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Chemistry of Fischer-type rhenacyclobutadiene complexes. I. Deprotonation, addition/substitution of nucleophilic reagents at α-carbon, and insertion of heteroatoms into rhenium–carbon bonds

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Abstract

The rhenacyclobutadienes $(CO)_4Re(\eta^2$- $C(R)C(CO_2Me)C(OR'))$ (**2**) undergo a number of reactions that mirror those of Fischer alkoxycarbene complexes. Thus, $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(OEt))$ (**2a**) can be deprotonated by LDA, Na[OBu-*t*], or $Na[CH(CO_2Me)_2]$ to give the ylide-like conjugate base $[(CO)_4Re(\eta^2\text{-}C({=}CH_2)C(CO_2Me)C(OEt)]^-$ (**3**), which was isolated as PPN(**3**). Li(**3**) undergoes deuteriation with DCl/D_2O and alkylation with Et_3OPF_6 at $ReC{=}CH_2$, with the latter reaction affording $(CO)_4Re(\eta^2\text{-}C(CH_2Et)C(CO_2Me)C(OEt))$ (**4**). Repetition of the sequence deprotonation-ethylation on **4** generates $(CO)_4Re(\eta^2\text{-}C(CHEt_2)C(CO_2Me)C(OEt))$ (**5**). The nature of the alkoxy substituent in **2** can be varied by use of the rhenacyclobutenones $Na[(CO)_4Re(\eta^2\text{-}C(R)C(CO_2Me)C(O))]$ (Na(**1**)) in conjunction with AcCl and R′OH to produce a series of new complexes (R = Ph, R′ = Et (**2b**); R = Me, $R' = CH_2CH{=}CH_2$ (**2c**), $(CH_2)_3C{\equiv}CH$ (**2d**), Me (**2e**)). Aminolysis of **2a** with the primary and secondary amines $PhNH_2$, $HO(CH_2)_2NH$, *p*-$TolNH_2$, and Et_2NH yields the aminorhenacyclobutadiene complexes $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(NHR'$ or $NR'_2))$ ($R'_2 = Et_2$ (**6a**); R′ = Ph (**6b**), $(CH_2)_2OH$ (**6c**), *p*-Tol (**6d**)). These complexes display lesser carbene-like character than their alkoxy counterparts **2**, as evidenced by ^1H and ^{13}C NMR spectroscopic properties and lack of reactivity toward LDA by **6a**. Reactions of each **2a** and **6a** with $PPhMe_2$ at low temperature afford $(CO)_4Re(\eta^2\text{-}C(Me)(PPhMe_2)C(CO_2Me)C(OEt))$ (**7**) and $(CO)_3(PPhMe_2)Re(\eta^2\text{-}C(Me)C(CO_2Me)C(NEt_2))$ (**9**), respectively, further in agreement with the more carbenoid nature of **2a** than **6a**. **7** undergoes conversion to $(CO)_3(PPhMe_2)Re(\eta^2\text{-}C(Me)C(CO_2Me)C(OEt))$ (**8**) upon heating. **2a** reacts with each of $(NH_4)_2[Ce(NO_3)_6]$, DMSO, $EtNO_2/Et_3N$, and Me_3NO under various conditions to afford one or both of the oxygen atom insertion products into the Re=C bonds, $(CO)_4Re(\kappa^2\text{-}OC(Me)C(CO_2Me)C(OEt))$ (**10**) and $(CO)_4Re(\kappa^2\text{-}C(Me)C(CO_2Me)C(OEt)O)$ (**11**). In contrast, no reaction occurred between **2a** and S_8 on heating. However, **6a** was converted to the NH insertion product $(CO)_4Re(\kappa^2\text{-}NHC(Me)C(CO_2Me)C(NEt_2))$ (**12**) by the action of $H_2NNH_2 \cdot H_2O$ at 0 °C. All new compounds were characterized by a combination of elemental analysis, mass spectrometry, and IR and NMR spectroscopy.

Keywords: Rhenium complexes; Metallacyclobutadiene complexes; Fischer carbene complexes; Deprotonation reactions; Aminolysis reactions; Insertion reactions

1. Introduction

We have previously reported the synthesis of rhenacyclobutenone complexes $Na[(CO)_4Re(\eta^2\text{-}C(R)C(CO_2Me)C(O))]$ (Na(**1**)) by reaction of $Na[Re(CO)_5]$ with the activated alkynes $RC{\equiv}CCO_2Me$ (R = H, Me, CO_2Me) [1,2]. Alkylation of Na(**1**) with Et_3OPF_6 furnished the

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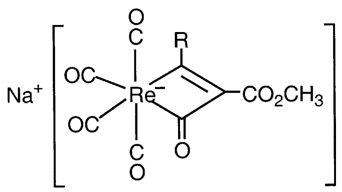
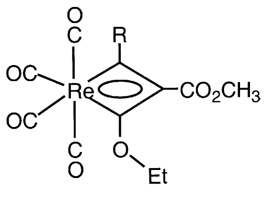
corresponding rhenacyclobutadiene complexes $(CO)_4Re(\eta^2\text{-}C(R)C(CO_2Me)C(OEt))$ (**2**).

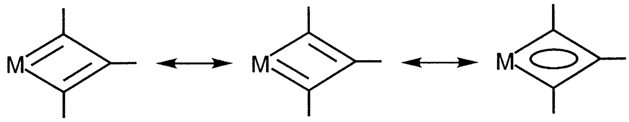


Na(**1**)



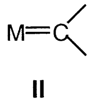
2

Structural, spectroscopic [1,2] and limited reaction chemistry studies on **2** [1–3] have indicated that these complexes may be regarded as metallacyclobutadiene analogues of Fischer-type carbenes [4], in the same sense that Schrock metallacyclobutadienes [5] are related to Schrock-type carbenes (alkylidenes) [6] (cf. **I** and **II**). Fischer carbene and metallacyclobutadiene complexes generally contain a low oxidation state transition metal in conjunction with carbonyl ligands, are often stabilized by the presence of a heteroatom bonded to carbene carbon, and show electrophilic properties. In contrast, Schrock alkylidene and metallacyclobutadiene complexes incorporate metal in a high formal oxidation state and behave as nucleophiles. [2]



I

metallacyclobutadiene



II

metal carbene/alkylidene

Since their discovery in 1964 [8], Fischer carbene complexes have shown extensive reaction chemistry and are considered to be one of the most versatile reagents in organic synthesis [9,10]. To explore chemical analogies between Fischer carbene and metallacyclobutadiene complexes, we have investigated several aspects of reaction chemistry of **2** and related rhenacyclobutadienes. Reported in this paper are our studies directed at developing further methods of synthesis of Fischer rhenacyclopentadiene complexes and at expanding the scope of their addition/substitution reactions with nucleophiles as well as insertion reactions of heteroatoms into Re=C bonds. The accompanying paper is concerned with reactions of **2** and derivatives with alkynes and sulfonium ylides and with rearrangements induced by nitriles and pyridine [11].

2. Experimental

2.1. General procedures and measurements

Reactions and manipulations of air-sensitive compounds were conducted under an atmosphere of dry argon by use of standard procedures [12]. Solvents were dried [13], distilled under argon, and degassed before use. Elemental analyses were carried out by M-H-W Laboratories, Phoenix, AZ and Guelph Chemical Laboratories Ltd, London, Ont., Canada. IR and NMR (^1H, ^2H, ^{13}C, and ^{31}P) spectra were obtained as previously described [14,15]. Mass spectra were recorded on a Kratos VG70-250S spectrometer by using either electron impact (EI) or fast atom bombardment (FAB) techniques. All listed mass peaks are those of ions containing ^{187}Re. Column chromatography was done on silica gel (Merck grade 60, 230–240 mesh).

2.2. Materials

Reagents were procured from various commercial sources and used as received. A solution of $Na[Re(CO)_5]$ in THF was prepared as described previously [2]. Rhenacyclobutenone $Na[(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(O)]$ (Na(**1a**))) was synthesized according to a procedure reported in the literature [2], but generally on a larger (ca. 4 times) scale, which resulted in the formation of purer product (less polynuclear rhenium carbonyl impurity). The complex $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(OEt))$ (**2a**) was obtained by treatment of Na(**1a**) with Et_3OPF_6 [2] (Method 1) or with AcCl and EtOH (Method 2, cf. Section 2.4.1.).

2.3. Deprotonation reactions of $(CO)_4Re(\eta^2\text{-}C(Me)C(CO_2Me)C(OEt))$ (2a) and deuteriation or alkylation of resultant $M[(CO)_4Re(\eta^2\text{-}C(=CH_2)C(CO_2Me)C(OEt))]$ (M(3): M = Li, Na, PPN)

2.3.1. Synthesis of $PPN[(CO)_4Re(\eta^2\text{-}C(=CH_2)C(CO_2Me)C(OEt))]$ (PPN(3): $PPN=(Ph_3P)_2N$)

A solution of **2a** (0.349 g, 0.770 mmol) in 20 ml of THF at −78 °C was treated with 1 equivalent of LDA (lithium diisopropylamide) in hexane (0.970 ml, 0.8 M)

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[2] However, some metal carbene/alkylidene complexes show amphiphilic properties [7].