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Reactivity with Alkene and Alkyne of Pentamethylcyclopentadienyl Half-Sandwich Diazoalkane Complexes of Ruthenium

Gabriele Albertin,^{*a} Stefano Antoniutti,^a Marco Bortoluzzi,^a Alessandra Botter^a and Jesús Castro^b

^a *Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, Via Torino 155, 30172 Mestre Venezia, Italy.*

Departamento de Química Inorgánica, Universidade de Vigo, Facultade de Química, Edificio de Ciencias Experimentais, 36310 Vigo (Galicia), Spain.

* Corresponding author. E-mail address: albertin@unive.it

ABSTRACT

Treatment of diazoalkane complexes $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{N}_2\text{CAr}_1\text{Ar}_2)\{\text{P}(\text{OR})_3\}\text{L}]\text{BPh}_4$ (**1–5**) [$\text{Ar}_1 = \text{Ar}_2 = \text{Ph}$, $\text{Ar}_1 = \text{Ph}$, $\text{Ar}_2 = p\text{-tolyl}$, $\text{Ar}_1\text{Ar}_2 = \text{C}_{12}\text{H}_8$; $\text{R} = \text{Me}$, Et ; $\text{L} = \text{P}(\text{OR})_3$, PPh_3] with ethylene and maleic anhydride (ma) afforded η^2 -alkene derivatives $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\eta^2\text{-CH}_2=\text{CH}_2)\{\text{P}(\text{OR})_3\}(\text{PPh}_3)]\text{BPh}_4$ (**7**, **8**) and $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\eta^2\text{-ma})\{\text{P}(\text{OR})_3\}\text{L}]\text{BPh}_4$ (**6**, **9**), respectively. Acrylonitrile also reacted with diazoalkane complexes **1–5** to give dipolar (3+2) cycloaddition, affording 3*H*-pyrazole derivatives $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)\{\eta^1\text{-}\overline{\text{N}=\text{NC}(\text{C}_{12}\text{H}_8)\text{CH}(\text{CN})\text{CH}_2}\}\{\text{P}(\text{OR})_3\}(\text{PPh}_3)]\text{BPh}_4$ [**A**] and $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)\{\eta^1\text{-}\overline{\text{N}=\text{NC}(\text{C}_{12}\text{H}_8)\text{CH}_2\text{C}(\text{H})\text{CN}}\}\{\text{P}(\text{OR})_3\}(\text{PPh}_3)]\text{BPh}_4$ [**B**] (**10**, **11**). Treatment of complexes **1–5** with acetylene $\text{HC}\equiv\text{CH}$ under mild conditions (1 atm, room temperature) led to dipolar cycloaddition, affording 3*H*-pyrazole complexes $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)\{\eta^1\text{-}\overline{\text{N}=\text{NC}(\text{Ar}_1\text{Ar}_2)\text{CH}=\text{CH}}\}\{\text{P}(\text{OR})_3\}\text{L}]\text{BPh}_4$ (**12**, **15**), whereas reaction with terminal alkynes $\text{HC}\equiv\text{CR}$ gave vinylidene derivatives $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)\{\text{C}=\text{C}(\text{H})\text{R}\}\{\text{P}(\text{OR})_3\}\text{L}]\text{BPh}_4$ (**13**, **14**, **16**, **17**). The complexes were characterised spectroscopically (IR and ¹H, ³¹P, ¹³C NMR) and by X-ray crystal structure determination of $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)\{\eta^1\text{-}\overline{\text{N}=\text{NC}(\text{C}_{12}\text{H}_8)\text{CH}=\text{CH}}\}\{\text{P}(\text{OEt})_3\}_2]\text{BPh}_4$ (**12**). A DFT study on the reaction of diazoalkane complexes with $\text{CH}_2=\text{CH}_2$ is also reported.

Keywords: Diazoalkane; Ruthenium; Half-sandwich; Pentamethylcyclopentadienyl; Alkene and alkyne; Cycloaddition; Synthesis

Introduction

Transition metal complexes containing diazoalkanes as ligands have attracted interest for a long time [1–3], not only because of the different coordination mode and reactivity shown by coordinated $\text{N}_2\text{CAr}_1\text{Ar}_2$ groups, but also due to their potential use in the synthesis of metal carbene derivatives [4,5]. Diazoalkane is also of interest as a model for the dinitrogen fixation process [6].

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