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Bresciani G., Volante S., Biancalana L., Zacchini S., Pampaloni G., Marchetti F. (2023). Piano stool iron complexes with isocyanide ligands. JOURNAL OF ORGANOMETALLIC CHEMISTRY, 1001, 1-10 [10.1016/j.jorganchem.2023.122851].

Availability:

This version is available at: <https://hdl.handle.net/11585/951027> since: 2024-06-06

Published:

DOI: <http://doi.org/10.1016/j.jorganchem.2023.122851>

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<https://doi.org/10.1016/j.jorganchem.2023.122851>

This is the final peer-reviewed accepted manuscript of:

G. Bresciani, S. Volante, L. Biancalana, S. Zacchini, G. Pampaloni, F. Marchetti, "Piano stool iron complexes with isocyanide ligands", *J. Organomet. Chem.*, **2023**, *1001*, 122851.

The final published version is available online at:
<https://doi.org/10.1016/j.jorganchem.2023.122851>

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Piano Stool Iron Complexes with Isocyanide Ligands

Giulio Bresciani,^{a,c} Stefania Volante,^a Lorenzo Biancalana,^{a,c} Stefano Zacchini,^{b,c} Guido Pampaloni,^{a,c}

Fabio Marchetti ^{a,c,*}

^a University of Pisa, Dipartimento di Chimica e Chimica Industriale, Via G. Moruzzi 13, I-56124 Pisa, Italy.

^b University of Bologna, Dipartimento di Chimica Industriale “Toso Montanari”, Viale del Risorgimento 4, I-40136 Bologna, Italy.

^c CIRCC, Via Celso Ulpiani 27, I-70126 Bari, Italy.

Corresponding Author

*E-mail address: fabio.marchetti@unipi.it

Webpage: https://people.unipi.it/fabio_marchetti/

ORCID-ID:

Giulio Bresciani: 0000-0003-4239-8195

Stefania Volante: 0009-0006-1837-0650

Lorenzo Biancalana: 0000-0002-9276-0095

Stefano Zacchini: 0000-0003-0739-0518

Guido Pampaloni: 0000-0002-6375-4411

Fabio Marchetti: 0000-0002-3683-8708

Abstract

Complexes [FeCpI(CO)(CNR)] [**2a-f**; R = 2,6-C₆H₃Me₂ = Xyl, 4-C₆H₄OMe, CH₂Ph, CH₂P(O)(OEt)₂, CH₂SO₂(4-C₆H₄Me), Me; Cp = η⁵-C₅H₅] and [FeCpI(CNR)₂] [**3a-f**; R = Xyl, 4-C₆H₄OMe, CH₂Ph, CH₂P(O)(OEt)₂, Me] were obtained in 58-73% yields from the thermal reactions of [FeCpI(CO)₂] (**1**) in toluene with one/two equivalents of CNR, respectively, in the presence of [Fe₂Cp₂(CO)₄] as catalyst. The 1:2 molar reaction of **1** with CNMe resulted in the prevalent formation of [FeCp(CO)(CNMe)₂]I, **4f** (86% yield). The reactions of **1** and **3a-c** with an excess of CF₃SO₃CH₃ afforded the triflate adducts [FeCp(OSO₂CF₃)L₂] (L = CO, **1**^{TF}; Xyl, **3a**^{TF}; 4-C₆H₄OMe, **3b**^{TF}; CH₂Ph, **3c**^{TF}), in 62-78% yields, via CH₃I elimination. All products were characterized by elemental analysis, IR and multinuclear NMR spectroscopy, moreover the molecular structures of **2a**, **2e** and **3a** were ascertained by single crystal X-ray diffraction. The potential of **1**, **2a-f** and **3a-f** as catalysts in the bulk polymerization of *rac*-lactide was examined.

Keywords: Organometallic chemistry; piano stool iron complexes; isocyanide ligand; electrophilic abstraction; lactide polymerization

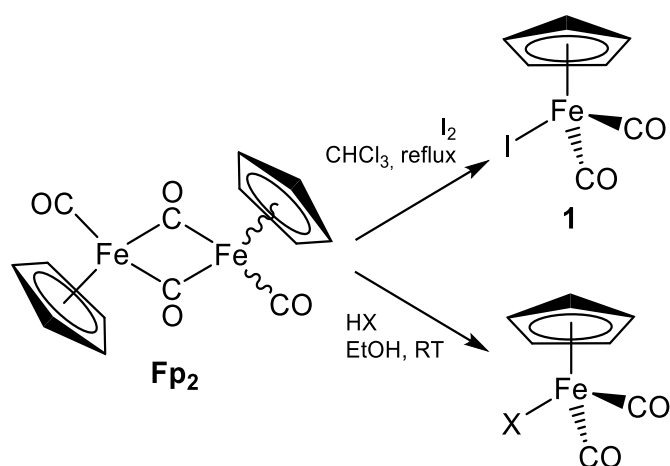
Introduction

The dimeric compound [Fe₂Cp₂(CO)₄] (Fp₂; Cp = η⁵-C₅H₅)^{1,2} is commercially available and inexpensive, and constitutes a convenient entry into the organometallic chemistry of di-^{3,4,5} and mono-iron complexes.^{6,7,8,9} Fp₂ exists as interconverting *cis* and *trans* isomers, and its reactions with halogens or hydrogen halides proceed with oxidative (Fe^I → Fe^{II}) cleavage of the carbonyl bridges leading to mononuclear complexes (Scheme 1).^{10,11} Among the latter, the piano-stool iodide complex [FeCpI(CO)₂], **1**,^{12,13} has been widely employed as a starting material to obtain a variety of derivatives which have been investigated for their possible applications as catalytic precursors,¹⁴ anticancer drug

candidates^{15,16,17,18} and CO-releasing molecules.¹¹ Different strategies have been explored to modify the coordination set around the iron(II) center in **1**. The thermal substitution of one CO ligand may be not selective, since iodide dissociation becomes competitive in some cases,^{19,20} thus, metal-based catalysts²¹ or UV-irradiation²² are usually required to favor the clean formation of CO-substitution products. Instead, the trimethylamine-N-oxide strategy,²³ consisting in the elimination of a CO ligand as CO₂ and largely applied to transition metal carbonyl cyclopentadienyl compounds,^{24,25,26} here is not viable due to the insufficient electrophilic character of the carbon monoxide ligands linked to the iron(II) centers. The reactions of **1** with N-heterocyclic carbenes (NHC) proceed with substitution of the iodide,²⁷ which can in turn replace one CO ligand upon prolonged irradiation with visible light, to give complexes of general formula [FeCpI(NHC)(CO)].^{28,29} Remarkably, the introduction of a NHC ligand provides robustness to the metallic structure and enhances the catalytic activity of the iron center.³⁰ Thus, complexes with the general formulas [FeCp(CO)₂(NHC)]I and [FeCpI(CO)(NHC)] have been reported to promote the hydrosilylation of carbonyl species^{31,32} and carbon dioxide,³³ the transfer hydrogenation of ketones^{34,35} and other processes involving different organic moieties.^{30,36,37,38}

Isocyanides are versatile reagents in organometallic chemistry,^{39,40,41,42} and it has been demonstrated that their introduction as ligands within an organo-iron structure may enable reactivity patterns including both nucleophilic^{43,44,45} and electrophilic additions,^{46,47} and supply catalytic properties to related complexes.⁴⁸ The thermal reaction between **1** and a small series of isocyanides (CNR) was previously conducted in benzene at reflux, to yield related mono- and bis- carbonyl substitution products.^{49,50} More specifically, complexes [FeCpI(CNR)(CO)] (R = ^tBu, Xyl, CH₂Ph) were prepared by treatment of **1** with one equivalent of CNR, in the presence of 5 mol% [Fe₂Cp₂(CO)₄] as catalyst.⁵¹ Instead, when two equivalents of isocyanide are employed, the bis-substituted products [FeCpI(CNR)₂] are prevalently obtained, in admixture with lower amounts of [FeCp(CNR)₃]I. Using a different approach, dinuclear complexes of the type [Fe₂Cp₂(CNAr)₄], containing aryl-isocyanide ligands, can be efficiently converted to [FeCpI(CNAr)₂] by means of I₂ oxidation.⁵²

In the framework of our interest in the chemistry of metal-isocyanide systems,^{3,47,44,45,53} here we expand the range of iron piano-stool complexes with isocyanide ligands, which were synthesized from **1** by an optimized synthetic procedure. The new complexes have been investigated for their reactivity with electrophiles, and their potential as lactide polymerization catalysts is preliminarily assessed. The synthesis of polylactide, i.e. a biocompatible and biodegradable polyester material, from the ring opening polymerization of lactide, is an important reaction^{54,55} whereby tin(II) 2-ethylhexanoate is industrially employed as an efficient catalyst despite unfavorable toxicity issues. The advance of alternative catalytic systems based on environmentally benign metals is highly desirable, and in this regard iron compounds represent a potentially ideal choice,⁵⁶ as surveyed in an excellent review recently published in *Organometallics*.⁵⁷



Scheme 1. Synthesis of piano-stool iron(II) carbonyl complexes by oxidation of commercial diiron(I) precursor with halogen reactants (X = Cl, Br).

Results and discussion

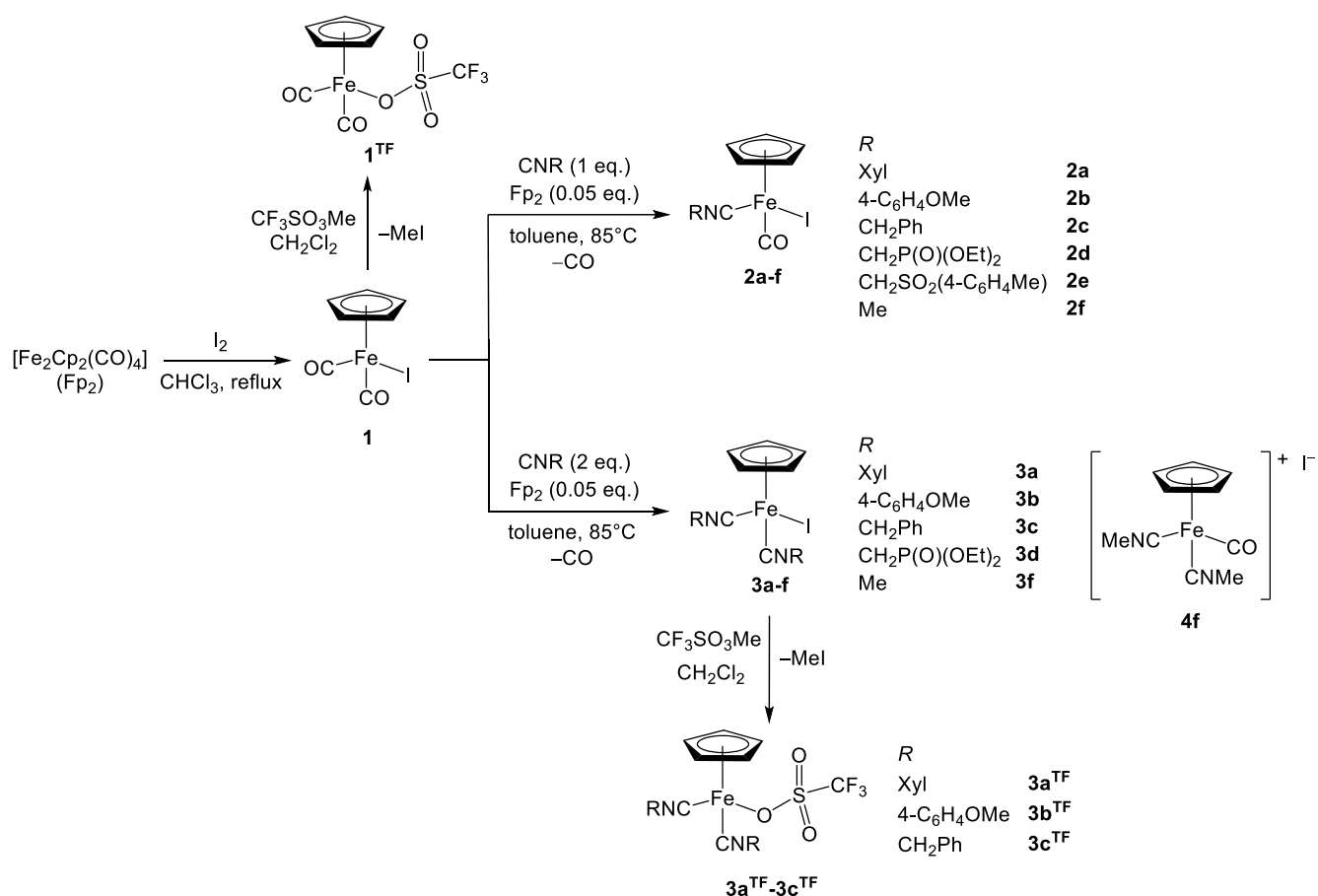
1) Synthesis and structural characterization of mono- and bis-isocyanide complexes

Complex **1** was prepared from Fp₂ using a slightly optimized literature procedure (see Experimental for details). Then, the mono-isocyanide adducts **2a-f** were synthesized by CO substitution reactions, performed at ca. 85 °C in toluene in the presence of Fp₂ as catalyst (Scheme 2). A similar procedure led

to the synthesis of the related bis-isocyanide compounds **3a-d**. The use of toluene as solvent was effective and represents an improvement with respect to the use of the more hazardous benzene reported in the literature (see Introduction). Interestingly, the reaction involving 4-toluenesulfonylmethyl isocyanide led to the mono-substituted derivative **2e** as largely prevalent product even when the isocyanide was used in a three-fold molar excess. On the other hand, the bis-methylisocyanide **3f** was isolated in a very poor yield from **1** and CNMe (1:2 molar ratio), the salt **4f** being the prevalent product of this reaction.

Compounds **2b,d,e** and **3b,d** are new; instead, the 2,6-dimethylphenyl and benzyl isocyanide adducts (**2a,c** and **3a,c**) were previously obtained from **1**,⁵¹ while **2f** was alternatively prepared from I₂ oxidation reaction of diiron methyl isocyanide precursors.⁵⁸ Furthermore, **4f** was reported from the reaction of K[FeCp(CO)(CN)] with excess MeI in refluxing MeCN;⁵⁹ **4f** and **3f** were also obtained in low yields (8-15%) from [Fe₂Cp₂(CO)_n(CNMe)_{4-n}]/I₂ (n = 0-2) in CH₂Cl₂.^{58,60}

All products were purified by silica chromatography, and finally isolated in 58-73% (**2a-f**), 43-64% (**3a-d**) and 86% (**4f**) yields. They were fully characterized by elemental analysis, IR (in CH₂Cl₂ solution) and multinuclear NMR spectroscopy (CDCl₃). The salient spectroscopic features are comparatively displayed in Table 1.



Scheme 2. Synthesis of cyclopentadienyl iron(II) complexes: CO/CNR substitution reactions and iodide replacement by triflate via electrophilic abstraction. Xyl = 2,6-C₆H₃Me₂.

Table 1. Comparative view of IR and NMR data for iron(II) cyclopentadienyl complexes. ^aCH₂Cl₂ solution; ^bNMR spectra recorded in CDCl₃ solution unless otherwise specified; ^ctoluene-d₈ solution.

	IR (ū/cm ⁻¹) ^a		¹ H NMR (δ/ppm) ^b	¹³ C NMR (δ/ppm) ^b		
	CO	CN	Cp	Cp	CO	CN
1	2041, 1996	=	5.05 ^c	83.9 ^c	214.0 ^c	=
2a	1983	2128	4.86	82.4	217.1	172.7
2b	1982	2134	4.83	82.6	217.3	168.9
2c	1980	2166	4.75	82.1	217.6	162.9
2d	1982	2162	4.79	82.3	217.1	167.7
2e	1989	2140	4.82	83.0	216.2	177.3
2f	1978	2185	4.74	81.8	217.8	159.6
3a	=	2120, 2072	4.73	80.9	=	180.7
3b	=	2121, 2082	4.68	80.6	=	177.8
3c	=	2149, 2114	4.47	79.1	=	171.8
3d	=	2146, 2111	4.51	80.0	=	176.6
3f	=	2165, 2135	4.42	78.6	=	168.4
4f	2025	2228, 2208	5.24	85.0	221.6	148.0
1^{TF}	2073, 2029	=	5.30			
3a^{TF}	=	2139, 2101	5.24	84.5	=	168.7
3b^{TF}	=	2174, 2133	5.13	84.1	=	163.7

3c^{TF}	=	2199, 2158	4.97	82.5	=	159.0
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The IR spectra of **2a-f** show a diagnostic band for the carbonyl ligand in the narrow interval 1978-1989 cm^{-1} , and the lowest wavenumber value was recorded for **2f**, in agreement with the relatively strong electron-donor ability of methyl isocyanide enhancing the Fe \rightarrow CO back-donation. On the other hand, the triple C-N bond gives rise to an intense absorption in the range 2128-2185 cm^{-1} , which is straightforwardly correlated with the R substituent, i.e. increased electro-donation from R corresponds to a higher C \equiv N stretching frequency. This trend is substantially preserved in the bis-isocyanide adducts **3a-f**. The cationic charge in **4f** determines an increase of the isocyanide stretching frequencies compared to **3f**, thus suggesting that back-donation from iron(II) directed to the isocyanide ligands play some role in **3a-f**. In the NMR spectra, the Cp resonance is upfield shifted ongoing from **1** to **2a-f** and then to **3a-f**, indicating a shielding effect provided by the isocyanide ligands. The ^{13}C NMR resonance for the CO ligand is also upfield shifted in **2a-f** compared to **1**, which is in alignment with the increased degree of back-donation in the former complexes, consequent to the substitution of one CO ligand with the CNR. The molecular structures of $[\text{FeCpI}(\text{CO})(\text{CNXyl})]$, **2a**, $[\text{FeCpI}(\text{CO})\{\text{CH}_2\text{SO}_2(4\text{-C}_6\text{H}_4\text{Me})\}]$, **2e** and $[\text{FeCpI}(\text{CNXyl})_2]$, **3a**, were elucidated by single crystal X-ray diffraction studies (Figure 1 and Table 2). To date, $[\text{FeCpI}\{\text{CN}(2,6\text{-C}_6\text{H}_4(\text{iPr})_2)_2\}]^{52}$ and $[\text{FeCpI}(\text{CO})_2]$ (**1**)⁶¹ are the only other crystallographically characterized complexes of type $[\text{FeCp}^X\text{I}(\text{CNR})_n(\text{CO})_{(2-n)}]$ (Cp^X = any η^5 -cyclopentadienyl ligand; $n = 1, 2$) reported in the literature; two additional examples containing Cl instead of I are known.^{62,63} Complexes **2a**, **2e** and **3a** display typical piano-stool geometries. The structure of **2a** can be compared to the strictly related structure of $[\text{FeCp}'\text{I}(\text{CO})(\text{CNXyl})]$ ($\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{Me}$):⁶⁴ the Fe-CO, Fe-CN and isocyanide C-N bond distances are very similar in the two complexes, while the main effect of the methyl group on the cyclopentadienyl ring is a significant elongation of the Fe-I bond in $[\text{FeCp}'\text{I}(\text{CO})(\text{CNXyl})]$ (2.616 Å) compared to **2a** [2.538(3) Å]. In **2e** compared to **2a**, a significant decrease of the Fe-CO bond distance can be observed [1.802(5)Å vs. 1.874(19)Å], highlighting the electron withdrawing character of

xylyl-isocyanide. In the bis-isocyanide adduct **3a**, the main bonding parameters do not dramatically differ than those present in the related mono-isocyanide complex **2a**.

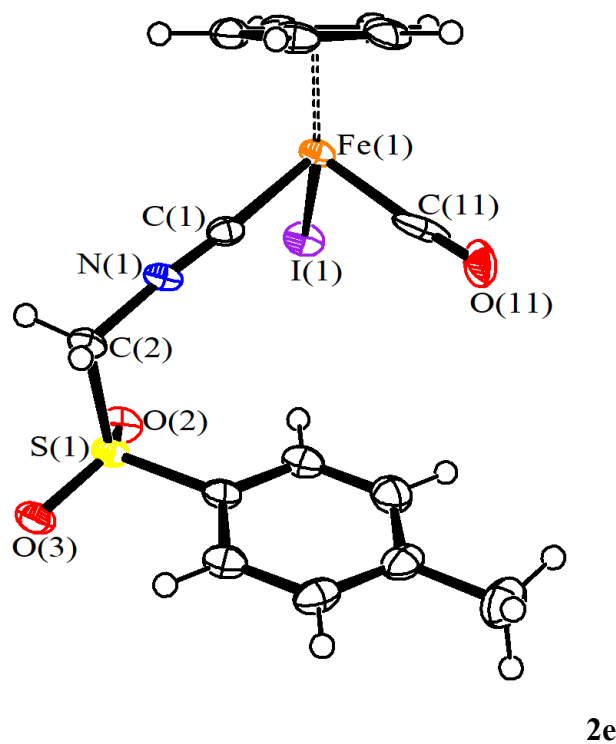
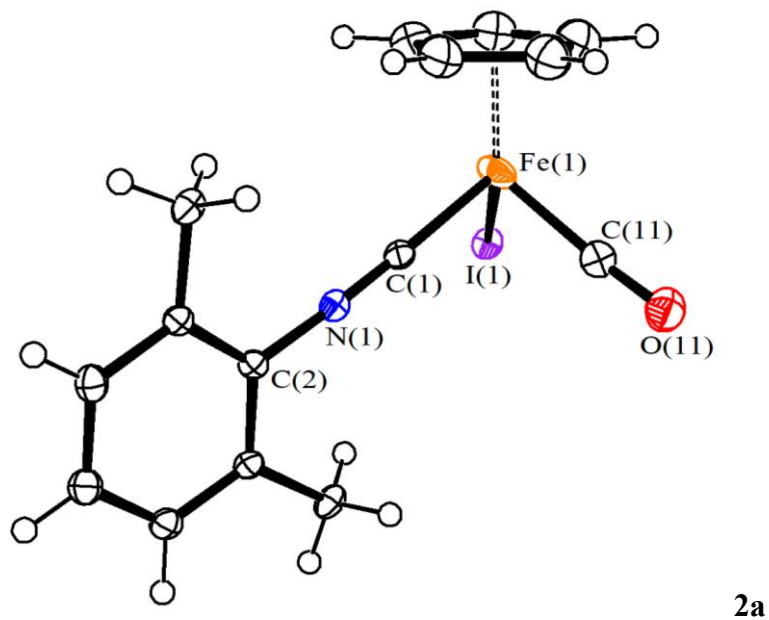


Figure 1. Views of the molecular structures of **2a** and **2e**. Displacement ellipsoids are at the 50% probability level.

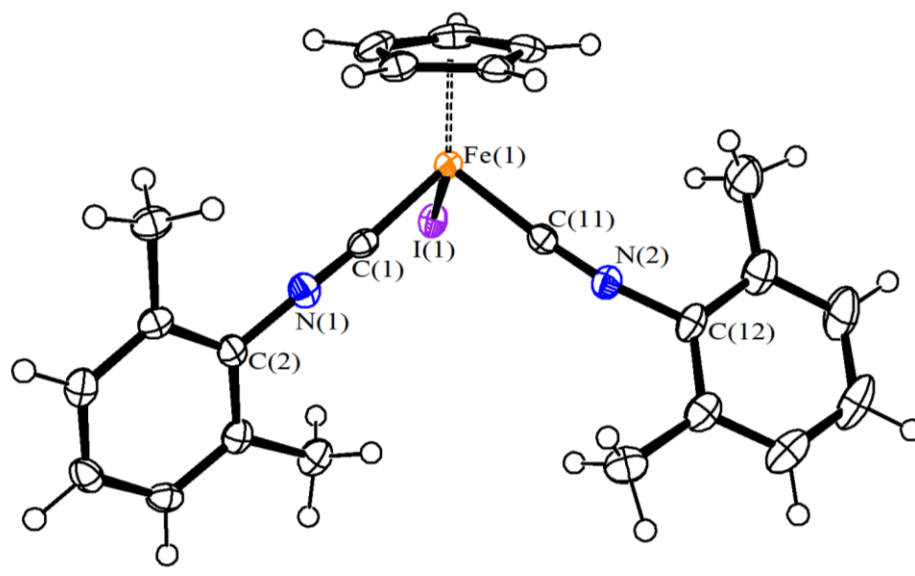


Figure 2. Views of the molecular structure of **3a**. Displacement ellipsoids are at the 50% probability level.

Table 2. Selected bond lengths (Å) and angles (°) for **2a**, **2e** and **3a**.

	2a	2e	3a
Fe(1)-Cp _{av}	2.12(3)	2.091(11)	2.086(7)
Fe(1)-I(1)	2.538(3)	2.5991(6)	2.6279(5)
Fe(1)-C(1)	1.833(12)	1.832(4)	1.820(3)
Fe(1)-C(11)	1.874(19)	1.802(5)	1.827(3)
C(1)-N(1)	1.164(15)	1.155(5)	1.160(4)
N(1)-C(2)	1.387(15)	1.411(5)	1.396(4)
C(11)-O(11)	1.152(18)	1.126(7)	-
C(11)-N(2)	-	-	1.165(4)
N(2)-C(12)	-	-	1.400(4)
C(1)-Fe(1)-C(11)	92.9(10)	96.1(2)	95.69(13)
C(1)-Fe(1)-I(1)	92.0(4)	89.36(12)	90.62(10)
C(11)-Fe(1)-I(1)	91.3(10)	89.06(17)	90.96(10)
Fe(1)-C(1)-N(1)	177.9(12)	176.3(4)	175.6(3)
Fe(1)-C(11)-X*	175(3)	175.8(7)	175.5(3)
C(1)-N(1)-C(2)	177.3(13)	170.2(4)	175.0(3)
C(11)-N(2)-C(12)	-	-	167.6(3)

* X = O(11), **2a**; N(2), **3a**.

2) Reactivity with methyl triflate and *rac*-lactide

There is a rich chemistry around the formation of bridging aminocarbyne ligands from the alkylation of isocyanide ligands in diiron and diruthenium complexes, otherwise examples of monoiron aminocarbyne complexes are rather circumscribed.^{46,47,65} Therefore, we came interested in exploring the reactivity of the bis-isocyanide complexes **3a-f** with a typical alkylating agent such as methyl triflate. Interestingly, the isocyanide ligands were not affected by the addition of methyl triflate in excess. This fact may be explained with the insufficient iron(II) to CNR back-bonding, inhibiting the *basicity* of the nitrogen; note that most cases of isocyanide alkylation in diiron complexes concern iron(I) species. It should be noted that, according to our result, Ruiz and co-workers evidenced the *electrophilicity* of isocyanides in $[\text{FeCp}(\text{CNR})(\text{CO})_2]^+$ and $[\text{FeCp}(\text{CNR})_2(\text{CO})]^+$ (R = Xyl or Cy), undergoing addition of mono-methylamine to afford di-aminoalkylidene species.⁴³

The triflate adducts **3a^{TF}**-**3c^{TF}** were cleanly obtained from **3a-c**, resulting from iodide abstraction by means of CH_3^+ (Scheme 2). Accordingly, in situ NMR experiments confirmed the formation of one equivalent of methyl iodide as by-product. Interestingly, **3a-c** were unreactive towards HSO_3CF_3 (triflic acid), revealing that the methyl cation plays a crucial role despite the relatively low energy of the carbon-iodine bond in CH_3I .^{66,67}

The synthesis of a triflate complex was extended to the bis-carbonyl **1**, converting into **1^{TF}** (Scheme 2). The formation of **1^{TF}** from **1** was previously achieved by silver salt metathesis.^{68,69} The analogous Cp* complex was obtained from the decomposition of a cationic carbene complex bearing triflate as the counteranion, and it was X-ray characterized showing that the triflate behaves as a monodentate oxygen ligand.⁷⁰

The triflate complexes **3a^{TF}**-**3c^{TF}** are not air-stable and were conserved at $-30\text{ }^\circ\text{C}$ under N_2 atmosphere. Their IR spectra (in CH_2Cl_2) exhibit two absorptions related to the isocyanide ligands at higher wavenumbers ($\Delta\tilde{\nu} = 20\text{-}50\text{ cm}^{-1}$) compared to **3a-c**, indicating a decreased $\text{Fe} \rightarrow \text{CNR}$ π back-donation,

supplied by $\text{I}^-/\text{CF}_3\text{SO}_3^-$ substitution. The NMR signals related to the Cp and CO ligands are downfield shifted in **3a^{TF}**-**3c^{TF}** compared to **3a-c**, otherwise the ^{13}C resonance for the isocyanide CN carbon is more shielded in **3a^{TF}**-**3c^{TF}** than in **3a-c** (e.g. for **3b/3b^{TF}**: $\delta/\text{ppm} = 177.8$ and 163.7 ppm, respectively). The triflate ligand manifests itself with a singlet in the ^{19}F NMR spectrum, occurring at 74.7 ppm in **1** and at ca. 78 ppm in **3a^{TF}**-**3c^{TF}**.

In 2022, Albrecht and coworkers reported the superior catalytic activity in the ROP (Ring Opening Polymerization) of bulk *rac*-lactide provided by a family of $[\text{FeCpI}(\text{CO})(\text{NHC})]$ complexes.⁷¹ These catalysts outperformed previously reported iron catalysts and the industrially used tin(II) bis-2-ethylhexanoate, and work effectively even when technical grade lactide is employed. Based on this recent literature result, we decided to screen the ability of the here reported mono- and bis-isocyanide complexes to promote the lactide polymerization reaction. The bis-carbonyl compound **1** was included in the present study. The conversion of the monomer into the polymer was determined by ^1H NMR spectroscopy (see Table 3 and Experimental for details). We found that **1** is moderately able to produce polylactide, with a conversion of 32% after 2.5 h at 150 °C. Compounds containing aryl-isocyanides, diethyl isocyanomethylphosphonate and 4-toluenesulfonylmethyl isocyanide performed worse than **1** (conversion values between 5 and 23%). On the other hand, the replacement of one carbonyl ligand with methylisocyanide (**2f**) and especially benzylisocyanide (**2c**) resulted in an enhancement of the conversion up to 48%. Working under analogous experimental conditions ($T = 150$ °C, *rac*-lactide/catalysts ratio = 1000, reaction time = 2 h), Albrecht obtained 91% yield of polymer by using a triazolylidene iron(II) cyclopentadienyl iodide catalyst.

The lower activity exhibited by the cationic bis-methylisocyanide complex **4f** with respect to the related **2f** suggests that the polymerization reaction may be favored by the presence of a weakly bound ligand such as the iodide, allowing the coordination of the reaction substrate to a cationic iron(II) center.

Table 3. Polymerization reaction of *rac*-lactide catalyzed by piano-stool iron complexes. Reaction conditions: catalyst 0.1 mol%; reaction time = 2.5 h; temperature = 150 °C. Conversion calculated by ¹H NMR.

<i>R</i>		Conversion(%) ^a		Conversion(%) ^a
	1	32		
Xyl	2a	16	3a	12
4-C ₆ H ₄ OMe	2b	11	3b	20
CH ₂ Ph	2c	48	3c	21
CH ₂ P(O)(OEt) ₂	2d	20	3d	23
CH ₂ SO ₂ (4-C ₆ H ₄ Me)	2e	5		
Me	2f	36	4f	16

Conclusions

We report a systematic study on the synthesis of iron(II) cyclopentadienyl complexes with one or two isocyanide ligands, their characterization and some insights into their reactivity. The interaction with a strong alkylating agent such as methyl triflate does not affect the isocyanide ligands, instead it results in electrophilic iodide abstraction offering a new route to the formation of triflate adducts. Mixed carbonyl complexes bearing an alkyl-substituted isocyanide ligand revealed a fair potential in the polymerization reaction of *rac*-lactide, in comparison with outstanding iron catalysts reported so far. This preliminary outcome suggests that, in the place of largely studied NHC adducts, the versatile isocyanide moiety, whose steric and electronic properties are easily tunable by the choice of the substituent (R), may deserve attention in the future design of iron(II) piano stool complexes for catalytic applications.

Experimental

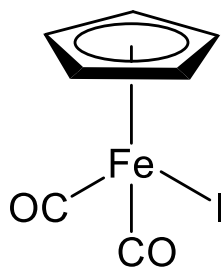
1) Synthesis and characterization of complexes.

General details. Reactants and solvents were purchased from Alfa Aesar, Merck, Strem or TCI Chemicals, and were of the highest purity available. Methyl isocyanide was prepared according to the

literature and stored at $-30\text{ }^{\circ}\text{C}$;⁷² an aliquot (10 μL) was titrated by ^1H NMR (CDCl_3) using Me_2SO_2 as internal standard;⁷³ contaminated labware was treated with EtOH/HCl . Complexes **2a**, **2c**, **3a** and **3c** were prepared by a slight modification of the literature procedure.⁵¹ Reactions were conducted under N_2 atmosphere using standard Schlenk techniques. Products were stored in air once isolated. Dichloromethane and toluene were dried with the solvent purification system mBraun MB SPS5, while chloroform was distilled from P_2O_5 . IR spectra of solutions were recorded using a CaF_2 liquid transmission cell ($2300\text{-}1500\text{ cm}^{-1}$) on a Perkin Elmer Spectrum 100 FT-IR spectrometer. IR spectra were processed with Spectragryph software.⁷⁴ ^1H and ^{13}C NMR spectra were recorded on Jeol JNM-ECZ500R or JNM-ECZ400R instruments equipped with a Royal HFX Broadband probe at 298 K. Chemical shifts (expressed in parts per million) are referenced to the residual solvent peaks⁷⁵ or to external standards⁷⁶ (^{19}F to CFCl_3 , ^{31}P to 85% H_3PO_4). NMR spectra were assigned with the assistance of ^1H - ^{13}C (*gs*-HSQC and *gs*-HMBC) correlation experiments.⁷⁷ Elemental analyses were performed on a Vario MICRO cube instrument (Elementar).

[FeCpI(CO)₂], 1 (Figure 3).^{10,78}

Figure 3. Structure of **1**.



$[\text{FeCp}(\text{CO})_2]_2$ (1.20 g, 3.39 mmol) and I_2 (1.03 g, 4.07 mmol) were placed in a 50 mL two-neck round bottom flask equipped with a condenser, and then 18 mL of CHCl_3 were added. The mixture obtained was stirred at reflux temperature for 30 minutes. The disappearance of the precursor was monitored by liquid IR spectroscopy. After cooling at room temperature, the reaction mixture was transferred into a

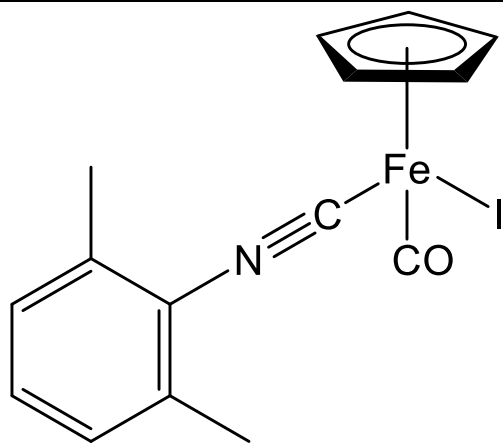
separatory funnel and washed with 25 mL of an aqueous solution of Na₂S₂O₃ (0.4 g/mL). The organic phase was separated and the solvent was evaporated under reduced pressure. The residue was dissolved in CH₂Cl₂ and this solution was filtered over celite. The filtrate was taken to dryness under vacuum and suspended in heptane for 2 h, filtered and then washed with 5 mL of pentane. The dark brown-violet solid obtained was finally dried under vacuum. Yield: 1.60 g (78 %). Similar results were obtained by performing the reaction in CH₂Cl₂ at ambient temperature for 15 h. IR (CH₂Cl₂): $\tilde{\nu}/\text{cm}^{-1} = 2041\text{vs (CO)}, 1996\text{vs (CO)}$. IR (toluene): $\tilde{\nu}/\text{cm}^{-1} = 2037\text{vs (CO)}, 1994\text{vs (CO)}$. ¹H NMR (CDCl₃): $\delta/\text{ppm} = 5.05$ (s, Cp). ¹H NMR (CD₂Cl₂): $\delta/\text{ppm} = 5.06$ (s, Cp). ¹H NMR (toluene-d₈): $\delta/\text{ppm} = 4.02$ (s, Cp). ¹³C{¹H} NMR (toluene-d₈): $\delta/\text{ppm} = 214.0$ (CO); 83.9 (Cp).

[FeCpI(CO)(CNR)] [R = Xyl, 2a; R = 4-C₆H₄OMe, 2b; R = CH₂Ph, 2c; R = CH₂P(O)(OEt)₂, 2d; R = CH₂SO₂(4-C₆H₄Me), 2e; R = Me, 2f].

General procedure. A solution of **1** (ca 1 mmol) and [FeCp(CO)₂]₂ (5 mol%) in toluene (10-20 mL) was treated with the appropriate isocyanide (ca. 1 eq.). The mixture was heated at 85 °C under stirring for 15 minutes. The conversion of the starting material was monitored by IR spectroscopy. The crude was cooled to room temperature and then charged on a silica column packed with petroleum ether: unreacted **1** was eluted using petroleum ether/toluene mixtures with increasing relative content of toluene, then the fraction corresponding to the desired product was collected using a specific eluent. The solvent was removed under reduced pressure, and the residue was suspended in a mixture of Et₂O (5 mL) and pentane (35 mL). After filtration, the isolated solid was dried under vacuum.

[FeCpI(CO)(CNXyl)], 2a (Figure 4).

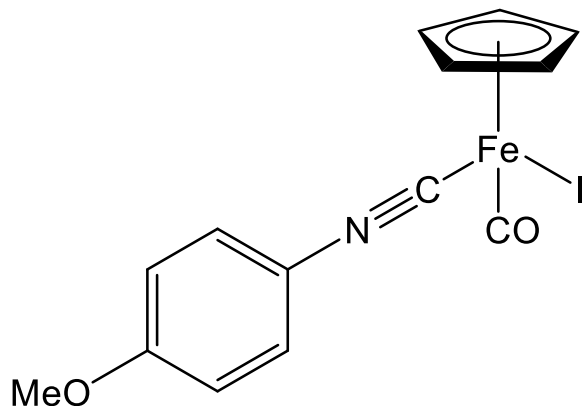
Figure 4. Structure of **2a**.



From **1** (150 mg, 0.494 mmol), $[\text{FeCp}(\text{CO})_2]_2$ (9 mg, 0.05 mmol) and 2,6-dimethylphenylisocyanide (CNXyl, 65 mg, 0.50 mmol). Chromatography: toluene/Et₂O (9/1 v/v). Dark-brown solid, yield 117 mg (58%). Anal. calcd. for C₁₅H₁₄FeINO: C, 44.26; H, 3.47; N, 3.44. Found: C, 44.05; H, 3.57; N, 3.31. IR (CH₂Cl₂): $\tilde{\nu}/\text{cm}^{-1}$ = 2128vs (C≡N), 1983s (CO). ¹H NMR (CDCl₃): δ/ppm = 7.08 (br, 3 H, C₆H₃); 4.86 (s, 5 H, Cp); 2.45 (s, 6 H, Me). ¹³C{¹H} NMR (CDCl₃): δ/ppm = 217.1 (CO); 172.7 (C≡N); 135.0, 127.8 (C₆H₃); 128.9, 128.0 (C-*ipso*); 82.4 (Cp); 18.9 (Me). Crystals suitable for X-ray analysis were collected by slow evaporation of an acetone solution of **2a**.

[FeCpI(CO){CN(4-C₆H₄OMe)}], 2b (Figure 5).

Figure 5. Structure of **2b**.

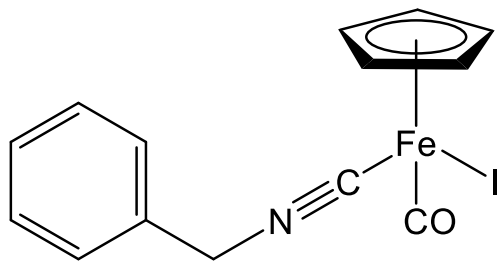


From **1** (253 mg, 0.833 mmol), $[\text{FeCp}(\text{CO})_2]_2$ (15 mg, 0.04 mmol) and 4-methoxyphenylisocyanide (112 mg, 0.841 mmol). Chromatography: toluene. Brown solid, yield 210 mg (62%). Anal. calcd. for C₁₄H₁₂FeINO₂: C, 41.11; H, 2.96; N, 3.42. Found: C, 40.94; H, 3.08; N, 3.29. IR (CH₂Cl₂): $\tilde{\nu}/\text{cm}^{-1}$ =

2134vs (C≡N), 1982vs (CO). ^1H NMR (CDCl_3): $\delta/\text{ppm} = 7.26, 6.84$ (d, $^3J_{\text{HH}} = 8.3$ Hz, 4 H, C_6H_4); 4.83 (s, 5 H, Cp); 3.80 (s, 3 H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta/\text{ppm} = 217.3$ (CO); 168.9 (C≡N); 159.6 (O-Carom); 127.6, 114.7 (C_6H_4); 122.3 (N-Carom); 82.6 (Cp); 56.0 (OMe).

[FeCpI(CO)(CNCH₂Ph)], 2c (Figure 6).

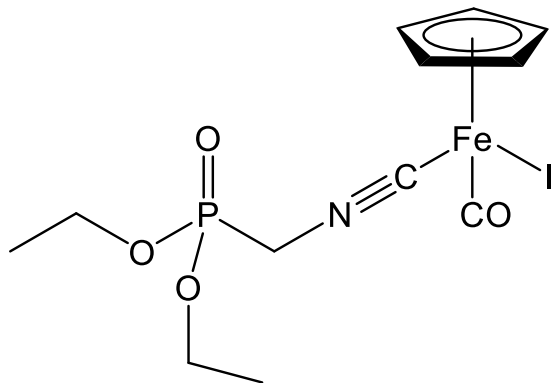
Figure 6. Structure of 2c.



From **1** (180 mg, 0.592 mmol), $[\text{FeCp}(\text{CO})_2]_2$ (10 mg, 0.03 mmol) and benzyl isocyanide (0.072 mL, 0.59 mmol). Chromatography: toluene/diethyl ether (4:1 v/v). Dark-brown solid, yield 144 mg (62%). Anal. calcd. for $\text{C}_{14}\text{H}_{12}\text{FeINO}$: C, 42.79; H, 3.08; N, 3.56. Found: C, 42.45; H, 3.11; N, 3.70. IR (CH_2Cl_2): $\tilde{\nu}/\text{cm}^{-1} = 2166$ vs (C≡N), 1980vs (CO). ^1H NMR (CDCl_3): $\delta/\text{ppm} = 7.39$ (m, 5 H, Ph); 5.00 (s, 2 H, CH_2); 4.75 (s, 5 H, Cp). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta/\text{ppm} = 217.6$ (CO); 162.9 (C≡N); 152.0 (*Cipso*); 133.2, 129.2, 129.0, 128.7, 126.7 (Ph); 82.1 (Cp); 49.2 (CH_2).

[FeCpI(CO){CNCH₂P(O)(OEt)₂}], 2d (Figure 7).

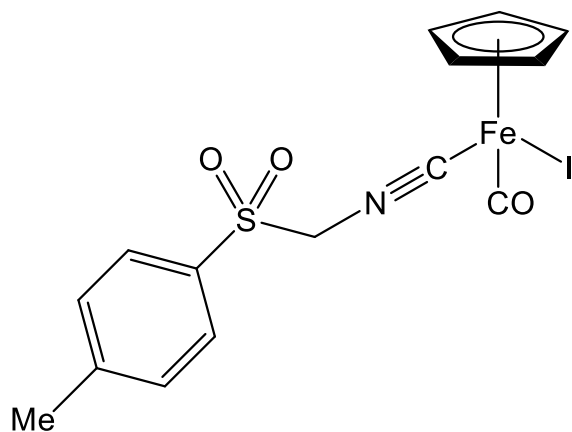
Figure 7. Structure of 2d.



From **1** (190 mg, 0.625 mmol), $[\text{FeCp}(\text{CO})_2]_2$ (11 mg, 0.03 mmol) and diethyl isocyanomethylphosphonate (0.10 mL, 0.63 mmol). Chromatography: $\text{Et}_2\text{O}/\text{acetone}$ (1/1 v/v). Dark-brown solid, yield 201 mg (71%). Anal. calcd. for $\text{C}_{12}\text{H}_{17}\text{FeINO}_4\text{P}$: C, 31.82; H, 3.78; N, 3.09. Found: C, 31.50; H, 3.58; N, 3.21. IR (CH_2Cl_2): $\tilde{\nu}/\text{cm}^{-1} = 2162\text{vs}$ ($\text{C}\equiv\text{N}$), 1982s (CO). ^1H NMR (CDCl_3): $\delta/\text{ppm} = 4.79$ (s, 5 H, Cp); 4.26 (m, 4 H, OCH_2); 4.11 (d, 2 H, $^2J_{\text{HH}} = 12.5$ Hz, NCH_2); 1.40 (m, 6 H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta/\text{ppm} = 217.1$ (CO); 167.7 ($\text{C}\equiv\text{N}$); 82.3 (Cp); 64.1 (d, $^2J_{\text{C-P}} = 6.4$ Hz, OCH_2); 41.2 (d, $^1J_{\text{C-P}} = 154.3$ Hz, NCH_2); 16.6 (d, $^3J_{\text{C-P}} = 5.4$ Hz, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta/\text{ppm} = 14.9$.

$[\text{FeCpI}(\text{CO})\{\text{CNCH}_2\text{SO}_2(4\text{-C}_6\text{H}_4\text{Me})\}]$, **2e (Figure 8).**

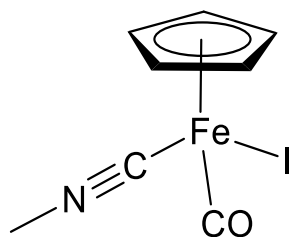
Figure 8. Structure of **2e**.



From **1** (150 mg, 0.494 mmol), $[\text{FeCp}(\text{CO})_2]_2$ (9 mg, 0.02 mmol) and 4-toluenesulfonylmethyl isocyanide (96 mg, 0.49 mmol). Chromatography: Et_2O . Brown solid, yield 154 mg (66%). Anal. calcd. for $\text{C}_{15}\text{H}_{14}\text{FeINO}_3\text{S}$: C, 38.24; H, 3.00; N, 2.97; S, 6.81. Found: C, 37.75; H, 3.16; N, 2.81; S, 6.65. IR (CH_2Cl_2): $\tilde{\nu}/\text{cm}^{-1} = 2140\text{vs}$ ($\text{C}\equiv\text{N}$), 1989vs (CO). ^1H NMR (CDCl_3): $\delta/\text{ppm} = 7.89, 7.42$ (m, 4 H, C_6H_4); 4.91 (s, 2 H, CH_2); 4.82 (s, 5 H, Cp); 2.46 (s, 3 H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta/\text{ppm} = 216.2$ (CO); 177.3 ($\text{C}\equiv\text{N}$); 147.0 (Me-Carom); 132.6 (S-Carom); $130.7, 129.3$ (C_6H_4); 83.0 (Cp); 64.4 (CH_2); 22.0 (Me). Crystals suitable for X-ray analysis were collected by slow diffusion of pentane into a dichloromethane solution of **2e**.

$[\text{FeCpI}(\text{CO})(\text{CNMe})]$, **2f (Figure 9).**

Figure 9. Structure of **2f**.



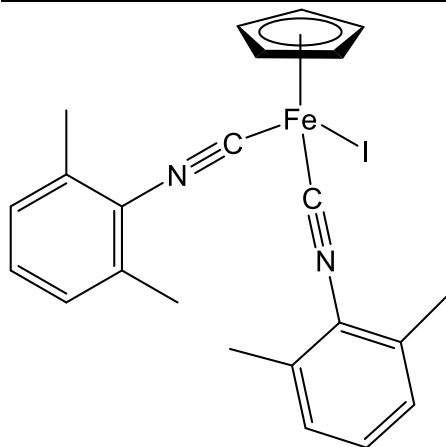
From **1** (311 mg, 1.02 mmol), [FeCp(CO)₂]₂ (18 mg, 0.05 mmol) and methyl isocyanide (68 μL, 15.2 mol/L, 1.03 mmol). Chromatography: Et₂O. The residue was triturated with pentane, the suspension was filtered and the resulting solid was washed with pentane. Ochre-brown/green solid, yield: 237 mg (73%); contains a trace amount (< 3 %) of [FeCpI(CNMe)₂]. IR (CH₂Cl₂): $\tilde{\nu}/\text{cm}^{-1}$ = 2185vs (C≡N), 1978vs (CO). ¹H NMR (CDCl₃): δ/ppm = 4.74 (s, 5 H, Cp), 3.55 (s, 3 H, Me). ¹³C{¹H} NMR (CDCl₃): δ/ppm = 217.8 (CO), 159.6 (br, C≡N), 81.8 (Cp), 31.2 (Me).

[FeCpI(CNR)₂] [**R** = Xyl, **3a**; **R** = 4-C₆H₄OMe, **3b**; **R** = CH₂Ph, **3c**; **R** = CH₂P(O)(OEt)₂, **3d**].

General procedure. A solution of **1** (*ca* 1 mmol) and [FeCp(CO)₂]₂ (5 mol%) in toluene (30 mL) was treated with the appropriate isocyanide (2 eq.). The mixture was heated at 85 °C and stirred for 15 minutes. The conversion of the starting material into the desired product was checked by IR spectroscopy. The crude was cooled to room temperature and then charged on a silica column. A first red fraction containing [FeCp(CO)₂]₂ and a small portion of **2a-d** were separated using toluene and the appropriate eluent, respectively, then the use of more polar solvents allowed to collect the desired product. Solvent was removed under reduced pressure, and the residue was reprecipitated using a mixture of Et₂O (5 mL) and pentane (35 mL). After filtration, the solid was dried under vacuum.

[FeCpI(CNXyl)₂], **3a** (**Figure 10**).

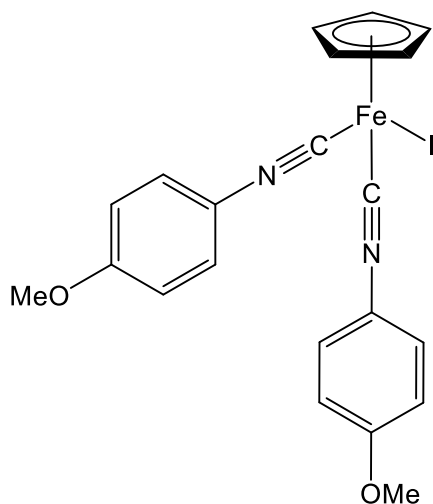
Figure 10. Structure of **3a**.



From **1** (308 mg, 1.01 mmol), $[\text{FeCp}(\text{CO})_2]_2$ (18 mg, 0.05 mmol) and 2,6-dimethylphenyl isocyanide (290 mg, 2.21 mmol). Chromatography: Et_2O . Dark-brown solid, yield 329 mg (64%). Anal. calcd. for $\text{C}_{23}\text{H}_{23}\text{FeIN}_2$: C, 54.15; H, 4.54; N, 5.49. Found: C, 54.42; H, 4.65; N, 5.34. IR (CH_2Cl_2): $\tilde{\nu}/\text{cm}^{-1} = 2120$ vs ($\text{C}\equiv\text{N}$), 2072vs ($\text{C}\equiv\text{N}$). ^1H NMR (CDCl_3): $\delta/\text{ppm} = 7.07$ (m, 6 H, C_6H_3); 4.73 (s, 5 H, Cp); 2.49 (s, 12 H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta/\text{ppm} = 180.7$ ($\text{C}\equiv\text{N}$); 134.9, 127.9, 127.2 (C_6H_3); 130.0 (*C-*ipso**); 80.9 (Cp); 19.3 (Me). Crystals suitable for X-ray analysis were collected by slow evaporation of an acetone solution of **3a**.

[FeCpI{CN(4-C₆H₄OMe)}₂], **3b (Figure 11).**

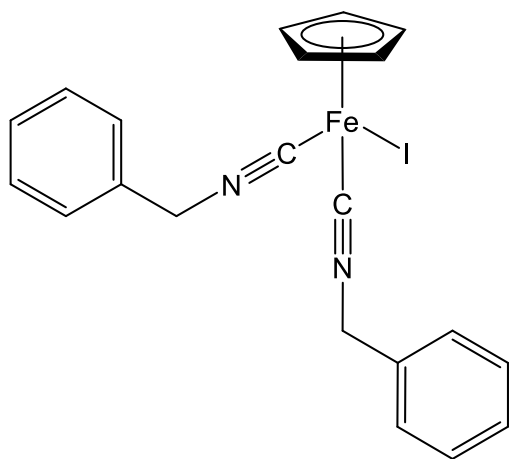
Figure 11. Structure of **3b**.



From **1** (253 mg, 0.83 mmol), $[\text{FeCp}(\text{CO})_2]_2$ (15 mg, 0.04 mmol) and 4-methoxyphenylisocyanide (238 mg, 1.75 mmol). Chromatography: acetone. Brown solid, yield 205 mg (48%). Anal. calcd. for $\text{C}_{21}\text{H}_{19}\text{FeIN}_2\text{O}_2$: C, 49.06; H, 3.73; N, 5.45. Found: C, 49.25; H, 3.58; N, 5.38. IR (CH_2Cl_2): $\tilde{\nu}/\text{cm}^{-1} = 2121\text{vs} (\text{C}\equiv\text{N}), 2082\text{vs} (\text{C}\equiv\text{N})$. $^1\text{H NMR}$ (CDCl_3): $\delta/\text{ppm} = 7.30, 6.85$ (m, 8 H, $^2J_{\text{HH}} = 8.7$ Hz, C_6H_4); 4.68 (s, 5 H, Cp); 3.80 (s, 6 H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta/\text{ppm} = 177.8 (\text{C}\equiv\text{N}); 158.8 (\text{O-Carom}); 127.3, 114.4 (\text{C}_6\text{H}_4); 123.6 (\text{N-Carom}); 80.6 (\text{Cp}); 55.7 (\text{OMe})$.

$[\text{FeCpI}(\text{CNCH}_2\text{Ph})_2]$, **3c (Figure 12).**

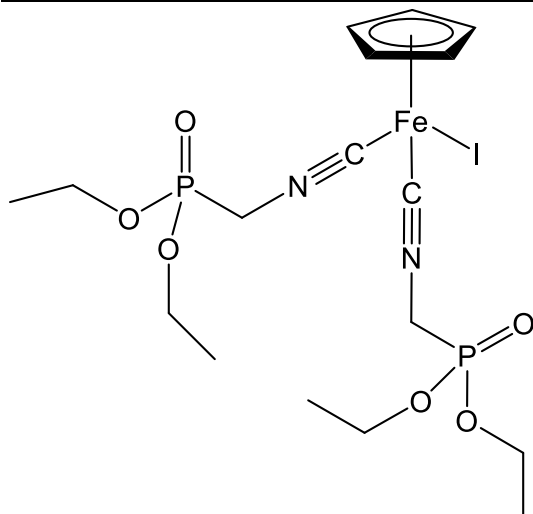
Figure 12. Structure of **3c**.



From **1** (273 mg, 0.898 mmol), $[\text{FeCp}(\text{CO})_2]_2$ (16 mg, 0.05 mmol) and benzyl isocyanide (0.22 mL, 1.8 mmol). Chromatography: Et_2O . Brown solid, yield 252 mg (58%). Anal. calcd. for $\text{C}_{21}\text{H}_{19}\text{FeIN}_2$: C, 52.31; H, 3.97; N, 5.81. Found: C, 52.14; H, 3.78; N, 5.84. IR (CH_2Cl_2): $\tilde{\nu}/\text{cm}^{-1} = 2149\text{vs} (\text{C}\equiv\text{N}), 2114\text{vs} (\text{C}\equiv\text{N})$. $^1\text{H NMR}$ (CDCl_3): $\delta/\text{ppm} = 7.38\text{-}7.27$ (m, 10 H, Ph); 4.98 (s, 4 H, CH_2); 4.47 (s, 5 H, Cp). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta/\text{ppm} = 171.8 (\text{C}\equiv\text{N}); 134.3, 128.9, 128.1, 126.5$ (Ph); 79.1 (Cp); 48.9 (CH_2).

$[\text{FeCpI}\{\text{CNCH}_2\text{P}(\text{O})(\text{OEt})_2\}_2]$, **3d (Figure 13).**

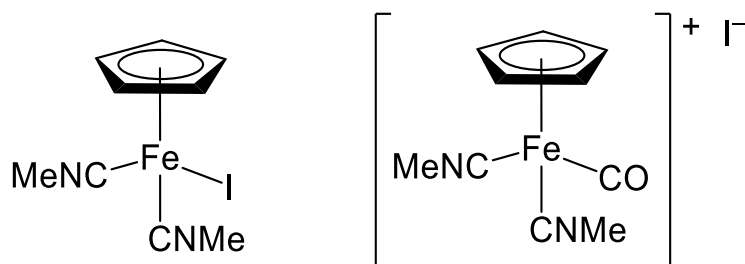
Figure 13. Structure of **3d**.



From **1** (243 mg, 0.800 mmol), $[\text{FeCp}(\text{CO})_2]_2$ (14 mg, 0.04 mmol) and diethyl isocyanomethylphosphonate (0.26 mL, 1.6 mmol). Chromatography: acetone. Dark-brown solid, yield 207 mg (43%). Anal. calcd. for $\text{C}_{17}\text{H}_{29}\text{FeIN}_2\text{O}_6\text{P}_2$: C, 33.91; H, 4.85; N, 4.65. Found: C, 33.58; H, 4.92; N, 4.52. IR (CH_2Cl_2): $\tilde{\nu}/\text{cm}^{-1} = 2146\text{vs} (\text{C}\equiv\text{N}), 2111\text{vs} (\text{C}\equiv\text{N})$. ^1H NMR (CDCl_3): $\delta/\text{ppm} = 4.51$ (s, 5 H, Cp); 4.25 (m, 8 H, OCH_2); 4.12 (m, 4 H, NCH_2); 1.38 (m, 12 H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta/\text{ppm} = 176.6$ ($\text{C}\equiv\text{N}$); 80.0 (Cp); 64.0 (d, $^2J_{\text{C-P}} = 6.2$ Hz, OCH_2); 41.2 (d, $^1J_{\text{C-P}} = 154.9$ Hz, NCH_2); 16.7 (d, $^3J_{\text{C-P}} = 5.3$ Hz, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta/\text{ppm} = 16.1$.

$[\text{FeCpI}(\text{CNMe})_2]$, **3f and $[\text{FeCp}(\text{CO})(\text{CNMe})_2]\text{I}$, **4f** (Figure 14).**

Figure 14. Structures of **3f** (left) and **4f** (right)



A dark brown solution of **1** (305 mg, 1.00 mmol) and $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ (18 mg, 0.050 mmol, 5% mol) in toluene (10 mL) was treated with methyl isocyanide (130 μL , 15.2 mol/L, 1.98 mmol). The Schlenk tube

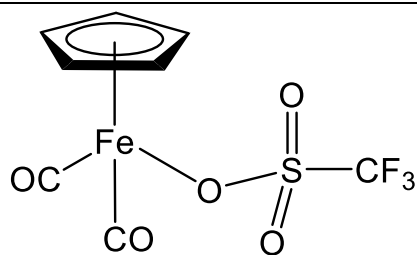
was immersed into an oil bath at 75 °C and gas evolution was observed. The mixture was stirred for 35 minutes at 75 °C leading to the formation of a yellow precipitate. Next, the suspension was cooled to room temperature and filtered on a G4 sintered-glass filter. The resulting yellow solid was washed with toluene, petroleum ether and dried under vacuum (room temperature). Yield: 286 mg, 86% of $[\text{FeCp}(\text{CO})(\text{CNMe})_2]\text{I}$, **4f**. The dark red-brown filtrate was taken to dryness under vacuum and analyzed by IR (CH_2Cl_2). Therefore, the residue was dissolved in few mL of toluene and moved on top of a silica column (d = 2.3 cm, h = 4 cm). Impurities were eluted with toluene, then a dark red-brown band and two dark green-brown bands were sequentially eluted with Et_2O . Volatiles were removed under vacuum. IR analyses of the three residues allowed their identification as a **1** + $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ mixture, **2f** (17 mg, 5.3% yield) and **3f** (21 mg, 6.3% yield), respectively. **3f**. IR (CH_2Cl_2): $\tilde{\nu}/\text{cm}^{-1} = 2165\text{s}$ ($\text{C}\equiv\text{N}$), 2135s ($\text{C}\equiv\text{N}$). ^1H NMR (CDCl_3): $\delta/\text{ppm} = 4.42$ (s, 5 H, Cp), 3.36 (s, 3 H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta/\text{ppm} = 168.4$ (br, $\text{C}\equiv\text{N}$), 78.6 (Cp), 31.2 (Me). **4f**. IR (CH_2Cl_2): $\tilde{\nu}/\text{cm}^{-1} = 2228\text{s}$ ($\text{C}\equiv\text{N}$), 2208 ($\text{C}\equiv\text{N}$), 2025s (CO). ^1H NMR (CDCl_3): $\delta/\text{ppm} = 5.24$ (s, 5 H, Cp), 3.69 (s, 3 H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta/\text{ppm} = 221.6$ (CO), 148.0 (br, $\text{C}\equiv\text{N}$), 85.0 (Cp), 33.0 (Me).

$[\text{FeCp}(\text{OSO}_2\text{CF}_3)\text{L}_2]$ (L = CO, **1^{TF}**; Xyl, **3a^{TF}**; L = 4-C₆H₄OMe, **3b^{TF}**; L = CH₂Ph, **3c^{TF}**).

A solution of the selected complex (ca. 0.1 mmol) in dichloromethane (10 mL) was treated with methyl trifluoromethanesulfonate (1.5–2 eq). The mixture was stirred for 5 h at room temperature, then the solvent was removed under reduced pressure to afford a residue which was dissolved in Et_2O (5 mL) and reprecipitated with pentane (40 mL). After filtration, the solid product was dried under vacuum. The same reactions were performed in CDCl_3 from ca. 0.05 mmol of starting complex, and ^1H NMR spectra of the mixtures evidenced the formation of CH_3I ($\delta = 2.16$ ppm).

$[\text{FeCp}(\text{OSO}_2\text{CF}_3)(\text{CO})_2]$, **1^{TF}** (Figure 15).

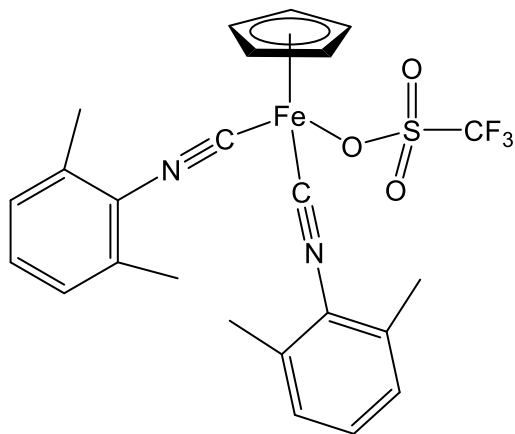
Figure 15. Structure of **1^{TF}**.



From **1** (160 mg, 0.527 mmol) and methyl trifluoromethanesulfonate (0.189 mL, 1.65 mmol). Brown solid, yield 120 mg (70%), stored at -30 °C. Anal. calcd. for C₈H₅F₃FeO₅S: C, 29.47; H, 1.55; S, 9.83. Found: C, 29.70; H, 1.36; S, 9.98. IR (CH₂Cl₂): $\tilde{\nu}/\text{cm}^{-1}$ = 2073vs (CO), 2029vs (CO). ¹H NMR (CDCl₃): δ/ppm = 5.30 (s, 5 H, Cp). ¹⁹F{¹H} NMR (CDCl₃): δ/ppm = -74.7 (s, CF₃).

[FeCp(OSO₂CF₃)(CNXyl)₂], 3a^{TF} (Figure 16).

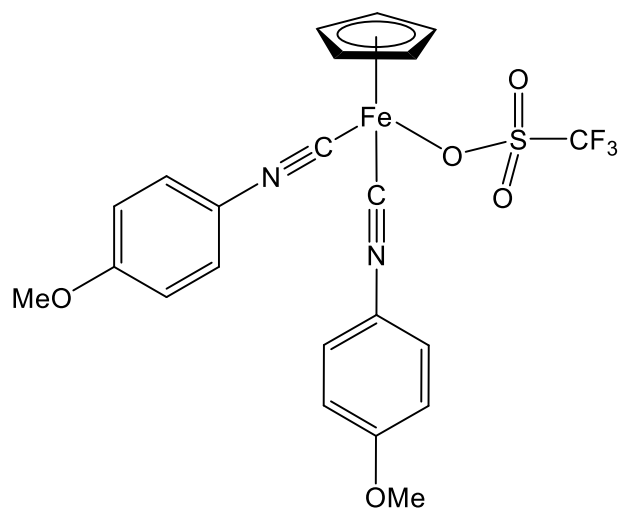
Figure 16. Structure of **3a^{TF}**.



From **3a** (138 mg, 0.270 mmol) and methyl trifluoromethanesulfonate (43 μ L, 0.38 mmol). Dark-brown solid, yield 112 mg (78%), stored at -30 °C. Anal. calcd. for C₂₄H₂₃F₃FeN₂O₃S: C, 54.15; H, 4.35; N, 5.26; S, 6.02. Found: C, 54.38; H, 4.48; N, 5.05; S, 6.18. IR (CH₂Cl₂): $\tilde{\nu}/\text{cm}^{-1}$ = 2139vs (C≡N), 2101vs (C≡N). ¹H NMR (CDCl₃): δ/ppm = 7.12 (m, 6 H, C₆H₃); 5.24 (s, 5 H, Cp); 2.41 (s, 12 H, Me). ¹³C{¹H} NMR (CDCl₃): δ/ppm = 168.7 (C≡N); 134.8, 129.2, 128.4, 128.3 (C₆H₃); 84.5 (Cp); 18.9 (Me). ¹⁹F{¹H} NMR (CDCl₃): δ/ppm = -78.0 (s, CF₃).

[FeCp(OSO₂CF₃){CN(4-C₆H₄OMe)₂}, 3b^{TF} (Figure 17).

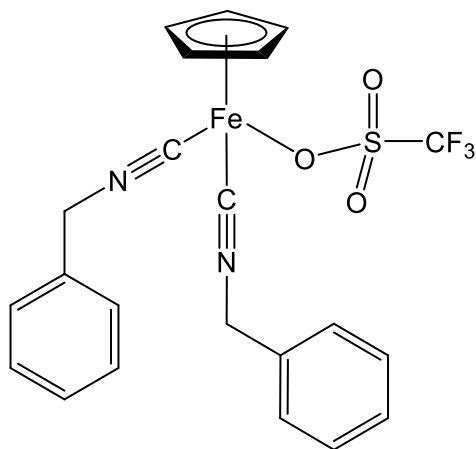
Figure 17. Structure of **3b^{TF}**.



From **3b** (108 mg, 0.210 mmol) and methyl trifluoromethanesulfonate (46 μ L, 0.41 mmol). Brown solid, yield 67 mg (62%), stored at -30 °C. Anal. calcd. for C₂₂H₁₉N₂SO₅F₃Fe: C, 49.27; H, 3.57; N, 5.22; S, 5.98. Found: C, 49.02; H, 3.65; N, 5.08; S, 6.10. IR (CH₂Cl₂): $\tilde{\nu}/\text{cm}^{-1}$ = 2174m (C≡N), 2133vs (C≡N). ¹H NMR (CDCl₃): δ/ppm = 7.41, 6.93 (m, 8 H, ²J_{HH} = 8.8 Hz, C₆H₄); 5.13 (s, 5 H, Cp); 3.83 (s, 6 H, Me). ¹³C{¹H} NMR (CDCl₃): δ/ppm = 163.7 (C≡N); 160.1 (O-Carom); 128.0, 114.9 (C₆H₄); 121.4 (N-Carom); 84.1 (Cp); 55.8 (OMe). ¹⁹F{¹H} NMR (CDCl₃): δ/ppm = -77.9 (s, CF₃).

[FeCp(OSO₂CF₃)(CNCH₂Ph)₂], 3c^{TF} (Figure 18).

Figure 18. Structure of **3c^{TF}**.



From **3c** (160 mg, 0.332 mmol) and methyl trifluoromethanesulfonate (67 μ L, 0.59 mmol). Brown solid, yield 118 mg (71%), stored at -30 °C. Anal. calcd. for $C_{22}H_{19}N_2SO_3F_3Fe$: C, 52.40; H, 3.80; N, 5.55; S, 6.36. Found: C, 52.12; H, 3.92; N, 5.43; S, 6.48. IR (CH_2Cl_2): $\tilde{\nu}/cm^{-1} = 2199m$ ($C\equiv N$), 2158vs ($C\equiv N$). 1H NMR ($CDCl_3$): $\delta/ppm = 7.32, 7.28$ (m, 10 H, Ph); 4.97 (s, 5 H, Cp); 4.80 (s, 4 H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta/ppm = 159.0$ ($C\equiv N$); 133.1, 129.2, 128.7, 126.9 (Ph); 82.5 (Cp); 49.3 (CH_2). $^{19}F\{^1H\}$ NMR ($CDCl_3$): $\delta/ppm = -77.9$ (s, CF_3).

2) X-ray crystallography

Crystal data and collection details for **2a**, **2e** and **3a** are reported in Table 4. Data were recorded on a Bruker APEX II diffractometer equipped with a PHOTON2 detector using Mo-K α radiation. The structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2 .⁷⁹ Hydrogen atoms were fixed at calculated positions and refined using a riding model.

The crystals of **2a** appeared to be non-merohedrally twinned. The TwinRotMat routine of PLATON was used to determine the twinning matrix and to write the reflection data file (.hkl) containing the twin components.⁸⁰ Refinement was performed using the instruction HKLF 5 in SHELXL and a BASF parameter, which refined as 0.247(6).

Table 4. Crystal data and measurement details for **2a**, **2e** and **3a**.

	2a	2e	3a
Formula	$C_{15}H_{14}FeINO$	$C_{15}H_{14}FeINO_3S$	$C_{23}H_{23}FeIN_2$
FW	407.02	471.08	510.18
T, K	100(2)	100(2)	100(2)
λ , Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$C2/c$	$P2_1/c$	$P\bar{1}$
a , Å	20.6305(10)	12.9753(9)	7.4306(5)
b , Å	13.9252(6)	16.4668(11)	9.1317(6)
c , Å	13.6845(7)	8.0587(5)	15.6310(10)
α , °	90	90	89.573(2)
β , °	131.2770(10)	103.712(2)	87.166(2)

γ , °	90	90	78.640(2)
Cell Volume, Å ³	2954.5(2)	1672.76(19)	1038.57(12)
Z	8	4	2
D_c , g·cm ⁻³	1.830	1.871	1.631
μ , mm ⁻¹	3.101	2.882	2.222
F(000)	1584	920	508
Crystal size, mm	0.18 × 0.14 × 0.10	0.18 × 0.14 × 0.07	0.19 × 0.16 × 0.11
θ limits, °	1.966-25.025	1.615-25.048	2.27525.996
Reflections collected	17638	17889	13020
Independent reflections	2608 [$R_{int} = 0.0598$]	2960 [$R_{int} = 0.0560$]	4056 [$R_{int} = 0.0348$]
Data / restraints / parameters	2608 / 172 / 206	2960 / 54 / 228	4056 / 0 / 248
Goodness on fit on F^2 ^a	1.200	1.157	1.099
R_1 ($I > 2\sigma(I)$) ^b	0.0990	0.0338	0.0285
wR_2 (all data) ^c	0.2566	0.08091	0.0672
Largest diff. peak and hole, e Å ⁻³	4.148 / -2.614	1.386 / -0.440	0.780 / -0.503

^a Goodness on fit on $F^2 = [\sum w(F_O^2 - F_C^2)^2 / (N_{ref} - N_{param})]^{1/2}$, where $w = 1/[\sigma^2(F_O^2) + (aP)^2 + bP]$, where $P = (F_O^2 + 2F_C^2)/3$; N_{ref} = number of reflections used in the refinement; N_{param} = number of refined parameters. ^b $R_1 = \sum ||F_O| - |F_C|| / \sum |F_O|$. ^c $wR_2 = [\sum w(F_O^2 - F_C^2)^2 / \sum w(F_O^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_O^2) + (aP)^2 + bP]$, where $P = (F_O^2 + 2F_C^2)/3$.

3) *rac*-Lactide polymerization reactions

General procedure. *rac*-Lactide (500-800 mg) and the selected catalyst (0.1 mol%) were introduced into a Schlenk tube, which was evacuated and then filled with dinitrogen. The mixture was heated at 150 °C under stirring for 2.5 h. The final mixture was allowed to cool to room temperature and dissolved in CH₂Cl₂ (ca. 5 mL). A small aliquot of the dichloromethane solution was dried under vacuum, the resulting residue was dissolved in CDCl₃ (0.7 mL) and this solution was analyzed by ¹H NMR spectroscopy. The conversion percentage was calculated based on the integral values related to *rac*-lactide ($\delta = 5.1, 1.6$ ppm) and polylactide ($\delta = 5.2, 1.7$ ppm).

Acknowledgements

We thank the University of Pisa for financial support (Fondi di Ateneo 2022).

Supporting Information Available

NMR spectra of products. CCDC reference numbers 2267916 (**2a**), 2267917 (**2e**) and 2267918 (**3a**) contain the supplementary crystallographic data for the X-ray studies reported in this work. These data are available free of charge at <http://www.ccdc.cam.ac.uk/structures>.

The authors declare no competing financial interests.

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