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Preliminary communication

FORMATION OF ARENE(CARBENE)RUTHENIUM COMPLEXES VIA VINYLIDENERUTHENIUM INTERMEDIATES

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Summary

$RuCl_2(PR_3)(\eta^6\text{-}C_6Me_6)$ (PR_3 = PMe_3; PMe_2Ph) reacts at room temperature with alkyne RC≡CH and $NaPF_6$ in methanol to produce the (alkoxy)alkylcarbeneruthenium complexes $[Ru(=C(OMe)CH_2R)Cl(PR_3)(\eta^6\text{-}C_6Me_6)]^+PF_6^-$ (R = Ph, ^{t}Bu, H) via a vinylideneruthenium intermediate. Use of 4-hydroxybutyne-1 leads to intramolecular cyclisation and formation of $[Ru(=CCH_2CH_2CH_2O)Cl(PMe_3)(C_6Me_6)]PF_6$.

Areneruthenium(II) complexes such as $RuCl_2(PR_3)(\eta^6\text{-}C_6Me_6)$ (**1**) have recently been shown [1] to be efficient catalyst precursors for the addition of carbamates to terminal alkynes to give vinyl carbamates. The regioselectivity of the addition suggested that the activation of the alkyne might proceed via a vinylideneruthenium intermediate. Although the M(η^2-alkyne) → M(η^1-vinylidene) rearrangement is well documented [2], especially in the cyclopentadienylruthenium(II) series [3], it has not been observed with areneruthenium(II) derivatives. Our attempts to isolate vinylideneruthenium complexes from **1** were initially unsuccessful, but we have found now that these intermediates can be trapped with alcohol to produce new (alkoxy)alkylideneruthenium complexes containing arene ligands.

To a suspension of 1 mmol (0.41 g) of **1a** [4] in 30 ml of methanol were added 1 mmol of phenylacetylene and 1 mmol $NaPF_6$. On stirring at room temperature a yellow precipitate formed rapidly, and this was recrystallized from dichloromethane/ether to give a 60% (0.395 g) yield of **2a** (Scheme 1). Only one isomer was observed by NMR spectroscopy. The ^{1}H NMR spectrum showed an AB system for the methylene protons, a signal consistent with a chiral ruthenium centre. In $^{13}C\{^1H\}$ NMR, the carbene-carbon resonance appeared at low field, as expected for a cationic carbene complex, and at 223 K only the resonance due to the CH_2–C(Ph) carbon nuclei disappeared, indicating a coalescence related to the rotation around the (Ru)CCH_2C(Ph) bonds. (^{1}H NMR (300.13 MHz, CD_2Cl_2, 300 K) δ(ppm): 7.35 (m, Ph), 5.04 and 4.50 (AB system, CH_2Ph, ^2J(HH) 13 Hz), 4.59 (s, OMe), 2.01 (s,

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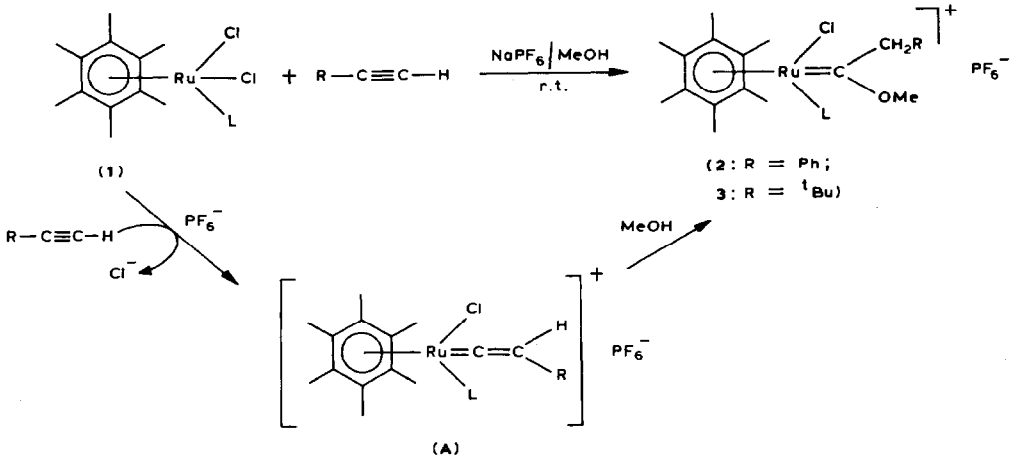
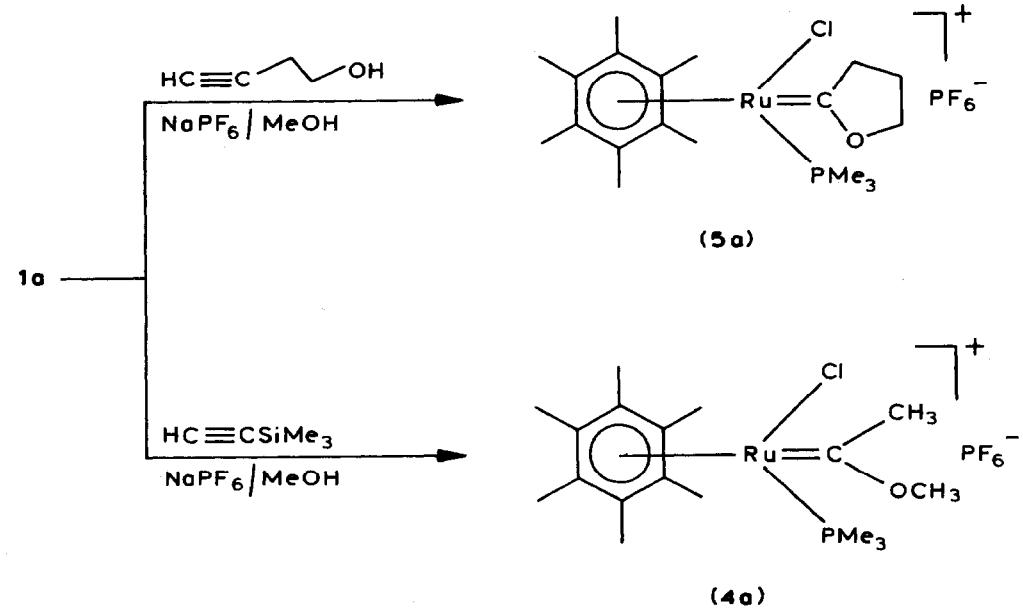


SCHEME 1

C_6Me_6), 1.44 (d, PMe_3, ^2J(PH) 10.6 Hz); ^{31}P NMR (32.38 MHz, CD_3COCD_3, 309 K) δ (ppm): 6.48 (s, PMe_3), 145.1 (sept, PF_6^-); ^{13}C {^1H} NMR (75.47 MHz, CD_2Cl_2, 300 K) δ (ppm): 323.0 (d, Ru=*C*, ^2J(PC) 20.6 Hz), 108.1 (s, C_6Me_6), 68.0 (s, OMe), 56.7 (s, CH_2), 16.6 (s, C_6Me_6), 16.2 (d, PMe_3, ^1J(PC) 35 Hz)).

Under similar conditions reaction of complex **1b** [4] with phenylacetylene gave **2b** in 58% yield. The carbeneruthenium complex **3a** (56%) was obtained by reaction of



SCHEME 2

TABLE 1

NMR DATA FOR CARBENE-RUTHENIUM COMPLEXES **2–5**

Complex	^{1}H NMR (300.13 MHz) δ(=C–CH_2)(ppm)(^2J(AB))	^{31}P NMR (32.38 MHz) $\delta(PR_3)$(s) [b] (ppm)	{^{1}H} ^{13}C NMR (75.47 MHz) δ(Ru=C)(ppm)(^2J(PC))
2a	5.04; 4.50 (13 Hz)	6.5	323.0 (20.6 Hz)
2b	5.49; 4.09 (12 Hz)	12.6	319.3 (19.8 Hz)
3a	3.70; 3.10 (20.6 Hz)	0.7	330.5 (16.1 Hz)
4a	2.98 (=C–CH_3)	10.5	330.9 (21.2 Hz)
5a	3.70; 3.30 (8 Hz) 5.18; 5.16 (23 Hz) [c]	8.6	317.4 (22.1 Hz)

[a] In CD_2Cl_2 at 300 K. [b] In addition, a septuplet was observed at ca δ −144 ppm, with respect to H_3PO_4 as external reference, for the PF_6^- anion. [c] O–CH_2.

1a with 2,2-dimethylbutyne-1. Complex **4a** was obtained in 60% yield by treating **1a** with trimethylsilylacetylene at room temperature (Scheme 2); its formation may involve a protonolysis of the C–Si bond by methanol as it was observed in carbene-platinum [5] and -tungsten complexes [6]. Reaction of complex **1a** with 4-hydroxybutyne-1 in methanol gave exclusively complex **5a**, isolated in 61% yield, indicating that the intramolecular addition of the alcohol function is favoured over addition of the solvent methanol. The complexes **2–5** gave satisfactory analyses, showed in the infrared absorptions at ca. 1280 cm^{-1} (C–OMe) and at 840 cm^{-1} (PF_6^-) and were characterized by NMR (Table 1).

The addition of an alcohol to an electrophilic vinylidene ligand is now well-established [2,7]. Thus the formation of the carbeneruthenium(II) complexes **2–5** probably proceeds via the addition of alcohol to the vinylidene ligand in the arene ruthenium(II) intermediates of type **A** (Scheme 1). The intermediates **A** may also be the active species in the additions to terminal alkynes catalyzed by precursors of type **1**.

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