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Reaction of $[(PEt_3)_3Rh\{C(N_2)SiMe_3\}]$ with terminal alkynes—synthesis of σ-alkynyl rhodium(III) complexes

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Abstract

Reaction of $[(PEt_3)_3Rh\{C(N_2)SiMe_3\}]$ with two equivalents of $HC\equiv CR$ (R = $SiMe_3$, Ph, or ${}^tBu$) affords the Rh^{III} complex $[(PEt_3)_3RhH(C\equiv CR)_2]$ in high yield, showing that the trimethylsilyldiazomethyl group behaves like an alkyl group. The reaction was followed by ^{31}P and ^1H NMR spectroscopy. The first step is the oxidative addition of alkyne to the metal, which is followed by elimination of trimethylsilyldiazomethane and formation of $[(PEt_3)_3Rh(C\equiv CR)]$.

Key words: Rhodium; Alkynes; Diazoalkanes; Synthesis; Hydride; Phosphine

1. Introduction

Reaction of alkynes with transition metal complexes is well documented since it generates a very rich inorganic, organometallic, and organic chemistry. Many examples of rhodium complexes with π-coordinated alkyne have been described [1] although σ-bonded alkynyl, hydridoalkynyl or vinylidene complexes were obtained by oxidative addition of terminal alkynes to basic metal centres [2,3]. Using $[RhCl(P^iPr_3)_2]$, Werner *et al.* studied the alkynyl-vinylidene rearrangement within the coordination sphere [4]. Increased interest in metal-alkynyl complexes has developed recently because they can give rise to linear conjugated molecules that may exhibit both second- and third-order non-linear optical activity [5,6]. Terminal alkynes are also synthons for organic cycles and heterocycles. An example is the reaction with organic diazoalkanes, which give pyrazoles through dipolar [2 + 3] cycloaddition, and cyclopentene after N_2 evolution [7].

It was thus of interest to study the reaction of alkynes with α-metallated diazoalkanes which combine the properties of a diazoalkane with those of a metal. This has not been done before because of the lack of suitable precursors. Since we prepared stable $[(PEt_3)_3Rh\{C(N_2)SiMe_3\}]$ (**1**) [8], we investigated its reaction with terminal alkynes $HC\equiv CR$ (R = $SiMe_3$, Ph or ${}^tBu$), and the results are reported here.

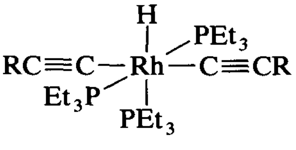
2. Results and discussion

$[(PEt_3)_3Rh\{C(N_2)SiMe_3\}]$ (**1**) dissolved in C_6H_6 reacts at 25°C under Ar with two molecules of alkyne, $HC\equiv CR$, to give quantitatively the Rh^{III} complexes (**2a–c**) *mer-trans* $[(PEt_3)_3RhH(C\equiv CR)_2]$, which have been isolated as orange, air-sensitive, oily solids. The reactions were followed by $^{31}P\{^1H\}$ and ^1H NMR spectroscopies and all followed a similar path.

$$\underset{\mathbf{1}}{[(PEt_3)_3Rh\{C(N_2)SiMe_3\}]} + 2\,HC\equiv CR \longrightarrow$$

$$\underset{\mathbf{2}}{[(PEt_3)_3RhH(C\equiv CR)_2]} + HC(N_2)SiMe_3$$

2a: R = $SiMe_3$
2b: R = Ph
2c: R = ${}^tBu$



To our knowledge they are the second example of bis(alkynyl)hydridorhodium complexes. The first exam-

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TABLE 1. Selected $^{31}P\{^1H\}$ and ^1H NMR parameters for **2a–c** and **3a–c**

Compound	δP_A (ppm)	δP_B (ppm)	J(Rh–PA) (Hz)	J(Rh–PB) (Hz)	J(P–P) (Hz)	δH (ppm)	J(Rh–H) * (Hz)	J(H–PA) (Hz)
2a [1]	−3	19	74	95	21	−10.38	13.5	166.9
2b [2]	−3	20	79	94	21	−10.19	13.4	170.5
2c [2]	−2	21	77	97	21	−10.65	12.0	171.9
3a [3]	24	20	128	137	38			
3b [4]	24	21	131	136	38			
3c [4]	25	21	133	135	38			

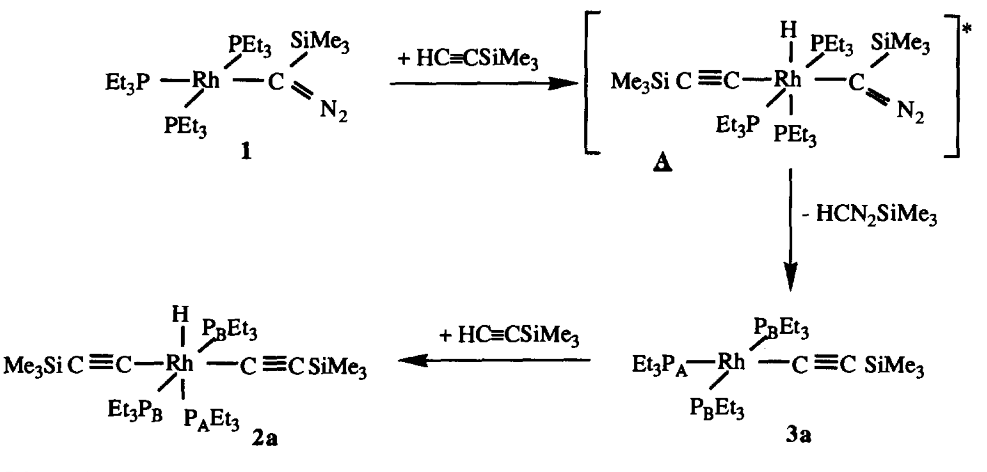
[1] $^{31}P\{^1H\}$: C_7D_8, 203 K; ^1H: C_7D_8, normal probe temperature. [2] C_7D_8, normal probe temperature. [3] C_7D_8, 183 K. [4] C_7D_8, 203 K.
* $J(\text{Rh–H}) = J(P_B\text{–H})$.

ple is the related PMe_3 compound that was synthesized by the reaction of HC≡CR with $[(PMe_3)_4Rh(C{\equiv}CR)]$ and structurally characterized [9].

Presence of the hydrido-ligand is deduced from the ^1H NMR spectrum, which shows a doublet of quadruplets characteristic of the *mer-trans* conformation (Table 1). The $^{31}P\{^1H\}$ NMR spectra are consistent with this conformation since they indicate an AB_2X system with coupling constants characteristic of a Rh^{III} centre. The sextuplet observed in the $^{13}C\{^1H\}$ NMR spectra confirms the equivalence of the two *trans*-alkyne carbon atoms. In contrast to the reaction of $[(PR_3)_nRhCl]$ (n = 2, 3, or 4) with alkyne, which gives alkynyl, hydridoalkynyl, and vinylidene derivatives, here the reaction is stereoselective and only complexes (**2**) have been observed.

It is possible to follow the addition of HC≡CR on (**1**) in deuterated benzene or toluene by ^{31}P and ^1H NMR spectroscopy. In every case a similar sequence of events was observed and we describe the experiment in the case of $HC{\equiv}CSiMe_3$. The reaction occurs stepwise. When the alkyne/complex ratio is about 1/2, the $^{31}P\{^1H\}$ NMR spectrum shows the multiplet characteristic of **1** and a second order AB_2X (X = Rh) multiplet attributed to $[(PEt_3)_3Rh(C{\equiv}CSiMe_3)]$, (**3a**), which becomes first order at −80°C. No signal due to free PEt_3 is apparent at low temperature, indicating that the first step is not a substitution process. The low temperature ^1H NMR spectrum for an alkyne: complex ratio of less than 0.5 shows two $SiMe_3$ singlets corresponding to **1** and **2a**, respectively, and the two signals of free $HC(N_2)SiMe_3$ [2.22 ppm (1H) and −0.02 ppm (9H)]. We could not isolate **3a** from the mixtures even at −70°C but it was successfully synthesized by reaction of lithio(trimethylsilyl)acetylene with $[(PEt_3)_3RhCl]$ at −78°C and its structure confirmed by IR and ^1H, ^{31}P, ^{13}C NMR spectroscopies and by comparison with the reported X-ray structure of the PMe_3 analogue [3].

When the amount of alkyne was increased, **2a** became the major species and for the ratio L/M > 2, it is the only complex present in solution. The corresponding ^1H NMR spectrum shows two new singlets in the



Scheme 1.

$SiMe_3$ region and two doublets at 6.51 and 5.93 ppm (J_{HH} = 19 Hz) in the alkene region besides **2a** and free trimethylsilyldiazomethane. These data are consistent with the stereoselective formation of the *E*-1,4-bis-(trimethylsilyl)but-1-ene-3-yne, $(SiMe_3)CH{=}CH{-}C{\equiv}C(SiMe_3)$ (**4**), resulting from the head-to-head coupling of two alkyne molecules. Larger quantities of trimethylsilylacetylene increased the amount of **4** as expected, since this coupling is known to be rhodium-catalyzed [10–12].

Scheme 1 suggests a mechanistic interpretation of the reaction course. The observation that **1** reacts with $HC{\equiv}CR$ to give **3**, (Table 1), led us to infer that the unobserved $[(PEt_3)_3RhH\{C(N_2)SiMe_3\}(C{\equiv}CR)]$ A resulting from oxidative addition of $HC{\equiv}CR$ to **1** is an unobserved intermediate. We have obtained previously the related Rh^{III} species $[(PMe_3)_3Rh\{C(N_2)SiMe_3\}IMe]$ by oxidative addition of MeI to $[(PMe_3)_4Rh\{C(N_2)SiMe_3\}]$, but we were unable to prepare the PEt_3 complex, which may be due to the larger steric hindrance of PEt_3 (cone angle of 123°) compared to PMe_3 (cone angle of 118°). Thus, formation of an unstable intermediate A remains probable, and it would give $[(PEt_3)_3Rh(C{\equiv}CR)]$ and free trimethylsilyldiazomethane through reductive elimination. This reaction is related to the reaction of terminal alkyne with $[(PMe_3)_4RhMe]$ which produces $(PMe_3)_4Rh(C{\equiv}CR)$ and methane. Consequently, trimethylsilyldiazomethane in **1** behaves like an alkyl group.

3. Experimental details

All operations were carried out under dinitrogen or in vacuum. Benzene was dried over sodium and distilled from sodium-benzophenone under dinitrogen. It was degassed by three freeze-thaw cycles before use. C_6D_6 (CEA) and PEt_3 were used as received. $[(PEt_3)_3Rh\{C(N_2)SiMe_3\}]$ was made by the published method [8]. Spectrometers: NMR; Bruker AC 200 and AC80, data in ppm referenced to $SiMe_4$ for ^1H and ^{13}C and to H_3PO_4 85% in D_2O for ^{31}P: IR; Perkin Elmer 577 and 983. Spectra in Nujol mulls or in NaCl cells (0.1 mm width), data in cm^{-1}.

3.1. *$[(PEt_3)_3RhH(C{\equiv}CSiMe_3)_2]$ (2a)*

$HC{\equiv}CSiMe_3$ (1.10 mmol) was added to a benzene solution (5 ml) of $[(PEt_3)_3Rh\{C(N_2)SiMe_3\}]$ (300 mg; 0.53 mmol). The solution was stirred for 15 min. Evaporation of the solvent *in vacuo* gave an orange oily product which, after recrystallization from pentane, produced **1** in good yield (90%). IR: $\nu(C{\equiv}C) = 2055$ cm^{-1}; $\nu(Rh{-}H) = 2005$ cm^{-1}; ^1H NMR (C_7D_8; probe temperature): −10.38 (dq, Rh–*H*, $^2J(PB{-}H) = 13.5$, $^2J(PA{-}H) = 166.9$, $^1J(Rh{-}H) = 13.5$); 0.24 (s, $(CH_3)_3Si$); 1.16 (q, $(CH_3CH_2)_3P_A$, $^3J(P{-}H) = 15$, $^3J(H{-}H) = 7.6$); 1.15 (q, $(CH_3CH_2)_3P_B$, $^3J(P{-}H) = 15$, $^3J(H{-}H) = 7.6$); 1.85 (m, $(CH_3CH_2)_3P_A$, $^3J(H{-}H) = 7.6$); 1.91 (m, $(CH_3CH_2)_3P_B$, $^3J(H{-}H) = 7.6$); $^{31}P\{^1H\}$ NMR (C_7D_8; 203 K): −3 (dt, $(CH_3CH_2)_3P_A$, $^1J(Rh{-}P) = 74$); 19 (dd, $(CH_3CH_2)_3P_B$, $^1J(Rh{-}P) = 95$, $^2J(P{-}P) = 21$); $^{13}C\{^1H\}$NMR (C_7D_8, RT): 1.7 (s, $(CH_3)_3Si$); 8.8 (s, $(CH_3CH_2)_3P$); 19.3 (d, $(CH_3CH_2)_3P_A$, $J(P{-}C) = 16$); 20.7 (t, $(CH_3CH_2)_3P_B$, $J(P{-}C) = 14$); 136.1 (dq, $Rh(CCSiMe_3)$, $J(P{-}C) = 16$; $J(Rh{-}C) = 32$); 112.8 (d, $Rh(CCSiMe_3)$, $J(Rh{-}C) = 5$).

3.2. *$[(PEt_3)_3Rh(C{\equiv}CSiMe_3)]$ (3a)*

1.5 ml of PEt_3 (0.01 mol) was added slowly to a suspension of 500 mg (1.3 mol) of $[\{RhCl(C_2H_4)_2\}_2]$ in ether (20 ml). The stirring was continued for 15 min, then the solvent was evaporated *in vacuo*. The resulting solid was allowed to react at −78°C with a solution of $LiC{\equiv}CSiMe_3$ [1.75 ml (2.8 mmol) of MeLi + 300 mg (3 mmol) of $HC{\equiv}CSiMe_3$ in ether (15 ml), −78°C, 25 min stirring]. The resulting solution was stirred at −78°C for 1 h and at 25°C for 15 min. Evaporation of the solvent gave a red solid which was recrystallized from pentane. (Yield: 80%). IR: $\nu(C{\equiv}C)$: 1998 cm^{-1}. ^1H NMR (C_7D_8, 293 K): 0.21 (s, $(CH_3)_3Si$); 0.92 (q, $(CH_3CH_2)_3P_A$, $^3J(P{-}H) = 15$, $^3J(H{-}H) = 7.4$); 0.92 (q, $(CH_3CH_2)_3P_B$, $^3J(P{-}H) = 15$, $^3J(H{-}H) = 7.5$); 1.36 (q, $(CH_3CH_2)_3P_A$, $^3J(H{-}H) = 7.4$); 1.85 (m, $(CH_3CH_2)_3P_B$, $^3J(H{-}H) = 7.5$); $^{31}P\{^1H\}$ NMR (C_7D_8, 183 K): 20 (dd, $(CH_3CH_2)_3P_B$, $^1J(Rh{-}P) = 137$); 24 (dt, $(CH_3CH_2)_3P_A$, $^1J(Rh{-}P) = 128$, $^2J(P{-}P) = 38$); $^{13}C\{^1H\}$ NMR (C_7D_8, 223 K): 2.1 (s, $(CH_3)_3Si$); 9.5 (s, $(CH_3CH_2)_3P_A$); 9.5 (s, $(CH_3CH_2)_3P_B$); 19.7 (t, $(CH_3CH_2)_3P_B$, $J(P{-}C) = 13$); 20.6 (d, $(CH_3CH_2)_3P_A$, $J(P{-}C) = 19$); 156.5 (ddt, $Rh(CCSiMe_3)$, $J(PA{-}C) = 84$, $J(PB{-}C) = 24$, $J(Rh{-}C) = 40$); 112.6 (dd, $Rh(CCSiMe_3)$, $J(Rh{-}C) = 11$, $J(PA{-}C) = 21$). Microanalysis calc. for $C_{23}H_{54}P_3RhSi$: H 9.82; C 49.82; found: H 9.78; C 48.96%.

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