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Synthesis and reactivity of (pyrazol-1-yl)acyl iron complexes



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ABSTRACT

Treatment of 1-methyl-3,5-dialkylpyrazoles with *n*-BuLi, and subsequently with iron carbonyl and iodine yielded (pyrazol-1-yl)acyl iron complexes $CH_2(CO)$ (3,5- R_2P_2)Fe(CO)₃I (R = Me or Prⁱ, Pz = pyrazol-1-yl). Reaction of $CH_2(CO)$ (3,5- Me_2P_2)Fe(CO)₃I with PhSNa gave a dimeric complex [$CH_2(CO)$ (3,5- Me_2P_2) Fe(CO)₂(SPh)]₂, while similar reactions of $CH_2(CO)$ (3,5- R_2P_2)Fe(CO)₃I with PySNa (Py = 2-pyridyl) gave mononuclear complexes $CH_2(CO)$ (3,5- R_2P_2)Fe(CO)₂(SPy), which exhibited an isomerization in solution. Treatment of the dimeric complex with PPh₃ at room temperature resulted in the decomposition of the starting material. Furthermore, this dimeric complex readily underwent reductive elimination to generate $CH_2(COSPh)$ (3,5- Me_2P_2) when heated at relatively low temperature, and thermal decomposition reaction to give PhSSPh in refluxing toluene solution. Reaction of mononuclear complexes with PPh₃ caused one carbonyl to be replaced by phosphine ligand to give complexes $CH_2(CO)$ (3,5- R_2P_2) Fe(CO) (PPh₃) (SPy). All these acyl iron complexes were fully characterized by IR and NMR spectroscopy, and their structures were unambiguously determined by X-ray crystallography.

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1. Introduction

The metal-acyl complexes are of great importance since they have proven to be excellent homogenous catalysts or crucial active intermediates in many important organic transformations [1-5], especially such as catalytic carbonylation reactions [6–9]. Furthermore, the metal-acyl unit has been introduced into the main chain of polymers to form potential functional organometallic materials [10,11], which develops the new application fields of metal-acyl complexes. In addition, since the successful elucidation of the structure of [Fe]-hydrogenase [12] indicated that an acyl-iron ligates to the active site of [Fe]-hydrogenase [13–15], many acyl iron complexes have been synthesized as biomimetic models for the active site of [Fe]-hydrogenase [16-25], which greatly promotes the development of metal-acyl complexes and widely broadens the potential application areas of metal-acyl complexes. Our recent investigations showed that polydentate pyrazolyl-based ligands could potentially be used to stabilize metal-acyl complexes [26–28]. These interesting results encouraged us to explore other related metal-acyl complexes based on pyrazolyl-based ligands. On the other hand, it is known that the chelation-assisted effect of

* Corresponding author. E-mail address: lftang@nankai.edu.cn (L.-F. Tang). polydentate ligands not only plays an important role in stabilizing metal-acyl complexes during their formation [29–31], but also significantly affects their reactivity [3]. As a part of our investigations on the metal-acyl complexes, in order to deeply understand the effect of the chelation-assisting roles of polydentate ligands on the reactivity and properties of the corresponding metal-acyl complexes, in this paper we describe the synthesis and reactivity of new pyrazolyl-based iron complexes containing bidentate (pyrazol-1-yl)acyl ligands.

2. Results and discussion

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

It is known that *N*-alkyl-3,5-dialkylpyrazoles underwent lithiation exclusively at the α -position of the *N*-alkyl groups [32], and the resulting lithium salts could react with various electrophiles, leading to the corresponding carbanions as important synthetic intermediates. Herein we find that treatment of the 1-lithio derivatives of 1,3,5-trimethylpyrazole and 1-methyl-3,5-diisopropylpyrazole with Fe(CO)₅ followed by I₂ yields (pyrazol-1-yl)acyl iron complexes **1** and **2** (Scheme 1). These two complexes were air-stable in the solid state and their solution could be manipulated in air for a short time without notable decomposition. They were fully characterized by IR and NMR spectroscopy.





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

The IR spectra of **1** and **2** showed that the characteristic acyl carbonyl (C=O) peak occurred at 1667 and 1676 cm⁻¹, respectively, lower than those in tridentate acyl ligated iron complexes, but higher than those in monodentate acyl ligated iron complexes [26]. The corresponding acyl carbons resonated at 254.0 ppm (**1**) and 254.2 ppm (**2**) in their ¹³C NMR spectra, which were comparable to those in monodentate and tridentate acyl ligated iron complexes [26]. In addition, the protons of the methylene group of these two complexes displayed an AB system in their ¹H NMR spectra, indicating that the five-membered metallacyclic structure was reserved in solution, which resulted in these two diastereotopic protons. Furthermore, four sets of proton and carbon signals of the isopropyl methyl groups were observed in the ¹H and ¹³C NMR spectra of **2**, reflecting that their free rotation was hindered possibly due to the repulsion among the bulky isopropyl groups.

2.2. Reaction of (pyrazol-1-yl)acyl iron complexes with ArSNa (Ar = Ph or 2-pyridyl)

Reaction of 1 with PhSNa gave a dimeric complex (3) (Scheme 1). The oxidative addition of thioesters to iron(0) to afford acyl thiolato iron complexes is known [16,17], but the dimeric complex readily underwent reductive elimination to generate S-phenyl (3,5dimethylpyrazol-1-yl)thioacetate (4) when heated at relatively low temperature (45 °C), and thermal decomposition reaction to give PhSSPh in refluxing toluene solution. Additionally, compound 4 was easily decomposed to afford PhSSPh with other uncharacterizable products when heated in refluxing toluene. Some analogous spectroscopic features were observed in complexes 1-3. For example, their IR spectra showed a resembling acvl carbonyl absorption peak. The ¹H NMR spectrum of **3** also displayed the inequivalent methylene protons, similar to those in 1 and 2. The structure of 3 was further confirmed by X-ray crystallography, and is shown in Fig. 1. The (pyrazol-1-yl)acyl group is bonded to the iron atom in a bidentate κ^2 -[N,C] chelating fashion. The Fe–S bond distances (2.347–2.408 Å) are unequal, but comparable to those reported in other acyl diiron complexes with the μ -SPh group, such as 2.3102–2.3972 Å in $Fe_2(SPh)_2[Ph_2PC_6H_4C(O)]_2(CO)_3$ [16]. The Fe-C_{acvl} and Fe-N bond distances are similar to the corresponding values reported for tridentate chelating bis(pyrazol-1-yl)acyl iron derivatives [26]. The C-C_{acyl} bond distance is 1.544(6) Å, close to those in monodentate acyl iron complexes, but slightly shorter than those in tridentate acyl iron complexes [26].

Reaction of 1 and 2 with PySNa (Py = 2-pyridyl) gave mononuclear complexes 5 and 6, respectively. The substitution of iodide by 2-pyridinethiolate caused the characteristic acyl carbonyl peaks of **5** (1650 cm⁻¹) and **6** (1655 cm⁻¹) in their IR spectra to significantly shift toward lower wave numbers compared to those of **1** and **2**, which should be attributed to the stronger donor ability of 2pyridinethiolate than iodide strengthening metal to carbonyl back bonding. The ¹H and ¹³C NMR spectra of **5** and **6** displayed two sets of proton and carbon signals, indicating the presence of isomers (Scheme 2). The assignment of isomers was based on the NOE experiments and the X-ray crystal structure determination of isomer **5A** (Fig. 2). Though the high similarity in the properties of **5A** and **5B** complicated the spectra, two sets of signals with a ratio of *ca*. 4/1 in CDCl₃ were clearly integrated for the two isomers respectively. For the signal set with larger integrals, strong correlation was observed in the NOESY spectrum between the methyl signal at 1.68 ppm and the aromatic proton at 8.10 ppm which should be the



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)–S(1) 2.347(2), Fe(1)–S(2) 2.408(1), Fe(1)–N(1) 2.033(4), Fe(1)–C(5) 1.938(5), Fe(2)–S(1) 2.402(1), Fe(2)–S(2) 2.347(2), Fe(2)–N(4) 2.039(3), Fe(2)–C(6) 1.945(5), C(5)–O(5) 1.213(5), C(6)–O(6) 1.217(5), C(5)–C(7) 1.544(6) Å; C(5)–Fe(1)–S(2) 166.6(2), C(5)–Fe(1)–N(1) 84.1(2), C(6)–Fe(2)–S(1) 171.4(2), C(6)–Fe(2)–N(4) 82.1(2), Fe(1)–S(1)–Fe(2) 98.19(5), Fe(1)–C(5)–O(5) 130.5(4), Fe(1)–C(5)–C(7) 112.9(3), Fe(2)–C(6)–C(13) 111.0(3), Fe(2)–C(6)–O(6) 131.9(4), C(6)–C(13)–N(3) 108.6(4), C(5)–C(7)–N(2) 110.4(4)°.

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