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Note

Alkyne insertion and coupling reactions mediated by the cycloheptatrienyl-bridged heterobimetallic complexes (μ-C_7H_7)$Ru(CO)_3M'(CO)_2$ ($M' = Rh, Ir$)

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ABSTRACT

Cycloheptatrienyl-bridged RuRh and RuIr pentacarbonyl complexes were found to undergo metal–carbon and carbon–carbon bond-forming reactions with hexafluoro-2-butyne to afford products in which coupling of the alkyne and cycloheptatrienyl group had occurred. Reaction of the RuRh complex occurred readily at room temperature whereas the RuIr complex required thermal activation of 100 °C, which resulted in incorporation of two alkyne units into the product.

1. Introduction

Heterobimetallic compounds are a class of bifunctional substrates which potentially offer some unique reactivity. As a result, there has recently been substantial interest into the catalytic activity of this type of compound. Thus, recent reviews into the catalytic behaviour of early/late transition metal heterobimetallic compounds [1] and rare earth-alkali metal complexes [2] have been published. However, heterobimetallic complexes do not always need to incorporate widely different metals to offer interesting chemistry. Regarding heterobimetallic complexes from adjacent or near-adjacent groups in the periodic table, the activation of a wide range of small molecules has been intensively studied [3] and one particular area that has been actively investigated is the activation of alkynes. For example, the hydrosilyation of alkynes has been accomplished using dithiolate bridged Pt–Ir complexes [4] and similar Ru–Rh complexes have been reported to mediate alkyne hydrogenation in addition to alkyne coupling [5]. Related hydrosulfido Ru–Mo complexes were also found to be active for the hydrogenation of alkynes [6]. By contrast, diphosphine bridged Ru–Re complexes have been reported to catalyse the coupling of formic acid and 1-alkynes to form enol esters [7] while alkyne-bridged W–Co and Mo–Co complexes have been able to mediate the Pauson–Khand reaction [8]. In this work, we report the insertion and coupling reactions of the activated alkyne hexafluoro-2-butyne (HFB) that occur with cycloheptatrienyl-bridged RuRh and RuIr complexes. We also report the X-ray crystal structure of the product obtained from the RuRh complex.

2. Experimental section

All preparations and subsequent manipulations were carried out using standard Schlenk techniques in an atmosphere of purified dinitrogen. Hexane, octane and CH_2Cl_2 were dried by standard methods, as were the deuterated solvents, CD_2Cl_2 and acetone-d_6. Hexafluoro-2-butyne (HFB) was purchased from S.C.M. Speciality Chemicals. NMR spectra were recorded on a Bruker WH 200 spectrometer. Assignments of all NMR spectra were made using homonuclear and heteronuclear decoupling experiments. For ^{19}F NMR, $CFCl_3$ was used as a calculated external standard. (μ-C_7H_7)$Ru(CO)_3Rh(CO)_2$ was made via addition of (cycloheptatrienyl)rutheniumtricarbonyl anion to (cyclooctadiene)rhodiumchloride dimer according to the literature method [9] and (μ-C_7H_7)$Ru(CO)_3Ir(CO)_2$ was prepared using an identical procedure [10]. Elemental microanalyses and mass spectrometry determinations were performed at the University of Alberta. The complete solid-state X-ray structural determination of compound **2** was carried out on a monoclinic crystal of **2** (space group $P2_1/n$) by Dr. R.G. Ball

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of the Structure Determination Laboratory at the University of Alberta. Details including crystallographic data and positional and thermal parameters are included in the Supplementary information.

2.1. *Preparation of (μ-C_7H_7)(μ-C_4F_6)$Ru(CO)_3Rh(CO)_2$ (**2**)*

(μ-C_7H_7)$Ru(CO)_3Rh(CO)_2$ (25 mg) was dissolved in hexane (10 ml) and freeze-thaw degassed. A slow stream of HFB was then bubbled through the reaction mixture for 1 min at room temperature. The red–brown solution was then stirred for 5 min with no colour change. The solvent was then removed to leave a brown residue which was chromatographed on a silica gel column (3 × 1.5 cm) eluting with hexane. The major orange band was collected and crystallized from hexane to afford yellow–orange crystals of **2** (16 mg, 45%).

Anal. Calcd. for $C_{16}H_7F_60_5RhRu$: C; 32.18, H; 1.35. Found: C; 32.35, H; 1.22.

M.S. (90 °C, 16 eV, 70 eV) $P^+ = 598$, $P^+ - n(C0)$, $n = 0–5$.

IR (ν_{CO}, hexane); 2089 (m), 2056 (s), 2035 (m), 2015 (m).

^1H NMR (22 °C, CD_2Cl_2; δ ppm, *J* Hz) δ 3.66 (1H, t, H7, $J_{H7-H1} = J_{H6-H7} = 7$), 4.12 (1H, t, H1, $J_{H1-H2} = J_{H7-H1} = 7$), 4.96 (1H, dd, H3, $J_{H2-H3} = 5.5$, $J_{H3-H4} = 9.5$), 5.10 (1H, dd, H2, $J_{H1-H2} = 7$, $J_{H2-H3} = 5.5$), 5.96 (1H, dd, H4, $J_{H3-H4} = 9.5$, $J_{H4-H5} = 6.5$), 6.04 (1H, dd, H6, $J_{H5-H6} = 9.5$, $J_{H6-H7} = 7$), 6.48 (1H, dd, H5, $J_{H4-H5} = 6.5$, $J_{H5-H6} = 9.5$).

^{13}C NMR (22 °C, CD_2Cl_2) δ 42.0 (C7), 73.2 (C3), 77.9 (C1), 80.1 (C2), 83.5 (C4), 127.2 (C5), 138.3 (C6), 101.1 (m,C8), 125.5 (q, CF_3, $J_{C-F} = 220$ Hz), 129.0 (q, CF_3, $J_{C-F} = 220$ Hz), 157.6 (m,C9), 188.8 (d, CO_{Rh}, $J_{Rh-C} = 80$ Hz), 189.6 (d, CO_{Rh}, $J_{Rh-C} = 70$ Hz), 192.6 (s, CO_{Ru}), 195.4 (s, CO_{Ru}), 197.7 (s, CO_{Ru}).

^{19}F NMR (22 °C, CD_2Cl_2) δ −61.1 (3F, q, $J_{F-F} = 14$ Hz, C_8CF_3), −40.2 (3F, dq, $J_{F-F} = 14$ Hz, $J_{Rh-F} = 3$ Hz, C_9CF_3).

2.2. *Preparation of (μ-C_7H_7)(μ-C_4F_6)$_2Ru(CO)_2Ir(CO)_2$ (**3**)*

(μ-C_7H_7)(μ-C_4F_6)$Ru(CO)_3Ir(CO)_2$ (50 mg) was dissolved in octane (10 ml) and freeze–thaw degassed. One atmosphere of HFB gas was then introduced to the frozen solution, which was then warmed to 100 °C and stirred for 2 h. The solvent was removed from the dark orange solution to leave an orange–brown residue which was washed with hexane (4 ml) and chromatographed on a silica gel column (9 cm × 1.5 cm) eluting with 40% CH_2Cl_2/hexane. A yellow–green band was collected and the solvent was removed to leave a cream solid which was recrystallized from CH_2Cl_2/hexane to give pale yellow-green crystals of **3** (40 mg, 51%).

Anal. Calcd. for $C_{19}H_7F_{12}OIrRu$: C; 27.81, H, 0.85, Found, C, 27.74, H, 0.84.

M.S. (FAB), $P^+ = 822$, $P^+ - n(C0)$, $n = 0–4$.

IR (ν_{CO}, hexane); 2095 (m), 2055 (s), 2049 (w), 2005 (m).

^1H NMR (22 °C, acetone-d_6); δ 3.13 (1H, dd, H4, $J_{H3-H4} = 7.5$, $J_{H4-H5} = 9$), 4.08 (1H, t, $J_{H1-H2} = J_{H7-H1} = 7.5$), 4.94 (1H, t, H3, $J_{H2-H3} = J_{H3-H4} = 7.5$), 5.14 (1H, t, H2, $J_{H1-H2} = J_{H2-H3} = 7.5$), 5.38 (1H, m, H7), 6.23 (1H, t, H5, $J_{H4-H5} = J_{H5-H6} = 9$), 6.62 (1H, dd, H6, $J_{H5-H6} = 9$, $J_{H6-H7} = 6$).

^{13}C NMR (22 °C, acetone-d_6; δ ppm, *J* Hz); δ 10.0 (q, C8, $J_{C-F} = 30$), 25.9 (s, C7), 33.2 (s, C4), 48.5 (m, C9), 61.1 (s, C1), 64.1 (s, C3), 71.1 (s, C2), 98.6 (m, C10), 124.0 (q, CF_3, $J_{C-F} = 280$), 124.5 (q, CF_3, $J_{C-F} = 280$), 129.5 (q, CF_3, $J_{C-F} = 275$), 130.0 (q, CF_3, $J_{C-F} = 280$), 133.7 (s, C6), 136.3 (s, C5), 159.8 (s, CO_{Ru}), 166.2 (s, CO_{Ru}), 191.4 (s, CO_{Ir}), 195.3 (s, CO_{Ir}).

^{19}F NMR (22 °C, acetone-d_6), δ −67.0 (br, C_8CF_3), −55.4 (m, $C_{10}CF_3$), −51.2 (qqd, $J_{F-F} = 14$, 9 Hz, $J_{H7-F} = 4$ Hz, C_9CF_3), −45.5 (q, $J = 16$ Hz, $C_{11}CF_3$).

3. Results and discussion

3.1. *Reaction of (μ-C_7H_7)$Ru(CO)_3Rh(CO)_2$ (**1a**) with HFB*

The reaction of (μ-C_7H_7)$Ru(CO)_3Rh(CO)_2$ (**1a**) with HFB was carried out by allowing a slow stream of HFB to bubble through a hexane solution of **1a** at R.T. Using IR spectroscopy it was determined that the starting material (**1a**) had been completely consumed within 5 min. Isolation of the yellow major band observed during column chromatography allowed a single product to be obtained. The IR spectrum of the product in the carbonyl region showed a four-band pattern between 2089 and 2015 cm^{-1}. Noticeably, these bands were at considerably higher frequency than the four-band pattern for **1a** (2064–1979 cm^{-1}) which is strongly indicative of decreased electron density on the metal centres. The product (**2**), which was formulated as $(C_7H_7)(HFB)RuRh(CO)_5$ by elemental analysis and mass spectrometric data was obtained in 45% yield and was analysed by ^1H, ^{19}F and ^{13}C NMR spectroscopy.

The ^1H NMR spectrum of **2** showed seven different signals for the C_7H_7 ring, indicating that the ring rotation which is observed for **1a** had been completely frozen out. The ^{19}F NMR spectrum gave two signals for two different CF_3 groups, one of which showed a small Rh coupling of 2 Hz in addition to the ^{19}F–^{19}F quartet coupling of 16 Hz. However, the ^{13}C NMR proved to be the most valuable for structure determination. In particular, there were three different types of C_7H_7 signal: Two signals due to an uncoordinated double bond were observed at 127 and 138 ppm, four signals due to coordinated double bonds were observed between 73 and 84 ppm, and a final signal, indicative of an sp^3 hybridised carbon atom was observed at 42 ppm. Further discussion and a figure of the ^{13}C NMR spectrum is presented in a later section. The NMR observations can be explained by assuming an insertion of an HFB molecule between a metal and the seven-membered ring has occurred. In order to confirm this and to identify exactly the interaction of the alkyne moiety with the two metals, an X-ray structure determination was carried out.

3.2. *Molecular structure of **2***

The molecular structure of **2** is given in Fig. 1 and selected interatomic distances are given in Table 1. It can be seen that the acetylenic bond has formally inserted between the Ru centre and

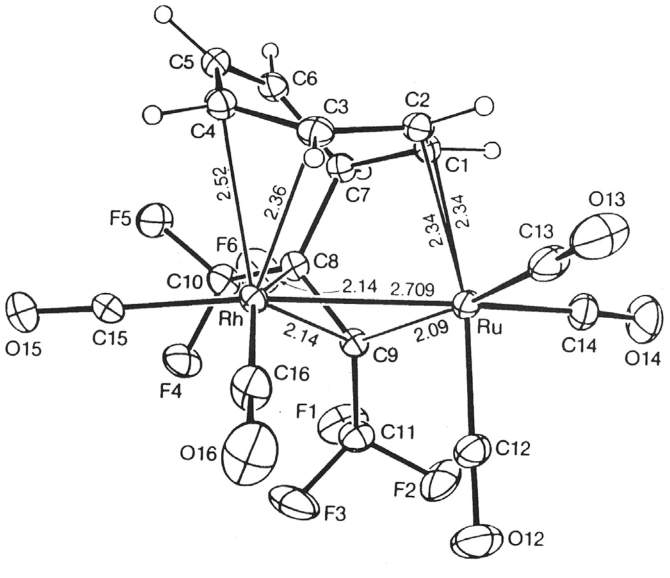

Fig. 1. Molecular structure of **2**.