

The photosubstitution of iodide in $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$. Synthesis of cyclopentadienyliron dicarbonyl- and carbonyl- phosphine complexes containing $\eta^1\text{-N-imidato}(1-)$ ligands

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Abstract

The photoreaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ -diisopropylamine with succinimide and phthalimide gave the corresponding $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{-}\eta^1\text{-N-imidato}$ complexes, which were converted into the $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{-}\eta^1\text{-N-imidato}$ complexes by refluxing with PPh_3 in toluene.

Introduction

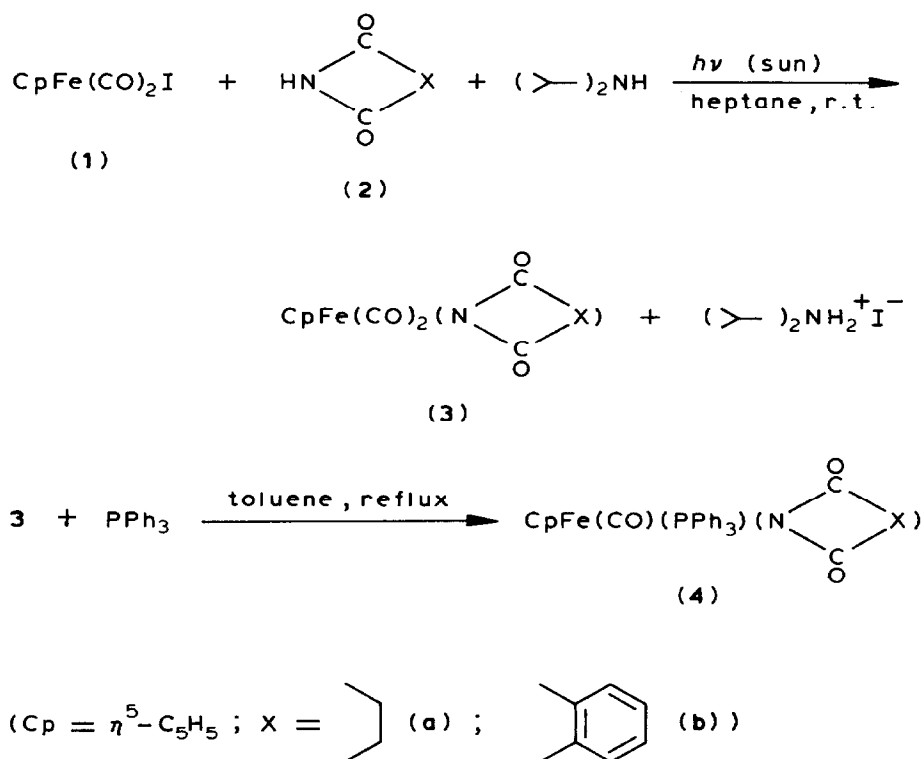
The nucleophilic substitution of halide in $\text{CpFe}(\text{CO})_2\text{X}$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) is a straightforward route to a variety of $\text{CpFe}(\text{CO})_2$ complexes [1]. In recent work [2] I have demonstrated that such a substitution can be achieved photochemically under mild conditions. Thus, $\text{CpFe}(\text{CO})_2\text{I}$ (**1**) reacts with pyrrole and indole in the presence of diisopropylamine, in sunlight, to afford the corresponding $\text{CpFe}(\text{CO})_2\text{-}\eta^1\text{-N-heterocyclic}$ complexes in 72 and 88% yield, respectively.

Here I describe an extension of this methodology for the synthesis of new $\text{CpFe}(\text{CO})_2\text{-}\eta^1\text{-N-imidato}$ complexes. In addition, chiral (racemic) $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{-}\eta^1\text{-N-imidato}$ complexes have been prepared for further studies of stereoselective reactions of imidato ligands.

Results and discussion

The cyclic imides **2a** and **2b** in heptane containing an excess of diisopropylamine, in the dark and at room temperature do not react with $\text{CpFe}(\text{CO})_2\text{I}$ (**1**). However, exposure to sunlight induces the replacement of iodide by imidato(1-) ligands.

The progress of the reaction can be monitored visually by the disappearance of the black crystals of **1** and the formation of a yellow reaction mixture (usually 1–2 sunny days are required to complete the reaction, carried out at the 5 mmol scale). The resulting imidato complexes **3a** and **3b** were isolated as yellow, air-stable



crystalline solids in 77 and 83% yields, respectively. Their structure was confirmed from their IR and ^1H NMR spectra as well as by elemental analyses (Table 1).

The relatively high IR metal-carbonyl and low imidato carbonyl stretching frequencies suggest that the iron–nitrogen bond in **3a** and **3b** has considerable ionic character. In fact, a recent study [3] has indicated that the η^1 -*N*-succinimidato(1-)

Table 1

Elemental analyses, IR and ^1H NMR spectral data

Complex	Elemental analysis (Found(calcd.)(%))				IR(CHCl_3 , cm^{-1})		^1H NMR (60 MHz, CDCl_3) δ (ppm)
	C	H	N	P	$\nu(\text{C}\equiv\text{O})$	$\nu(\text{C}=\text{O})$ (imide)	
3a	48.0	3.5	5.2	—	2060	1635	2.59, s, 4H; $(\text{CH}_2)_2$
	(48.04)	(3.30)	(5.09)	—	2010		5.02, s, 5H; Cp
3b	55.9	3.0	4.3	—	2060	1660	5.12, s, 5H; Cp
	(55.76)	(2.81)	(4.34)	—	2015		7.47, m, 4H; C_6H_4
4a	65.9	4.6	2.8	6.2	1975	1620	1.95, s, 4H; $(\text{CH}_2)_2$
	(66.03)	(4.75)	(2.75)	(6.08)			4.62, s, 5H; Cp
4b							7.2-7.5, m, 15H; PPh_3
	69.1	4.3	2.3	5.7	1970	1640	4.75, s, 5H; Cp
	(68.96)	(4.34)	(2.51)	(5.56)			7.2-7.5, m, 19H; $\text{C}_6\text{H}_4 + \text{PPh}_3$

ligand behaves as a pseudohalogen; (i.e. is a strong π acceptor and a moderate π donor).

The mechanism for the conversion of **1** into **3a** and **3b** has not been studied. Nevertheless, I think that it could be reminiscent of the photostimulated $S_{RN}1$ reactions of benzyl and aryl halides [4].

The complexes **3a** and **3b** when refluxed with one equivalent of PPh_3 in toluene gives the purple, air-stable carbonylphosphine complexes **4a** and **4b** in 85 and 92% isolated yield, respectively. The elemental analyses, IR and 1H NMR spectral data (Table 1) are in full accord with their formulation.

The chiral fragment $CpFe(CO)(PPh_3)$ gave rise to high stereoselectivities in a wide range of reactions of attached acyl ligands [5]. Similar high diastereoselectivities may be also expected for reactions of imidato ligands in **4a** and **4b**. A study of such reactions is currently under way.

Experimental

All the reactions described were carried out under argon. All the solvents and diisopropylamine (Fluka) were routinely dried and distilled prior to use. $CpFe(CO)_2I$ was prepared by a published procedure [6]. Other reagents were used as received (Fluka). The spectra were recorded with Specord 75 (IR) and Tesla BS 487 (60 MHz 1H NMR) spectrometers.

Preparation of $CpFe(CO)_2-\eta^1$ -N-imidato complexes 3a and 3b

To a 100 ml Schlenk tube were added heptane (60 ml), $CpFe(CO)_2I$ (**1**, 1.52 g, 5 mmol), imide **2a** or **2b** (5 mmol) and diisopropylamine (2.5 ml, ~ 18 mmol). The tube was exposed, with magnetic stirring, to sunlight. After 1–2 sunny days all the black crystals, (i.e. of **1**), had been consumed to give a yellow slurry. The solid was filtered off and extracted several times into ether. The combined extracts were concentrated to give the crude product, contaminated with 5–10% of unchanged imide. Repeated recrystallizations from ether gave analytically pure **3a** (77%) or **3b** (83%) as yellow, air-stable crystals.

Preparation of $CpFe(CO)(PPh_3)-\eta^1$ -N-imidato complexes 4a and 4b

A solution of **3a** or **3b** (2 mmol) and PPh_3 (524 mg, 2 mmol) in toluene (10 ml) was refluxed for 15 min. After being cooled to room temperature the red solution was filtered, the solvent was removed, and the residue was crystallized twice from chloroform/heptane. The products **4a** and **4b** were obtained as purple air-stable crystals in 85 and 92% yield, respectively.

Acknowledgment

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