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Terminal alkynes as a source of carbonyl-alkyl and carbonyl-acyl bipyridyl ruthenium complexes

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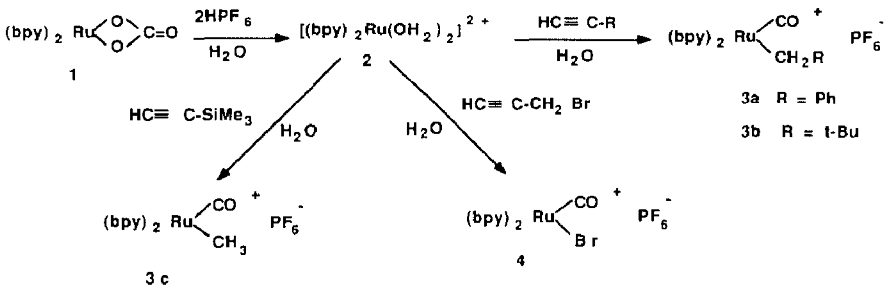
Abstract

Protonation of $(\widehat{N\ N})_2Ru(CO_3)$ with aqueous HPF_6 followed by reaction with terminal alkynes gives $(\widehat{N\ N})_2Ru(CO)(CH_2R)^+PF_6^-$ [$\widehat{N\ N}$ = 2,2′-bpy; R = H, t-Bu, Ph; $\widehat{N\ N}$ = bpy* = 4,4′-di-t-Bu-2,2′-bpy; R = Ph]. Reaction of $(bpy)_2Ru(CO_3)$ with propargyl bromide in water in the presence of HPF_6 yields $(bpy)_2Ru(CO)(Br)^+PF_6^-$, whereas reaction of $(bpy^{\star})_2Ru(CO_3)$ with HPF_6 and trimethylsilylacetylene in ethanol–water affords $(bpy^{\star})_2Ru(CO)(OH_2)^{2+}(PF_6^-)_2$. Use of propiolic acid results in the unexpected formation of $(\widehat{N\ N})_2Ru(CO)(COCH_3)^+PF_6^-$.

The stoichiometric reactions between terminal alkynes and organometallic ruthenium complexes have been found to give η^1-vinylidene ruthenium(II) complexes via π-alkyne intermediates [1,2]. Advantage has been taken of the high reactivity of vinylidene ruthenium complexes towards nucleophiles to prepare alkoxy-alkyl carbene complexes from alcohols [3,4] and acyl- or alkyl-carbonyl complexes from water [3]. Sullivan and Meyer also obtained a high yield synthesis of a carbonyl-benzyl ruthenium complex $[(bpy)_2Ru(CO)(CH_2Ph)](PF_6)$ from $(bpy)_2Ru(OH_2)_2^{2+}$ and phenyl acetylene in water [5]. As this approach seemed to provide a good route to a variety of ruthenium-alkyl complexes we decided to study the reaction of several terminal alkynes with 2,2′-bipyridine (bpy) and 4,4′-di-tert-butyl-2,2′-bipyridine (bpy*) ruthenium complexes in aqueous solution. In this communication we report some preliminary results and show that, depending on the nature of the alkyne and of the bipyridyl ligand used, the reaction leads to new carbonyl-alkyl complexes but also to carbonyl-aquo, -halogeno and -acyl complexes.

The diaquo ruthenium complex **2** can be generated in situ by addition of two equivalents of aqueous HPF_6 to the carbonato ruthenium complex **1** in water [5]. Addition of an excess of t-butylacetylene, followed by heating of the mixture in an autoclave for two hours, gives the neopentyl-carbonyl ruthenium complex **3b** as a red precipitate in 82% yield (Scheme 1). Under similar conditions the methyl-



Scheme 1

carbonyl complex **3c** is obtained in 51% yield from trimethylsilylacetylene. The formation of this compound may result from the protonolysis of the carbon–silicon bond. Attempt to prepare $(bpy)_2Ru(CO)(CH_2CH_2Br)^+$ from propargyl bromide failed, and the carbonyl-bromide complex **4** was exclusively obtained instead (Scheme 1). An elimination of ethene from a bromoethyl ruthenium intermediate could account for the formation of **4**. New compounds **3b,c** have been fully characterized by analytical and spectroscopic studies (Table 1). For example **3b** shows, like **3a** [5], a strong infrared absorption at 1915 cm^{-1} assigned to the carbonyl stretching vibration, and the methylene protons of the neopentyl ligand appear as an AB system, a signal consistent with a chiral ruthenium centre. The cyclic voltammogram of **3b** in acetonitrile reveals an irreversible oxidation of Ru(II) to Ru(III) [$E_p^a = 0.90$ V] whereas **3c** gives a Ru^{III}/Ru^{II} quasi-reversible wave at $E_{1/2} = 1.02$ V.

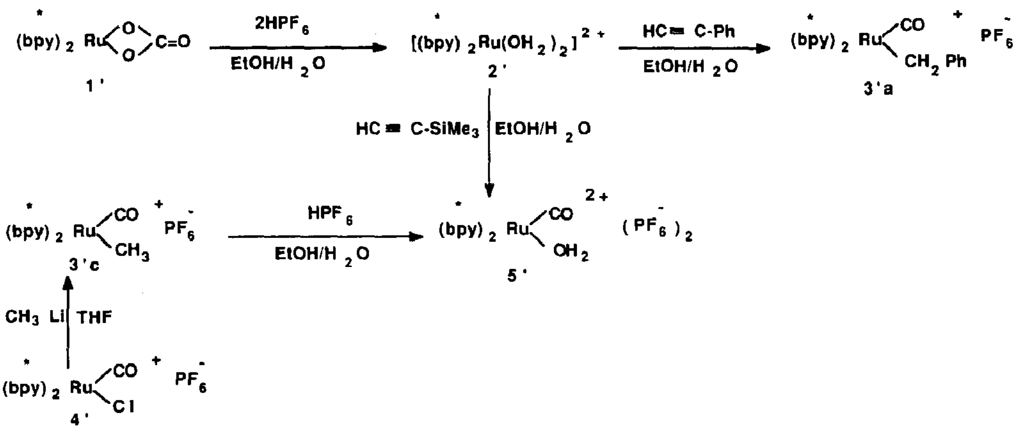
The reaction of **1′** [6] with aqueous HPF_6 and phenylacetylene in ethanol–water yields the ruthenium benzyl complex **3′a** (63%). The reaction with trimethylsilylacetylene proceeds differently and affords only the carbonyl-aquo complex **5′** (Scheme 2). Since the cleavage of metal–alkyl bond by acids is well known [7,8], **5′** could be produced by the breaking of the Ru–CH_3 bond by HPF_6 in **3′c**, followed by coordination of water. To confirm this suggestion **3′c** was prepared by treating the carbonyl-chloro complex **4′** [6] with methyl lithium in THF: addition of HPF_6 to an

Table 1

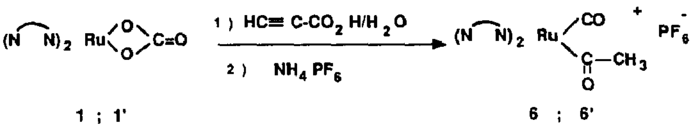
Selected spectroscopic and electrochemical data for complexes $[\widehat{N\,N}]_2Ru(CO)X^+PF_6^-$ (X = Cl, Br, CH_2R, $COCH_3$) and $(bpy^*)_2Ru(CO)(H_2O)^{2+}(PF_6^-)_2$.

Compound	ν(CO) (cm^{-1}) [a]	δ ^1H [b]	$E_{Ru^{III}/Ru^{II}}$ (V) [c]
3a	1930	3.20; 2.20 (dd, CH_2–, $^2J_{HH} = 10.3$) [d]	0.81 [g]
3b	1915	1.60; 0.45 (dd, CH_2–, $^2J_{HH} = 10.2$) [e]	0.90 [g]
3c	1920	0.15 (s, CH_3) [d]	1.02 [g]
3′a	1924	3.16; 2.04 (dd, CH_2–, $^2J_{HH} = 8.4$) [f]	0.80 [g]
3′c	1915	−0.19 [s, CH_3] [f]	0.90 [h]
4	1965	–	1.50 [h]
4′	1960	–	1.39 [h]
5′	1985	–	–
6	1940, 1600	2.11 [s, CH_3] [e]	1.02 [h]
6′	1935, 1595	2.17 [s, CH_3] [d]	0.96 [h]

[a] In Nujol. [b] all chemical shifts in ppm and coupling constants in Hz. [c] in CH_3CN–0.1 *M* Bu_4NPF_6, V vs SCE. [d] in CD_2Cl_2. [e] in CD_3CN. [f] in $CDCl_3$. [g] irreversible Ep^a. [h] reversible $E_{1/2}$.



Scheme 2



Scheme 3

ethanol–water solution of **3'** gives the expected complex **5'** (Scheme 2). Complexes **3'a-c** and **5'** were readily characterized spectrochemically and electrochemically (Table 1). Cyclic voltammetry of **3'c** shows a Ru^{III}/Ru^{II} wave at 0.90 V. The difference of 120 mV observed between **3c** and **3'c** clearly reflects the stronger donor character of the bpy * ligands, and can explain the higher reactivity of **3'c** towards protic electrophiles.

Propiolic acid also cleanly reacts with carbonato-ruthenium complexes **1** and **1'** in boiling water or ethanol–water mixture to give, after addition of NH_4PF_6, the unexpected yellow compounds **6** and **6'** in quantitative yields (Scheme 3). The identity of these new carbonyl-acyl ruthenium complexes has been established by infrared, ^1H, and ^{13}C NMR spectroscopy (Table 1). For **6** and **6'** the ν(CO) acetyl band appears at 1600 and 1595 cm^{-1}, respectively. In the ^{13}C NMR spectrum the acyl and carbonyl carbons in **6** give rise to a singlet at δ 262.2 and 203.5 ppm, respectively, in the typical range of δ ^{13}C shifts for acyl and terminal CO carbon nuclei [9]. The mechanism of the reaction has still to be established, and experiments are in progress aimed at isolating the intermediates.

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