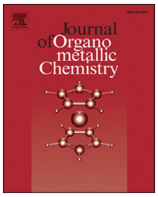
Journal of Organometallic Chemistry 780 (2015) 56–62

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem



Synthesis of acyl iron complexes based on bis(heteroaryl)methanes

Da-Wei Zhao, Xia-Li Liu, Xiao-Yan Zhang, Liang-Fu Tang*

Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China

ARTICLE INFO

Article history:
Received 14 October 2014
Received in revised form
23 December 2014
Accepted 30 December 2014
Available online 8 January 2015

Keywords:
Bis(heteroaryl)methane
Bis(pyrazol-1-yl)methane
1-Methylimidazole
Iron carbonyl
Metal–acyl complex

ABSTRACT

Treatment of the lithium salts, derived from the lithiation of bis(pyrazol-1-yl)methanes, bis(1-methylimidazol-2-yl)methane [$CH_2(mim)_2$] and 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine [$CH_2(3,5\text{-}Me_2Pz)(Py)$] using *n*-BuLi at low temperature, with iron carbonyl and iodine resulted in significantly different acyl iron derivatives. Reaction of bis(pyrazol-1-yl)methanes with *n*-BuLi, and subsequently with iron carbonyl and iodine yielded bis(pyrazol-1-yl)acyl iron complexes, while similar reaction of $CH_2(mim)_2$ gave valeryl iron complex $CH_2(mim)_2Fe(CO)_2(COBu\text{-}n)I$, which was also obtained by the sequential treatment of iron carbonyl with *n*-BuLi, $CH_2(mim)_2$ and iodine. Additionally, the consecutive reaction of $CH_2(3,5\text{-}Me_2Pz)(Py)$ with *n*-BuLi, iron carbonyl and iodine yielded (3,5-dimethylpyrazol-1-yl)(2-pyridyl)acyl iron complex. The corresponding valeryl iron complex $CH_2(3,5\text{-}Me_2Pz)(Py)Fe(CO)_2(COBu\text{-}n)I$ was obtained when iron carbonyl was reacted with *n*-BuLi, and subsequently with $CH_2(3,5\text{-}Me_2Pz)(Py)$ and iodine. However, analogous valeryl iron complexes supported by bis(pyrazol-1-yl)methanes could not be formed by these methods. The different electron-donating ability of these bis(heteroaryl)methanes and the distinct nucleophilicity of the bis(heteroaryl)methyl carbanions were possibly responsible for the diversification of reactivities. All these acyl iron complexes were fully characterized by IR and NMR spectroscopy, and their structures were unambiguously determined by X-ray crystallography.

Introduction

The metal–acyl complexes are crucial active intermediates in many catalytic carbonylation reactions [1,2]. It is important to capture these active species and elucidate their structures for a better understanding of the catalytic mechanism and would be illuminating in the design of new catalysts. In addition, recent investigations on [Fe]-hydrogenase suggest the presence of an acyl–iron ligation in the active site of [Fe]-hydrogenase [3–5], promoting the development of research on acyl iron complexes and expanding the scope of application of metal–acyl complexes [6–12]. A usual synthetic method of metal–acyl complexes is to treat the acylmetalate salts derived from the reaction of metal carbonyls and organolithium reagents with a soft electrophile [13]. It is found that the chelation effect of polydentate ligands plays an important role in stabilizing the metal–acyl complexes during their formation [14–16].

Bis(heteroaryl)methanes, especially bis(azaaryl)methanes, such as bis(pyrazol-1-yl)methanes [17], bis(1-methylimidazol-2-yl) methane [$CH_2(mim)_2$] [18–26] and bis(2-pyridyl)methane [27–29], have been used extensively in bioinorganic, coordination chemistry and organometallic fields owing to their versatile coordination behavior towards main group and transition metals. The deprotonation of their methylene group to give bis(heteroaryl)methyl carbanions has been also reported [20,25,30–35] and the resulting anions have been shown to react with various electrophiles to generate novel bridgehead functionalized bis(heteroaryl)methane ligands, which widely broaden the potential application areas of bis(heteroaryl)methanes [36,37]. Recently, we studied the reaction of bis(pyrazol-1-yl)methyllithium with tungsten carbonyl, which gave rise to novel bis(pyrazol-1-yl)acyl and bis(pyrazol-1-yl)methide tungsten derivatives [38], implying that pyrazolyl-based ligands could potentially be used to stabilize metal–acyl complexes. As an extension of our investigations on the reactivity of bis(pyrazol-1-yl) methyl anions, in this work we report the reaction of the lithium salts derived from the lithiation of bis(3,5-dialkylpyrazol-1-yl) methanes, $CH_2(mim)_2$ and 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine [$CH_2(3,5\text{-}Me_2Pz)(Py)$] with $Fe(CO)_5$ and halogen, which resulted in significantly different reaction patterns.

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* Corresponding author. Fax: +86 22 23502458.
E-mail address: lftang@nankai.edu.cn (L.-F. Tang).

http://dx.doi.org/10.1016/j.jorganchem.2014.12.039

Results and discussion

Synthesis of bis(pyrazol-1-yl)acyl iron complexes

Bis(pyrazol-1-yl)acyl iron complexes **1**–**3** were readily obtained by the reaction of bis(3,5-dialkylpyrazol-1-yl)methyllithium, prepared by the reaction of bis(3,5-dialkylpyrazol-1-yl)methanes with *n*-BuLi at low temperature [30], with $Fe(CO)_5$ followed by Br_2 or I_2 (Scheme 1). Complexes **4** and **5** were further generated by the salt elimination reaction of **1** and **3** with PhSNa. It should be pointed out that obvious decomposition was observed upon treatment of **1** or **3** with PhSNa, which is possibly responsible for the relatively low yields of **4** and **5**. All these bis(pyrazol-1-yl)acyl complexes **1**–**5** were air-stable in the solid state and their solution could be manipulated in air without notable decomposition. These complexes were fully characterized by IR and NMR spectroscopy, and their structures were unambiguously confirmed by X-ray crystallography.

The IR spectra of **1**–**5** showed the presence of the characteristic acyl carbonyl (C═O), which occurred at 1708–1729 cm^{-1}, significantly lower than those of two terminal carbonyls (C≡O) in a range of 1973–2046 cm^{-1}. Furthermore, the corresponding acyl carbon resonated at 245–248 ppm in the ^{13}C NMR spectra of **1**, **2** and **4**, which was similar to those of known acyl iron complexes [39,40]. In addition, four sets of proton signals of the isopropyl methyl groups were observed in the ^1H NMR spectra of **3** and **5**, indicating that they were diastereotopic, since the bulky isopropyl groups were inclined to limit their free rotation.

The crystal structures of **3** and **4** are presented in Figs. 1 and 2, respectively. The crystal structure of **2** is given in the Supplementary material. These three complexes share a similar fundamental framework. For example, bis(pyrazol-1-yl)acyl is bonded to the iron atom in a tridentate κ^3-[N,C,N] chelating fashion. The X-ray data reveal that complexes **2**–**4** also possess analogous structural parameters, such as similar Fe–C_{acyl}, Fe–N and C–C_{acyl} bond distances, as well as N–Fe–N and C–C_{acyl}–Fe angles. The Fe–C_{acyl} (1.932–1.947 Å) bond distances are comparable to those reported in other acyl iron complexes with chelating acyl ligands [7–9]. The Fe–N bond distances are in the range of 2.024–2.061 Å in complexes **2**–**4**, similar to the corresponding values reported for pyrazolyl ligated carbonyl iron derivatives, such as 1.992–2.082 Å in $TpFe(CO)_2(COMe)$ [41] and 2.021–2.057 Å in $TpFe(CO)(PMe_3)Me$ (Tp = Hydrotris(1-pyrazolyl)borate) [42].

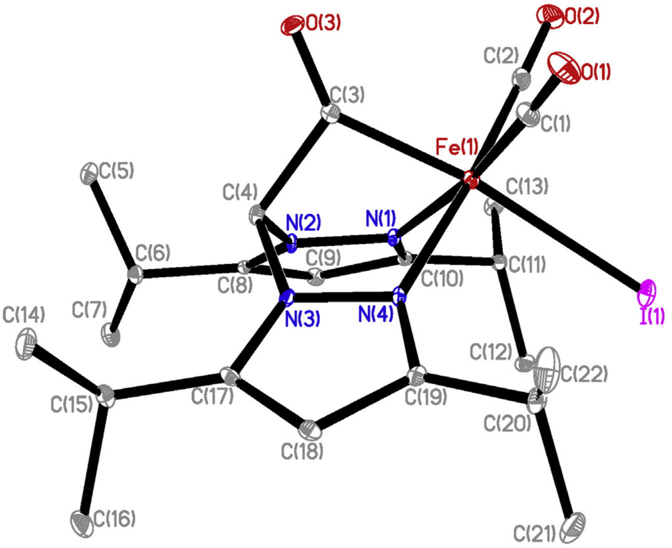
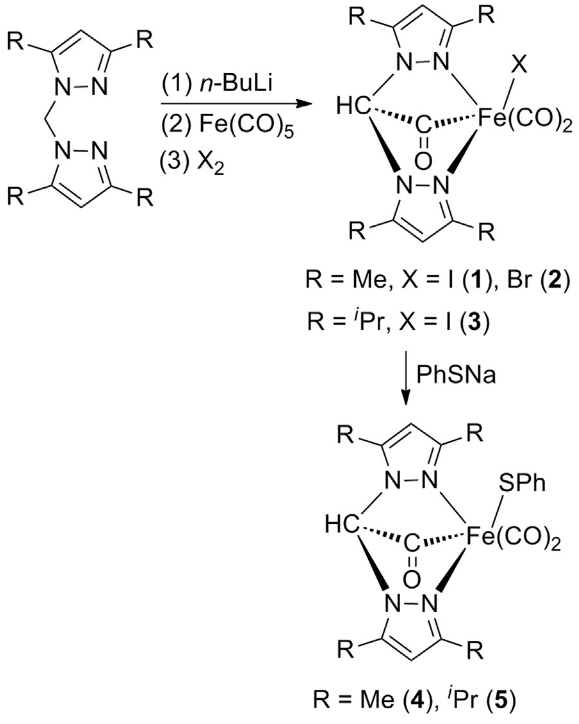


Fig. 1. The molecular structure of **3**. The thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (°): Fe(1)–I(1) 2.6875(8), Fe(1)–C(3) 1.944(2), Fe(1)–N(1) 2.061(2), Fe(1)–N(4) 2.024(2), C(3)–C(4) 1.597(3), C(3)–O(3) 1.190(3) Å; N(1)–Fe(1)–N(4) 88.93(7), N(2)–C(4)–N(3) 110.5(2), C(4)–C(3)–Fe(1) 100.3(1), Fe(1)–C(3)–O(3) 138.6(2), C(3)–Fe(1)–I(1) 172.03(7), C(14)–C(15)–C(17) 111.6(2)°.



Scheme 1. Synthesis of bis(pyrazol-1-yl)acyl iron complexes.

Synthesis of acyl iron complexes derived from $CH_2(mim)_2$ and $CH_2(3,5\text{-}Me_2Pz)(Py)$

Like bis(pyrazol-1-yl)methanes, $CH_2(mim)_2$ can act as a potential chelating bidentate ligand for various main group and transition metals [18–26]. The deprotonation of $CH_2(mim)_2$ at the methylene group, and subsequent reaction with various electrophiles have been reported in the literature [20,25,32–35]. However, we herein found that the reaction of the bis(1-methylimidazol-2-yl)methyl carbanions with $Fe(CO)_5$ did not occur, remarkably different from the above-mentioned reaction of the bis(3,5-dialkylpyrazol-1-yl)methyl carbanions under similar conditions. Treatment of the lithium salt generated in situ by the lithiation of $CH_2(mim)_2$ using *n*-BuLi with $Fe(CO)_5$ followed by I_2 only afforded valeryl iron complex $CH_2(mim)_2Fe(CO)_2(COBu\text{-}n)I$ (**6**) together with some insoluble solids, while the expected bis(1-methylimidazol-2-yl)acyl iron complex could not be obtained (Scheme 2). Based on these results and our previous study [25], it seems that bis(1-methylimidazol-2-yl)methyl carbanions show relatively low nucleophilicity towards organometallic reagents. The reason is still not completely clear, which may be related to the isomerism of bis(heteroaryl)methyl carbanions [43], leading to the decrease of their nucleophilicity.

The formation of **6** should be the result of a direct reaction of $CH_2(mim)_2$ with iron valerylate, which was supported by the verification experiment in which $Fe(CO)_5$ was consecutively treated with *n*-BuLi, $CH_2(mim)_2$ and I_2 to generate the same product. However, similar product could not be obtained when $CH_2(mim)_2$ was