 16.343(6), c = 9.209(6) Å, V = 3081 Å^3, Z = 4, μ = 6.7 cm^{-1}, D_c = 1.37 g cm^{-3}.
For 2 (R = Ph, L = C_2H_4): yellow crystal (0.16×0.20×0.13 mm^3), monoclinic, $P2_1/c$, a = 9.308(2), b = 16.89(2), c = 20.20(2) Å, β = 104.75(6)°, V = 3072 Å^3, Z = 4, μ = 5.8 cm^{-1}, D_c = 1.314 g cm^{-3}.
Unique data sets were measured at ca. 295 K to $2\theta_{max}$ = 55° (50° for 2) ($2\theta/\theta$ scan mode; monochromatic Mo-Kα radiation, λ 0.7107$_3$ Å); 3871 (5381) independent reflections were obtained, 2329 (3126) with $I > 3\sigma(I)$ being considered 'observed' and used in the full matrix least squares refinement after gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; (x, y, z, U_{iso})$_H$ were included constrained at estimated values. Conventional residuals R = 0.059 (0.045), R_w = 0.057 (0.042) based on $|F|$, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Computation used the XTAL 2.6 program system implemented by S.R. Hall [11]; neutral atom complex scattering factors were employed. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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[15] Typical preparation: ethene was bubbled into a solution of 1 (R = Bu^t) (100 mg, 0.16 mmol) in MeOH (20 ml) for 20 min at room temperature. Addition of excess NaOMe [from Na (92

mg) in MeOH (1 ml)] and brief warming to 50°C resulted in a colour change from red to yellow. Subsequent cooling (−10°C) afforded air-stable yellow crystals of $Ru(C_2Bu^t)(\eta-C_2H_4)(PPh_3)Cp^*$ (2, R = Bu^t, L = C_2H_4) (50 mg, 50%), m.p. 229–230°C (dec.), soluble in C_6H_6, CH_2Cl_2 and thf.

Selected data for 2. R = Bu^t, L = CO: IR (Nujol): ν(C≡C) 2100, ν(CO) 1928, 1911 cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 0.99 (s, 9H, Bu^t), 1.61 [d, J(HP) = 1.42 Hz), 15H, Cp*], 7.26–7.64 (m, 15H, Ph). ^{13}C NMR: $\delta(CDCl_3)$ 9.70 (C_5Me_5), 32.70 (CMe_3), 77.43 (C≡CBu^t), 96.83 (C≡CBu^t), 118.42 (C_5Me_5), 127.49–135.32 (m, Ph), 207.23 [d, J(CP) = 20.91 Hz), CO]. FAB MS (m/z): 608, M^+; 580, $[M-CO]^+$; 527, $[M-C_2Bu^t]^+$; 499, $Ru(PPh_3)Cp^*]^+$.

R = Bu^t, L = C_2H_4: IR (Nujol) ν(C≡C) 2094, ν(C=C) 1570 cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 0.94 (s, Bu^t), 1.50 (s, Cp*), 1.67 [d, J(HP) 4.20 Hz, C_2H_4]. ^{13}C NMR: $\delta(CDCl_3)$ 8.8 (C_5Me_5), 30.56 (CMe_3), 39.39 (C_2H_4), 90.92 (C≡CBu^t), 105.19 (C≡CBu^t), 124.21 (C_5Me_5). FAB MS (m/z): 608, M^+; 581, $[M-C_2H_4]^+$.

R = Ph, L = O_2: IR (Nujol) ν(C≡C) 2094, ν(O=O) 914 cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 1.53 (s, Cp*), 6.75–7.41 (m, 20H, Ph). FAB MS (m/z): 632, M^+; 616, $[M-O]^+$; 600, $[M-2O]^+$.

R = Bu^t, L = $P(OMe)_3$: IR (Nujol) ν(C≡C) 2086 cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 1.16 (s, Bu^t), 1.46 (s, Cp*), 3.34 [d, J(HP) 10.70 Hz, POMe], 7.25–7.80 (m, Ph). ^{13}C NMR: $\delta(CDCl_3)$ 9.50 (C_5Me_5), 32.90 (CMe_3), 51.95 [d, J(CP) = 5.90 Hz, POMe], 77.57 (C≡CBu^t), 93.42 (C≡CBu^t), 116.8 (C_5Me_5), 126.32–139.22 (m, Ph). FAB MS (m/z): 703, M^+; 624, $[M-C_2Bu^t]^+$.

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