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Wolff rearrangement in a transition-metal diazoalkane complex. Synthesis of the first η^1-ketenyl rhodium complex $[Rh\{C(CO)SiMe_3\}(CO)(PEt_3)_2]$

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Abstract

Reaction of carbon monoxide with $[Rh\{C(N_2)SiMe_3\}(PEt_3)_3]$ gives $[Rh\{C(CO)SiMe_3\}(CO)(PEt_3)_2]$ (3) in a high yield, Wolff-like rearrangement process. This is the first Rh^I η^1-ketenyl complex which has been characterized by ^1H, ^{13}C, ^{31}P NMR and IR spectroscopies.

1. Introduction

Organic diazoalkanes are exceedingly useful in organic synthesis, as precursors for carbenes, as reagents for heterocyclic synthesis *via* 1,3-dipolar cycloaddition, and for their rearrangement reactions [1]. By far the most useful process is the Wolff rearrangement of α-diazoketones, giving ketenes or ketene-derived products. This reaction has been used for ring contraction and for chain homologation. Two mechanisms have been proposed for this process. The first involves N_2 loss and formation of free carbene (Scheme 1). The second is a one-step concerted reaction.

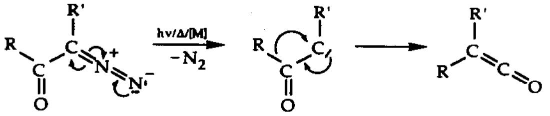
By comparison, the chemical reactivity of diazoalkanes *C*-bonded to transition metals is underdeveloped. This is related to the fact that α-metalated diazoalkanes are few in number and as yet limited to osmium [2], palladium [3], rhodium [4], and nickel [5]. However, their carbenoid character has been illustrated in the case of the rhodium and nickel complexes, the transient singlet α-metalated carbenes generated by photolysis being trapped by phosphine [4b,5].

Interest in the carbonylation of these species is increased by the fact that coupling of carbon monoxide with methyl and methylidyne ligands are possible steps in homogeneous and heterogeneous metal-catalyzed reduction of carbon monoxide by molecular hydrogen. Examples of these mechanisms are still scarce [6].

Here we describe the reaction of $[Rh\{C(N_2)SiMe_3\}(PEt_3)_3]$ (1) with carbon monoxide producing the first η^1-ketenyl complex of rhodium, 3, in a high-yield Wolff-rearrangement-like process. It is the first example of such a mechanism in α-metallated diazoalkanes.

2. Experimental part

All operations were performed under argon with dioxygen-free solvents using standard Schlenk techniques. $[Rh\{C(N_2)SiMe_3\}(PEt_3)_3]$ was prepared as already reported [4b]. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 983 spectrometer and in benzene or pentane solutions prepared in a glove box. The ^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ solution spectra were recorded on a Bruker WM 200 spectrometer in C_6D_6. Chemical shifts were referenced to the residual solvent signals for ^1H and ^{13}C NMR (C_6D_6; $^1H: \delta(^1H) = 7.27$;



Scheme 1.

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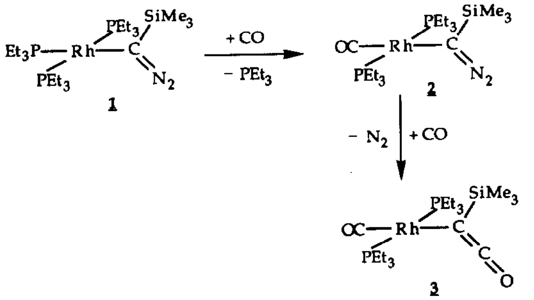


Scheme 2.

$\delta(^{13}C) = 128.4$ ppm) and for ^{31}P NMR to external H_3PO_4 (85% in D_2O, $\delta = 0$ ppm).

2.1. *Synthesis of [Rh{C(CO)SiMe₃}(CO)(PEt₃)₂] (3)*

CO was bubbled slowly through a solution of $[Rh\{C(N_2)SiMe_3\}(PEt_3)_3]$ (300 mg, 0.53 mmol) in C_6H_6 (5 ml) at room temperature until the red solution turned yellow. The solvent was evaporated *in vacuo*. Addition of 5 ml of pentane, filtration, and concentration produced **3** as a yellow solid in 95% yield. All attempts to obtain single crystals were unsuccessful.

3. Results and discussion

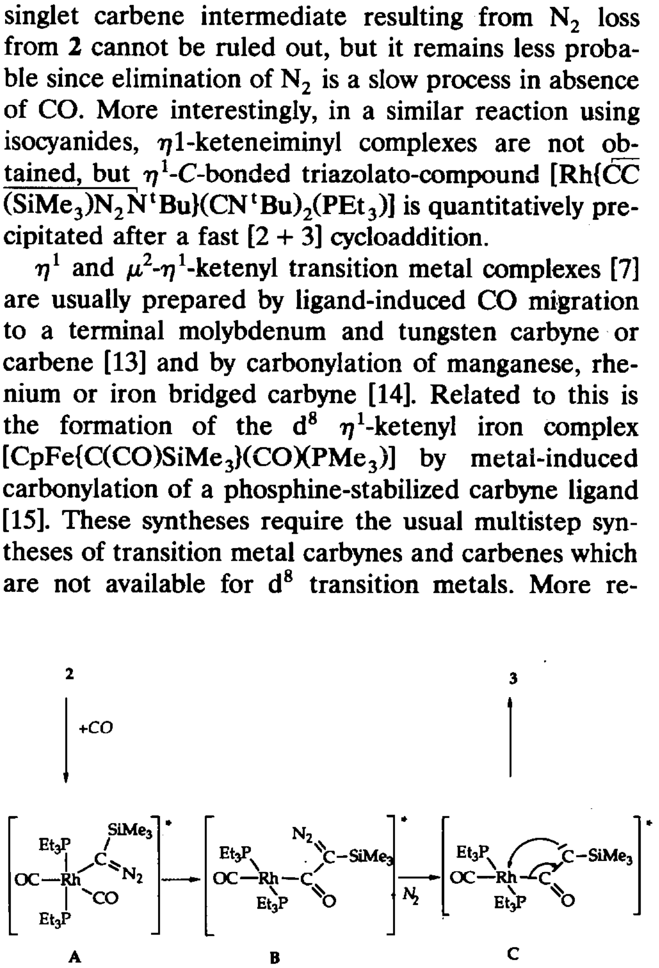
Bubbling CO slowly through a benzene solution of **1** produced a change from red to yellow. The reaction was followed by $^{31}P\{^1H\}$ NMR and IR spectroscopies and showed the successive formation of two species $[Rh\{C(N_2)SiMe_3\}(CO)(PEt_3)_2]$ (**2**) and $[Rh\{C(CO)SiMe_3\}(CO)(PEt_3)_2]$ (**3**) (Scheme 2) [7*]. Complex **2** was isolated by careful control of CO concentration (in the ratio CO/**1** = 1:1). An excess of CO gave the ketenyl compound **3**.

The η^1-ketenyl complex **3** was characterized by NMR and IR spectroscopies. The two strong infrared stretches at 2020 cm^{-1} and 1953 cm^{-1} confirmed the presence of both ketenyl and carbonyl. The $^{31}P\{^1H\}$ NMR spectrum displayed a doublet at 22 ppm (J(Rh–P) = 122 Hz) indicating *trans* phosphines. The ^1H NMR spectrum showed a broad resonance at 1.68 ppm (^2J(H–H) = 7.5 Hz) for the CH_2, a quintet at 1.00 ppm (^3J(P–H) = 15; ^3J(H–H) = 7.5 Hz) for the CH_3 groups of PEt_3 and one $SiMe_3$ resonance at 0.28 ppm (in the ratio $SiMe_3/PEt_3 = 1:2$). The ketenyl group was unambiguously characterized by $^{13}C\{^1H\}$ NMR spectroscopy by a singlet at 145.4 ppm corresponding to the sp carbon atom bonded to oxygen and a doublet of triplets at −7.6 ppm (^2J(P–C) = 10; ^1J(Rh–C) = 21 Hz) characteristic of the sp^2 carbon atom. These values are within the usual range for metal-coordinated ketenyl groups [8]. The doublet of triplets observed at 189.80 ppm was attributed to the terminal carbonyl ligand.

The first step in this reaction involves substitution of the phosphine *trans* to the diazoalkyl group of **1** by CO giving **2** [4b]. It is reasonable to assume that a second CO molecule then inserts into the $Rh–C(N_2)SiMe_3$ bond of **2** producing the rhodium-substituted α-diazoketone **B** with the five-coordinate complex **A** as intermediate (Scheme 3) [9*]. This has precedents in the synthesis of rhodium-acyl complexes [10] and in the reaction of $[Rh\{C(N_2)SiMe_3\}(PEt_3)_3]$ with isocyanides [6]. The most probable reaction is a Wolff-rearrangement-like process involving the rhodium-substituted α-diazoketone **B** giving **3** quantitatively. Thus the diazo moiety remains present at stage B [11]. Metal-assisted loss of N_2 during the B → C step may be facilitated by coordination of the terminal nitrogen atom to the unsaturated d^8 Rh^I fragment [12].

The possibility of direct addition of CO to the singlet carbene intermediate resulting from N_2 loss from **2** cannot be ruled out, but it remains less probable since elimination of N_2 is a slow process in absence of CO. More interestingly, in a similar reaction using isocyanides, η1-keteneiminyl complexes are not obtained, but η^1-*C*-bonded triazolato-compound $[Rh\{\overline{CC}(SiMe_3)N_2N^tBu\}(CN^tBu)_2(PEt_3)]$ is quantitatively precipitated after a fast [2 + 3] cycloaddition.

η^1 and μ^2-η^1-ketenyl transition metal complexes [7] are usually prepared by ligand-induced CO migration to a terminal molybdenum and tungsten carbyne or carbene [13] and by carbonylation of manganese, rhenium or iron bridged carbyne [14]. Related to this is the formation of the d^8 η^1-ketenyl iron complex $[CpFe\{C(CO)SiMe_3\}(CO)(PMe_3)]$ by metal-induced carbonylation of a phosphine-stabilized carbyne ligand [15]. These syntheses require the usual multistep syntheses of transition metal carbynes and carbenes which are not available for d^8 transition metals. More re-



Scheme 3.

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* Reference number with asterisk indicates a note in the list of references.

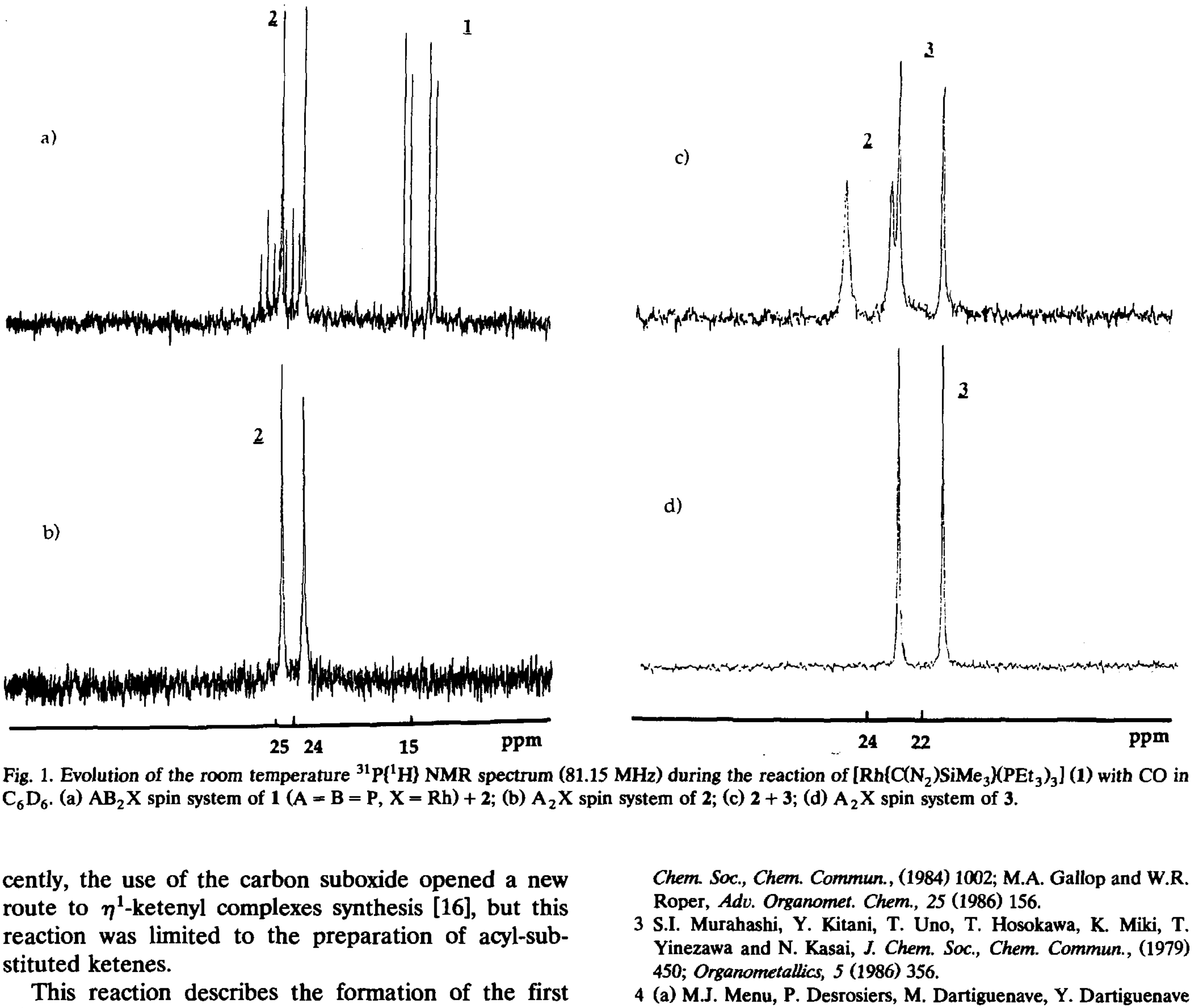

Fig. 1. Evolution of the room temperature $^{31}P\{^1H\}$ NMR spectrum (81.15 MHz) during the reaction of $[Rh\{C(N_2)SiMe_3\}(PEt_3)_3]$ (**1**) with CO in C_6D_6. (a) AB_2X spin system of **1** (A = B = P, X = Rh) + **2**; (b) A_2X spin system of **2**; (c) **2** + **3**; (d) A_2X spin system of **3**.

cently, the use of the carbon suboxide opened a new route to η^1-ketenyl complexes synthesis [16], but this reaction was limited to the preparation of acyl-substituted ketenes.

This reaction describes the formation of the first η^1-ketenyl rhodium complex by carbonylation of a rhodium-diazomethyl compound. This is important in the field of metal-induced carbonylation involving late-transition-metal carbyne species.

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