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Synthesis and structural characterization of (pyrazolyl)alkenyl Fischer carbene complexes of chromium and tungsten

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Abstract

Michael addition of substituted pyrazoles **2** to 1-alkynyl Fischer carbene complexes $(CO)_5M{=}C(OEt)(C{\equiv}CPh)$ (**1**) (**a**, M = Cr and **b** M = W) afforded (pyrazolyl)alkenyl Fischer carbene complexes $(CO)_5M{=}C(OEt)(CH{=}C(R^1R^2R^3pz)Ph)$ ($R^1R^2R^3pz$ = pyrazolyl) **3** (M = Cr) and **4** (M = W), respectively, with an exclusive (*E*)-configuration in mild to excellent yields. The reaction of **1a** and 3,5-dimethylpyrazole (**2b**) was monitored to demonstrate the formation and decomposition of complex **3b** by ^1H NMR measurements in $CDCl_3$ at 23 °C. Complexes **3** and **4** were characterized with ^1H, $^{13}C\{^1H\}$ NMR, IR spectroscopies and elemental analysis. When the substituted pyrazoles were 3-methylpyrazole (**2a**) and 3,5-di-*tert*-butylpyrazole (**2d**), molecular structures of the corresponding (pyrazolyl)alkenyl Fischer carbene complexes **3a** and **4d** were characterized by X-ray crystallographic study.

Keywords: Fischer carbene; Pyrazole; Michael addition; Chromium; Tungsten

1. Introduction

Fischer carbene complexes were first synthesized by Fischer and Maasböl in 1964 [1,2] and have been paid much attention in the last two decades because they can be rather readily prepared and manipulated to demonstrate diverse reactivity in organic synthesis [3]. Transformations from alkynyl carbene to alkenyl carbene complexes have been extensively investigated. Michael addition of dimethylamine to Fischer alkynylcarbene complexes was reported by Fischer and Kreissl [4] as early as 1972, followed by several other groups [5]. Michael-type addition of amines or N–H bond-containing compounds to α,β-unsaturated Fischer carbene complexes to form β-aminovinyl-substituted products has been considered a useful methodology for certain preparative organic synthesis because the resultant Michael-type adducts are usually reactive intermediates [6–18]. A rich chemistry of pyrazoles [19] and pyrazolato ligands [20–22] has been evolved since pyrazoles were first prepared in 1968 [23], due to the presence of pyrazolyl-containing compounds in nature and potential bioactivity of pyrazole derivatives as well as their good coordination ability as ligands. Pyrazole contains a reactive N–H bond which can be easily deprotonated to proceed a lot of reactions. However, up to date no β-pyrazolyl subsitituted alkenyl Fischer carbene complexes have been synthesized, although 1-methoxy-1-(5-pyrazole) Fischer carbene complexes were reportedly generated in the reactions of 1-alkynyl Fischer carbene

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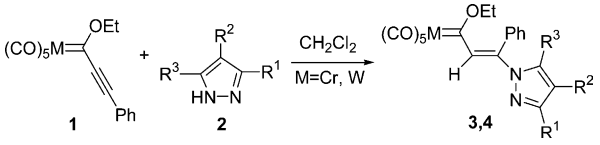
complexes with Me_3SiCHN_2 [24a] and $(CO)_5W$-C(OEt)(CH=C($C_3H_3N_2$)Ph) was detected by UV spectroscopy [24b]. Herein, we report the synthesis of (pyrazolyl)alkenyl Fischer carbene complexes **3** and **4** by the reactions of substituted pyrazoles **2** with 1-alkynyl Fischer carbene complexes **1a**,**b** (**a**, M = Cr; **b**, M = W) under mild conditions, as well as their structural characterization.

2. Results and discussion

2.1. Synthesis of (pyrazolyl)alkenyl carbene complexes 3 and 4

Treatment of the 1-alkynyl Fischer carbene complexes **1a** and **1b** with an equivalent amount of substituted pyrazole in dichloromethane at ambient temperature afforded (pyrazolyl)alkenyl Fischer carbene complexes **3** and **4** in mild to excellent yields (Eq. (1)). The reaction temperature was elevated to 38 °C due to the poor solubility of 3,5-di-*tert*-butylpyrazole and 3,5-di-phenylpyrazole in CH_2Cl_2. 3-Methylpyrazole exhibited very low reactivity to both complexes **1a** and **1b** and only 32.2% and 17.6% yields of the desired products were achieved over a period of 77–85 h for **1a** and **1b**, respectively.



(1)

2	R^1	R^2	R^3	3 (M = Cr), %	4 (M = W), %
2a	Me	H	H	**3a**, 32.2	**4a**, 17.6
2b	Me	H	Me	**3b**, ~77[a]	**4b**, 99.6
2c	Ph	H	Ph	**3c**, 60.5	**4c**, 90.4
2d	*t*-Bu	H	*t*-Bu	**3d**, 65.8	**4d**, 80.5
2e	Me	Me	Me	**3e**, 65.8	**4e**, 93.0
2f	Me	$PhCH_2$	Me	**3f**, 88.5	**4f**, 93.1

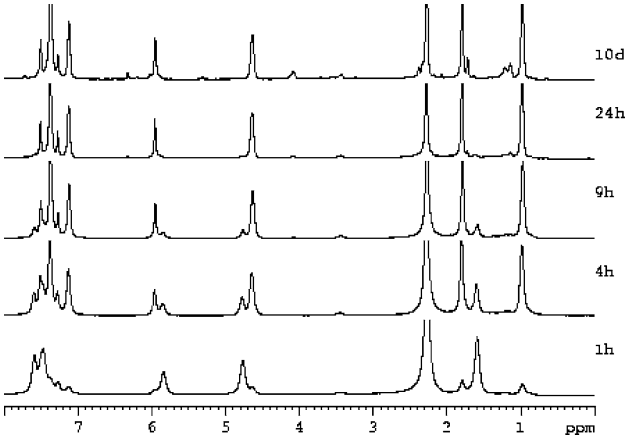
[a] Containing small amounts of decomposition products.

In the other cases, the tungsten carbene complex **1b** demonstrated higher reactivity (shorter reaction time) to the investigated substituted pyrazoles than its chromium analogue, leading to higher yields for the tungsten products (80.5–99.6%) and lower isolated yields for their chromium analogues (60.5–88.5%). It was observed that the chromium products were subject to decomposition on silica gel when the crude products were purified by column chromatography.

It is noteworthy that complex **4b** was obtained in 99.6% isolated yield while its chromium analogue, i.e., complex **3b** underwent decomposition under mild conditions to form some unidentified products when 3,5-dimethyl pyrazole was used. In order to understand the behavior of complex **3b**, Fischer carbene complex **1a** was treated with an equivalent amount of 3,5-dimethyl pyrazole (**2b**) in $CDCl_3$ in a 5-mL NMR tube at ambient temperature and the reaction was monitored by ^1H NMR measurements over a period of ten days (Scheme 1). The ^1H NMR measurements revealed that the reaction exclusively proceeded to form **3b** and the reaction was completed in 24 h at ambient temperature. It was noticed that the product, i.e., **3b**, gradually decomposed when the reaction solution was kept at ambient temperature for a longer time (e.g., 10 days). It was also observed that the reaction of **1a** with an excess of the pyrazole (2.0 equiv.) in $CDCl_3$ at ambient temperature did not lead to any formation of the de-ethoxy product, i.e., the 2,4-dipyrazolyl alkenylcarbene complex. Due to its decomposition at ambient temperature, the full characterization data for complex **3b** could not be collected, but its NMR data was tentatively assigned.

2.2. Spectroscopy of (pyrazolyl)alkenyl carbene complexes 3 and 4

The strong bands in the region 2069–1902 cm^{-1} of the IR spectra are characteristic of the typical patterns expected for a $M(CO)_5$ moiety in Fischer carbene complexes. The proton resonances of HC=C($R^1R^2R^3$pz)Ph in complexes **3** and **4** in $CDCl_3$ are shown in the region 8.20–7.31 ppm as singlets and those of the alkenyl complexes of chromium, **3**, are slightly shifted downfield as compared with their tungsten analogues. The ^{13}C resonances of the carbene carbons, i.e., Cr=C in complexes **3** are at 331.4–338.4 ppm and those of W=C in complexes **4** are at 310.5–304.6 ppm, while the ^{13}C NMR signals of typical β-aminoalkenyl Fischer carbene complexes exhibiting some conjugation between the metal carbene M=C and the alkenyl moiety are in the region ~270–290 ppm [7,10], and those of metal carbene M=C in $(OC)_5M$=



Scheme 1. Formation and decomposition of **3b** from the reaction of **1a** and 3,5-dimethylpyrazole (**2b**) monitored by ^1H NMR measurements in $CDCl_3$ at 23 °C.