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Reactions of $Ru(CO)ClH(C_5H_5N)(PPh_3)_2$ with 1-alkynes

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Abstract

$Ru(CO)ClH(C_5H_5N)(PPh_3)_2$ reacts with an equivalent of a monosubstituted alkyne in dichloromethane to give alkenyl derivative $Ru(CO)Cl((E)HC{=}CHR)(C_5H_5N)(PPh_3)_2$ ($R = n\text{-}C_3H_7$, $n\text{-}C_6H_{13}$, $n\text{-}C_8H_{17}$, CMe_3, Ph, COOMe, COOEt), resulting from a *cis*-insertion of the alkyne into the Ru–H bond. The reaction of the ruthenium hydride with an excess of an activated alkyne $HC{\equiv}CCOOR$ (R=Me, Et) in methanol under reflux yields the bis-insertion derivative $Ru(CO)Cl[RO\text{-}OCC{=}CHCH{=}CHCOOR](PPh_3)_2$ (R = Me, Et).

Introduction

We recently described the reactions of neutral and cationic ruthenium hydrido complexes $Ru(CO)ClH(PR_3)_2L$ ($L = PPh_3$, Me_2Hpz; R=Ph, $p\text{-}CH_3C_6H_5$) and $[Ru(CO)H(MeCN)_2(PPh_3)_2]A$ ($A{=}ClO_4$, PF_6) with alkynes [1–6]. The reaction generally involved insertion of the alkyne into the Ru–H bond, although in some instances bis-insertion derivatives [3,5,7] or unexpected products [4,5] were also isolated. We describe here a series of new alkenyl ruthenium complexes derived from the new neutral ruthenium complex $Ru(CO)ClH(C_5H_5N)(PPh_3)_2$ (**1**) by reaction with 1-alkynes $RC{\equiv}CH$ ($R = n\text{-}C_3H_7$, $n\text{-}C_6H_{13}$, $n\text{-}C_8H_{17}$, CMe_3, Ph, COOMe, COOEt).

Results and discussion

The reaction of hydride **1** with 1-alkynes takes place readily in dichloromethane at 23–40 °C to yield the (*E*)-alkenyl complexes **2–8** in excellent yields (eq. 1). The stereochemistry of the alkenyl ligands was assigned on the basis of the $^3J(^1H-^1H)$

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coupling constants, and is consistent with the *cis*-insertion of the 1-alkyne into the Ru–H bond observed with related ruthenium complexes [1–6,8].

$$\mathrm{Ru(CO)ClH(py)(PPh_3)_2 + HC{\equiv}CR \rightarrow Ru(CO)Cl(HC{=}CHR)(py)(PPh_3)_2} \qquad (1)$$

(**2**: $R = n\text{-}C_3H_7$; **3**: $R = n\text{-}C_6H_{13}$; **4**: $R = n\text{-}C_8H_{17}$; **5**: $R = CMe_3$; **6**: $R = Ph$; **7**: $R = COOMe$; **8**: $R = COOEt$)

The alkenyl ruthenium complexes obtained are six-coordinate species with a stereochemistry similar to that found in the analogous dimethyl pyrazole alkenyl ruthenium complexes [5], with mutually *trans* triphenylphosphine ligands and the alkenyl group *cis* to the carbonyl ligand, in an approximately octahedral coordination. The IR spectra showed $\nu(C{=}O)$ frequencies at 1910–1930 cm^{-1} for the pyridine complexes, similar to those observed for the dimethylpyrazole complexes (1923–1935 cm^{-1}); a *trans* stereochemistry between the CO and the alkenyl ligands shifts the $\nu(C{=}O)$ frequency to 1990 cm^{-1} in the related complex $[Ru(CO)(MeOOC{=}CHCOOMe)(MeCN)_2]ClO_4$ [6].

When the reactions of hydride **1** with an excess of methyl or ethyl propiolate were performed in methanol under reflux for 8 h, the bis-insertion derivatives $Ru(CO)Cl[ROOCC{=}CHCH{=}CHCOOR](PPh_3)_2$ (R = Me, **9**; R = Et, **10**) were obtained in 50–60% yield. These complexes were identical with those obtained in low yield from $Ru(CO)ClH(PPh_3)_3$ [3,7] and an excess of alkyne at room temperature. A higher temperature is probably required for the displacement of the coordinated pyridine from the insertion derivatives **7** and **8** by a second equivalent of the alkyne, which coordinates to the metal through the carbonyl oxygen [7].

Experimental

IR spectra were recorded on a Pye Unicam SP-3-300S spectrophotometer using KBr discs. Only the most significant IR frequencies are given in the details of the preparations. ^1H NMR spectra were measured on a Varian XL 300 (300 MHz) spectrometer in $CDCl_3$ solutions containing tetramethylsilane as internal standard. ^{13}C NMR spectrum was measured on a Bruker AM 200 (50 MHz) in deuterochloroform solution with the solvent as internal standard.

All reactions were carried out under nitrogen. Dichloromethane was freshly distilled from CaH_2 under argon. Elemental analyses were performed with a Perkin–Elmer 240C Elemental Analyzer.

$Ru(CO)ClH(PPh_3)_3$ was prepared as described previously [9].

$Ru(CO)ClH(py)(PPh_3)_2$ (1)

A suspension of the hydride $Ru(CO)HCl(PPh_3)_3$ (1.19 g, 12.5 mmol) in ethanol (100 ml) containing an excess of pyridine (8.0 ml, 106 mmol) was heated under reflux for 1 h. The resulting white solid was filtered off, washed with ethyl ether and hexane and dried under vacuum to give **1** (585 mg, 61%) as a white solid. A second crop (117 mg, 12%) of hydride was obtained from the filtrate after evaporation and trituration of the residue with ethyl ether and hexane. Combined yield: 73%. IR (cm^{-1}): 2008 m, 1937 vs, 1558 w. ^1H NMR: δ 8.78–8.66 (m, 1 H, py), 8.40–7.92 (m, 1 H, py), 7.60–7.54 (m, 12 H, Ph), 7.27–7.18 (m, 19 H, 18 H Ph and 1 H py), 6.48–6.34 (m, 1 H, py), 6.32–6.20 (m, 1 H, py), −13.52 (t, $J = 19.5$ Hz, 1 H). Anal. Found: C, 65.37; H, 4.68; N, 1.81. $C_{42}H_{36}ClNOP_2Ru$ calcd.: C, 65.58; H, 4.72; N, 1.82.

$Ru(CO)Cl(CH{=}CHC_3H_7)(py)(PPh_3)_2$ (2)

A solution of hydride **1** (120 mg, 0.16 mmol) and 1-n-pentyne (0.016 ml, 0.16 mmol) in dichloromethane (20 ml) was stirred at 23° C for 1 h. The solvent was evaporated and the resulting solid was triturated with ethyl ether, filtered off, dissolved in dichloromethane, and precipitated with hexane to yield **2** (130 mg, 73%) as a pale yellow powder. IR (cm^{-1}): 2950 w, 2910 w, 1910 vs, 1595 w. ^1H NMR: δ 8.50–8.45 (m, 2 H, py), 7.65–7.50 (m, 12 H, Ph), 7.35–7.21 (m, 7 H, 6 H Ph and 1 H py), 7.21–7.16 (m, 13 H, 12 H Ph and 1 H CH=), 6.58–6.65 (m, 2 H, py), 4.81–4.72 (dm, $J = 16.5$ Hz, 1 H, CH=), 1.88–1.80 (m, 2 H, CH_2), 1.12–1.00 (m, 2 H, CH_2), 0.66 (t, $J = 7.2$ Hz, 3 H, CH_3). Anal. Found: C, 67.31; H, 5.39; N, 1.66. $C_{47}H_{44}ClNOP_2Ru$ calcd.: C, 67.42; H, 5.30; N, 1.67.

$Ru(CO)Cl(CH{=}CHC_6H_{13})(py)(PPh_3)_2$ (3)

A solution of hydride **1** (211 mg, 0.27 mmol) and 1-n-octyne (0.081 ml, 0.55 mmol) in dichloromethane (15 ml) was stirred at 23° C for 90 min. The mixture was concentrated to ca. 2–3 ml and treated with hexane. The solid was filtered off and washed with hexane to yield **3** (175 mg, 73%) as a pale yellow solid. IR (cm^{-1}): 2950 w, 2910 m, 1910 vs, 1595 w. ^1H NMR: δ 8.51–8.45 (m, 2 H, py), 7.55–7.49 (m, 12 H, Ph), 7.33–7.21 (m, 7 H, 6 H Ph and 1 H py), 7.20–7.14 (m, 13 H, 12 H Ph and 1 H CH=), 1.88–1.82 (m, 2 H, CH_2), 1.23–1.00 (m, 8 H, 4 CH_2), 0.82 (t, $J = 7.0$ Hz, 3 H, CH_3). Anal. Found: C, 68.17; H, 5.74; N, 1.60. $C_{50}H_{50}ClNOP_2Ru$ calcd.: C, 68.29; H, 5.73; N, 1.59.

$Ru(CO)Cl(CH{=}CHC_8H_{17})(py)(PPh_3)_2$ (4)

A solution of hydride **1** (144 mg, 0.18 mmol) and 1-n-decyne (0.07 ml, 0.39 mmol) in dichloromethane (15 ml) was stirred at 23° C for 90 min. The mixture was treated as above to yield **4** (155 mg, 91%) as a pale yellow solid with identical IR to that of **3**. The ^1H NMR was also identical except for the multiplet at 1.23–1.00 corresponding to 12 H (6 CH_2). Anal. Found: C, 68.79; H, 6.01; N, 1.55. $C_{52}H_{54}ClNOP_2Ru$ calcd.: C, 68.82; H, 6.00; N, 1.54.

$Ru(CO)Cl(CH{=}CHCMe_3)(py)(PPh_3)_2$ (5)

A solution of hydride **1** (105 mg, 0.14 mmol) and 3,3-dimethyl-1-butyne (0.017 ml, 0.14 mmol) in dichloromethane (20 ml) was heated under reflux for 1 h, then evaporated. The residue was triturated with ethyl ether and the residual solid dissolved in dichloromethane and re-precipitated with hexane to give **5** (81 mg, 70%) as a greenish-yellow powder. IR (cm^{-1}): 2950 m, 1930 vs, 1595 w. ^1H NMR: δ 8.51–8.49 (m, 2 H, py), 7.55–7.49 (m, 12 H, Ph), 7.22–7.18 (m, 7 H, 6 H Ph and 1 H py), 7.17–7.11 (m, 13 H, 12 H Ph and 1 H CH=), 6.60–6.55 (m, 2H, py), 4.82 (dt, $J = 16.2$ Hz, 1.6 Hz, =CH), 0.64 (s, 9 H, CMe_3). Anal. Found: C, 67.85; H, 5.46; N, 1.66. $C_{48}H_{46}ClNOP_2Ru$ calcd.: C, 67.72; H, 5.45; N, 1.66.

$Ru(CO)Cl(CH{=}CHPh)(py)(PPh_3)_2$ (6)

A solution of hydride **1** (100 mg, 0.13 mmol) and phenylacetylene (0.014 ml, 0.13 mmol) in dichloromethane (20 ml) was heated under reflux for 1 h. The solution was evaporated and the residue was triturated with ethyl ether to give **6** (97 mg, 86%) as a crystalline light yellow solid. IR (cm^{-1}): 1920 vs, 1593 m, 1540 m. ^{1}H NMR: δ 8.75 (dt, J = 16.9, 3.2 Hz, 1 H, CH=), 8.53–8.51 (m, 2 H, py), 7.54–7.45 (m, 12 H, Ph), 7.28–7.20 (m, 7 H, 6 H Ph and 1 H py), 7.18–7.07 (m, 14 H, 12 H Ph and 2 H PhCCH), 6.90 (t, J = 7.1 Hz, 1 H, PhCCH), 6.85 (d, J = 7.3 Hz, 2 H PhCCH), 6.58 (t, J = 6.9 Hz, 2 H py), 5.78 (br d, J = 16.9 Hz, CH=). ^{13}C{^{1}H} NMR: δ 203.20 (t, J = 14.5 Hz), 154.00 (s), 153.77 (t, J = 14.5 Hz), 141.11 (s), 138.34 (s), 135.23 (s), 134.30 (t, J = 5.0 Hz, Ph$_3$P), 132.47 (t, J = 20.3 Hz, Ph$_3$P), 129.10 (s, Ph$_3$P), 127.67 (s), 127.40 (t, J = 4.5 Hz, Ph$_3$P), 124.19 (s), 123.61 (s), 123.40 (s). Anal. Found: C, 69.02; H, 4.89; N, 1.61. $C_{50}H_{42}ClNOP_2Ru$ calcd.: C, 68.92; H, 4.87; N, 1.61.

Ru(CO)Cl(CH=CHCOOMe)(py)(PPh$_3$)$_2$ (7)

A solution of hydride **1** (105 mg, 0.14 mmol) and methyl propiolate (0.012 ml, 0.14 mol) in dichloromethane (20 ml) was stirred at 23° C for 1 h. The solvent was evaporated and the residue was triturated with ethyl ether to give **7** (98 mg, 82%) as a light yellow solid. IR (cm^{-1}): 2950 w, 1928 vs, 1686 s, 1599 w, 1528 s. ^{1}H NMR: δ 10.46 (dt, J = 16.8, 1.9 Hz, CH=), 8.48–8.47 (m, 2 H, py), 7.48–7.41 (m, 12 H, Ph), 7.30–7.22 (m, 7 H, 6 H Ph and 1 H py), 7.21–7.14 (m, 12 H, Ph), 6.62 (t, J = 6.9 Hz, 2 H py), 5.61 (br d, J = 16.8 Hz, CH=), 3.50 (s, 3 H, Me). Anal. Found: C, 64.81; H, 4.74; N, 1.63. $C_{46}H_{40}ClNO_3P_2Ru$ calcd.: C, 64.76; H, 4.73; N, 1.64.

Ru(CO)Cl(CH=CHCOOEt)(py)(PPh$_3$)$_2$ (8)

A procedure analogous to that above gave **8** as a light yellow solid in 85% yield. IR (cm^{-1}): 2950 w, 2910 w, 1920 vs, 1680 s, 1598 w, 1527 s. ^{1}H NMR: δ 10.42 (br d, J = 16.6 Hz, CH=), 8.48–8.47 (m, 2 H, py), 7.48–7.42 (m, 12 H Ph), 7.30–7.21 (m, 7 H, 6 H Ph and 1 H py), 7.20–7.14 (m, 12 H Ph), 6.62 (t, J = 6.5 Hz, 2 H py), 5.59 (dt, J = 16.6, 1.5 Hz, CH=), 3.95 (q, J = 7.1 Hz, 2 H, CH$_2$), 1.16 (t, J = 7.1 Hz 3 H, CH$_3$). Anal. Found: C, 65.18; H, 4.90; N, 1.62. $C_{47}H_{42}ClNO_3P_2Ru$: C, 65.09; H, 4.88; N, 1.61.

$\overline{\text{Ru(CO)Cl[MeOO}}$CC=CH-CH=CHCOOMe](PPh$_3$)$_2$ (9)

A suspension of hydride **1** (312 mg, 0.4 mmol) and methyl propiolate (0.14 ml, 1.6 mmol) in methanol (50 ml) was heated under reflux for 8 h. The resulting yellow solid was filtered off, washed with methanol and ethyl ether, and dried to give **9** (170 mg, 49%). A second fraction was obtained from the filtrate after evaporation and treatment with hexane (31 mg, 9%; combined yield: 201 mg, 58%). The product was identical with that obtained from Ru(CO)ClH(PPh$_3$)$_3$ [3,7]. The corresponding reaction of ethyl propiolate gives $\overline{\text{Ru(CO)Cl[EtOO}}$CC=CH-CH=COOEt](PPh$_3$)$_2$ (**10**) in 55% yield, identical with that prepared from Ru(CO)ClH(PPh$_3$)$_3$ [3].

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