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Adding Diversity to Diiron Aminocarbyne Complexes with Amine Ligands

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Abstract: The reactions of the diiron aminocarbyne complexes $[Fe_2Cp_2(NCMe)(CO)(\mu\text{-}CO)\{\mu\text{-}CN(Me)(R)\}]CF_3SO_3$ (R = Me, **1a**^{NCMe}; R = Cy, **1b**^{NCMe}), freshly prepared from the tricarbonyl precursors **1a–b**, with primary amines containing an additional function (i.e., alcohol or ether) proceeded with the replacement of the labile acetonitrile ligand and formation of $[Fe_2Cp_2(NH_2CH_2CH_2OR')(CO)(\mu\text{-}CO)\{\mu\text{-}CN(Me)(R)\}]CF_3SO_3$ (R = Me, R′ = H, **2a**; R = Cy, R′ = H, **2b**; R = Cy, R′ = Me, **2c**) in 81–95% yields. The diiron-oxazolidinone conjugate $[Fe_2Cp_2(\mathbf{NH_2}^{OX})(CO)(\mu\text{-}CO)\{\mu\text{-}CN(Me)_2\}]CF_3SO_3$, **3**, was prepared from **1a**, 3-(2-aminoethyl)-5-phenyloxazolidin-2-one (**NH$_2$**^{OX}) and Me_3NO, and finally isolated in 96% yield. In contrast, the one pot reactions of **1a-b** with $NHEt_2$ in the presence of Me_3NO gave the unstable $[Fe_2Cp_2(NHEt_2)(CO)(\mu\text{-}CO)\{\mu\text{-}CN(Me)(R)\}]CF_3SO_3$ (R = Me, **4a**; R = Cy, **4b**) as unclean products. All diiron complexes were characterized by analytical and spectroscopic techniques; moreover, the behavior of **2a–c** and **3** in aqueous media was ascertained.

Keywords: organometallic chemistry; diiron complexes; aminocarbyne ligand; amine ligand; oxazolidinone

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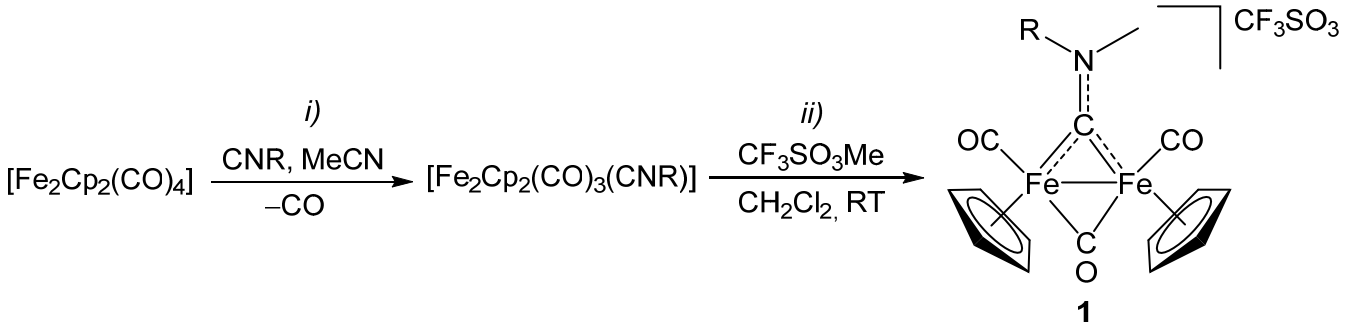
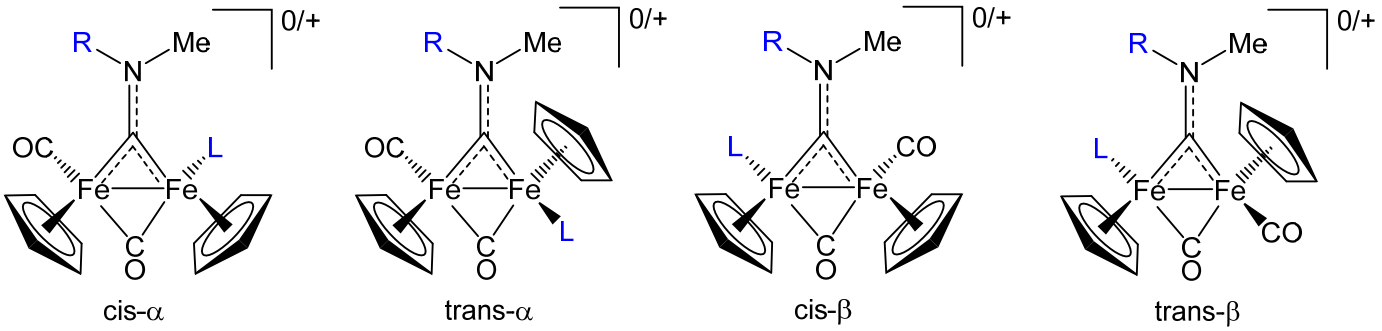
1. Introduction

The chemistry of diiron complexes has attracted considerable attention for several reasons. First, iron is an earth-abundant and environmentally benign element, its compounds are relatively cost-effective and nontoxic, and the advance of iron chemistry is an important step forward in the urgent demand for developing new sustainable synthetic processes [1–5]. The second point to be considered is that a bimetallic system is characterized by cooperative effects arising from the two metal centers working in concert, thus enabling uncommon reactivity patterns which would otherwise not be viable on related monometallic species [6–11]. Finally, and relevant to this last point, the inorganic unit of a class of hydrogenases [12,13], i.e., enzymes capable of producing dihydrogen from water, is based on an organo-diiron core; therefore, a variety of diiron complexes has been intensively investigated to efficiently mimic such natural catalysts in the perspective of a "hydrogen economy" [14–17]. The dimeric compound $[Fe_2Cp_2(CO)_4]$ (Cp = η^5-C_5H_5) is a commercially available, convenient and cheap starting material to access diiron organometallic chemistry [18–23]; in the last 20 years, our research in this field has focused on the synthesis and reactivity of derivatives containing a bridging aminocarbyne ligand [24,25]. These are obtained through a straightforward two-step procedure, consisting of the substitution of one carbon monoxide ligand with an isocyanide (CNR), followed by alkylation of the isocyanide ligand, which is usually performed with methyl triflate (Scheme 1) [26]. The {CN(Me)R} moiety possesses some iminium character; the carbyne–nitrogen bond is partially double, thus rotation of the amine group around the carbyne-N axis is hampered at room temperature and above.



Scheme 1. Typical two-step synthesis of diiron μ-aminocarbyne complexes from commercially available chemicals. R = alkyl or aryl (**i**,**ii**).

Remarkably, complexes of type **1**, and their cationic derivatives, are normally air-stable and rather inert in aqueous solutions, and these features have recently fueled the exploration of their potential use in medicine [27–29] and catalysis [30–32]. The replacement of one or two carbonyls from **1** is key to their derivatization, including C-C and C-N coupling reactions involving the carbyne center [24,25,33]. However, the simple introduction of one terminal ligand (L) different from CO may produce a significant impact on the physicochemical properties and aqueous stability of the resulting diiron aminocarbyne compounds [29,34]. In principle, the CO/L mono-substitution reaction may generate cationic or neutral adducts (depending on the charge of L) existing in different isomeric forms, i.e., cis and trans isomers (with reference to the mutual geometry of the Cp rings with respect to the Fe-Fe axis), and α and β isomers (with reference to the mutual orientation of L and the aminocarbyne R substituent), as seen in Scheme 2 [24,25]. Relevant to the latter point, it should be noted that the α/β isomerism, arising from the double bond nature of the carbyne–nitrogen linkage, may be not observed when both R and L are bulky units (i.e., the α isomer largely prevails) [35,36], and disappears when R = Me. In contrast, cis isomers are usually more stable than the corresponding trans isomers, the latter being observed due to a combination of steric and electronic factors [25,37]. The interconversion in solution between trans and cis forms, and consequently between α and β forms, is practicable in certain cases under thermal treatment, and possibly obeys the Adams–Cotton mechanism whereby ligands undergo site exchange through open-bridged structures [37–40].



Scheme 2. Possible isomers in diiron μ-aminocarbyne derivatives: the net positive charge of the complex is present if L = neutral, otherwise (L = monoanionic) the complexes are neutral. α/β forms are observable when R ≠ Me.

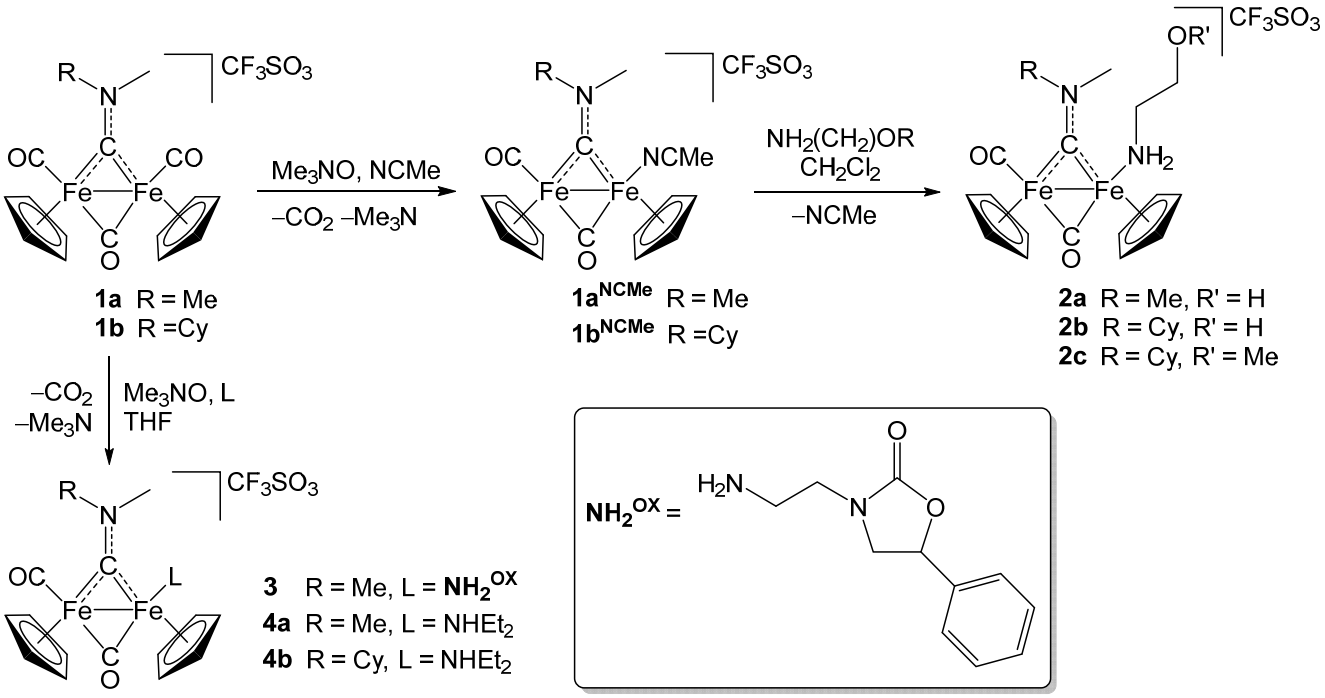
In this study, we report the synthesis, the spectroscopic characterization and the assessment of the behavior of a new series of diiron aminocarbyne complexes with primary amines bearing additional functions in aqueous media (solubility, stability).

2. Results and Discussion

2.1. Synthesis and Spectroscopic Characterization

The diiron aminocarbyne complexes **1a–b** were synthesized according to the procedure shown in Scheme 1. They are 36-electron compounds and comprise firmly bound ligands; therefore, the substitution of one CO with a more labile acetonitrile ligand was preliminarily carried out with the aim of allowing amine coordination. Consequently, **1a–b** were converted into the acetonitrile adducts using the trimethylamine-N-oxide (TMNO) strategy [41], which is commonly reliable with cationic complexes based on the $M_2Cp_2(CO)_3$ core (M = Fe, Ru) [42–45]. The resulting derivatives, $\mathbf{1a}^{\mathbf{NCMe}}$ and $\mathbf{1b}^{\mathbf{NCMe}}$ [46], were then employed as freshly prepared.

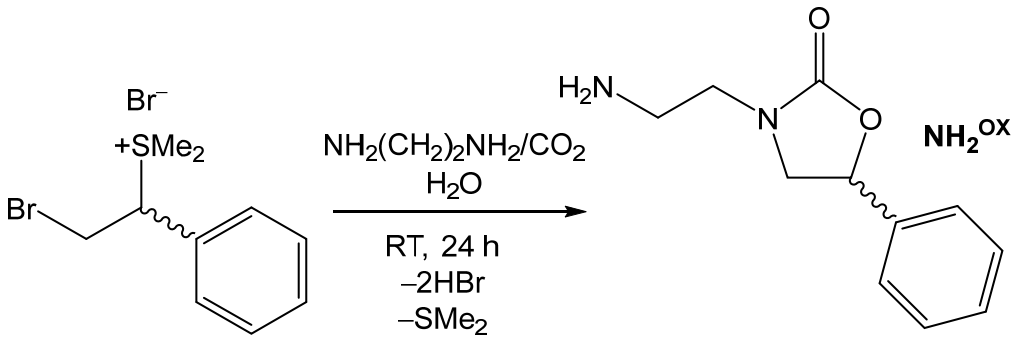
The reactions of $\mathbf{1a}^{\mathbf{NCMe}}$ and $\mathbf{1b}^{\mathbf{NCMe}}$ with ethanolamine and of $\mathbf{1b}^{\mathbf{NCMe}}$ with 2-methoxyethylamine were conducted at room temperature using an excess of the organic reagents and were continued with quantitative acetonitrile –amine substitution to afford the novel air-stable complexes **2a–c** in 81–95% yields (Scheme 3). No traces of O-coordinated adducts were detected, in alignment with the fact that N-coordination is favored over O-coordination for potential nitrogen/oxygen donors on soft metal centers [47,48], whereas O-coordination becomes easier with higher valent metal complexes [49].



Scheme 3. Routes for the synthesis of diiron μ-aminocarbyne complexes with amine ligands reported in this work.

Due to evidence that terminal amines form stable compounds with the $[Fe_2Cp_2(CO)_2\{\mu\text{-}CNMe(R)\}]$ scaffold, and that the synthesis reaction seems tolerant of additional heteroatom functions on the amine, we moved to evaluate the possibility of exploiting the amine coordination as a carrier of a bioactive fragment. In particular, oxazolidinones are five-membered cyclic carbamates which find important applications for their biological activity [50–52]. Reported synthetic procedures to obtain oxazolidinones are commonly metal-catalyzed and make use of aziridines as atom-economical starting materials [53–56]. In the framework of our interest in the chemistry of carbamates [57–60], we recently developed a catalyst-free method to access 5-aryl-2-oxazolidinones directly from aziridine precursors, amines and carbon dioxide, working at ambient temperature and pressure [61]. This strategy allows for unprecedented access to molecules with uncommon substituents on the nitrogen ring, including the -NH_2 group and the skeleton of several natural α-amino-acids [62].

We selected 3-(2-aminoethyl)-5-phenyloxazolidin-2-one ($\mathbf{NH_2}^{\mathbf{OX}}$) as an appropriate amine reagent towards diiron aminocarbyne acetonitrile complexes (Scheme 4).



Scheme 4. Catalyst-free synthesis of 3-(2-aminoethyl)-5-phenyloxazolidin-2-one ($\mathbf{NH_2}^{\mathbf{OX}}$) from (2-bromo-1-phenylethyl)dimethylsulfonium bromide, ethylenediamine and carbon dioxide in water (T = 298 K, pCO_2 = 1 atm).

The reaction of $\mathbf{NH_2}^{\mathbf{OX}}$ with freshly prepared $\mathbf{1a}^{\mathbf{NCMe}}$, in dichloromethane, proceeded smoothly at room temperature to afford the unprecedented diiron-oxazolidinone conjugate **3**; nevertheless, **3** was obtained in a purer form by allowing $\mathbf{NH_2}^{\mathbf{OX}}$ to react with **1a**, in tetrahydrofuran, in the presence of TMNO (Scheme 3). The same method was applied in the past to obtain diiron complexes analogous to **2a–c** and containing a terminal alkyl-amine ligand [63]. Thus, complex **3** was isolated in almost quantitative yield after the work-up. Compounds **2–3** are indefinitely stable in the solid state in air, well soluble and stable in dichloromethane and acetone, almost insoluble in diethyl ether and insoluble in hexane.

Note that $\mathbf{1b}^{\mathbf{NCMe}}$ did not react with aniline ($PhNH_2$) and gave only partial substitution with diethylamine (Et_2NH) and pyrrolidine [$(CH_2)_4NH$], suggesting that electronic ($PhNH_2$) and steric [secondary amine ≥ cyclic secondary amine > primary amine] factors are crucial to let the amine win the competition for coordination with N≡CMe. To favor the formation of the related adducts, these amines were added to a mixture of **1b** and TMNO in tetrahydrofuran. The reactions of **1b** with TMNO, in the presence of aniline or pyrrolidine, resulted in extensive decomposition; instead, **4b** was formed from **1b**/$NHEt_2$/TMNO and the analogous reaction from **1a**/$NHEt_2$/TMNO afforded **4a** (Scheme 3). Both **4a** and **4b** were obtained in admixture with inseparable impurities and are unstable species, undergoing progressive degradation at room temperature both in the solid state and in chlorinated solvents.

Compounds **2a–c** and **3** were characterized by IR and multinuclear NMR spectroscopy (see Supplementary Material), showing a general good degree of purity, whereas only a limited characterization was possible for **4a–b** due to the stability issues. As a general consideration, NMR spectroscopy characterization of **2–3**, and in general [$Fe_2Cp_2(CO)_4$] derivatives, is possible due to the diamagnetism of these species, which may be not associated with the presence of an iron–iron bond [64].

The IR spectra (CH_2Cl_2 solutions, 2300–1500 cm^{-1} spectral region) share a common pattern consisting of three main bands ascribable to the terminal and bridging carbonyl ligands, falling in narrow ranges of wavenumbers (respectively at 1970–1978 and 1797–1800 cm^{-1}, in CH_2Cl_2), and to the bridging carbyne–nitrogen bond. The latter band is strongly affected by the aminocarbyne substituents and was found at ca. 1575 cm^{-1} for R = Me (**2a**, **3** and **4a**) and ca. 1530 cm^{-1} for R = Cy (**2b**, **2c** and **4b**). For the sake of comparison, the corresponding CO absorptions in the parent complexes $\mathbf{1a–b}^{\mathbf{NCMe}}$ occur at ca. 1985 and 1815 cm^{-1} [42,46], clarifying the major σ-donation supplied by primary alkyl-amines compared to acetonitrile, resulting in a reinforced π back-bonding from the iron centers to the carbonyl ligands in **2–4**. Furthermore, the infrared band for the μ-CN moiety falls at higher frequencies in $\mathbf{1a–b}^{\mathbf{NCMe}}$ ($\mathbf{1a}^{\mathbf{NCMe}}$: 1584 cm^{-1} [42]; $\mathbf{1b}^{\mathbf{NCMe}}$: 1562 cm^{-1} [46]), indicating that the aminocarbyne ligand experiences a slightly increased back-donation

from the metal centers in **2–4** than in **1a–b^{NCMe}**, weakening the carbyne–nitrogen bond. Note that aminocarbyne ligands are usually regarded as strong π-acceptor ligands [24,65]. In **3**, the absorption related to the carbonyl belonging to the carbamate moiety occurs at 1751 cm^{-1}.

The ^{1}H NMR spectrum of **2a** shows two sets of resonances in a 4:1 ratio, which we attribute to cis and trans isomers (Scheme 2). A distinctive feature is provided by the ^{1}H and ^{13}C resonances of the N-Me units, which are quite close in the two isomers [cis: 4.73, 4.35 ppm (^{1}H) and 54.5, 52.8 ppm (^{13}C); trans: 4.80, 4.40 ppm (^{1}H) and 53.9, 52.7 ppm (^{13}C)]. In contrast, the NMR spectra of **2b–c** display two sets of resonances, which are likely more ascribable to α and β isomers differing in the orientation of the N-substituents with respect to the amine ligand (see Scheme 2) [25]. As a matter of fact, the signals related to N-Me undergo a significant shift going from one isomer to another [e.g., for **2b**: α isomer, 4.50 (^{1}H) and 45.1 ppm (^{13}C); β isomer, 4.09 (^{1}H) and 46.4 ppm (^{13}C)]. NMR resonances of **2b–c** were assigned to the two isomers (α and β) based on a comparison with literature data for similar complexes containing the aminocarbyne {CNMe(Cy)} group and terminal nitrogen ligands [46]; in particular, the N-bound methyl generally resonates, in the ^{1}H NMR spectra, at a lower chemical shift in the α isomer than in the β isomer, and the opposite trend is observed in the ^{13}C NMR spectra. Consistently, the α isomer is prevalent in both **2b** and **2c** (α/β ratio ≈ 2), placing the bulky cyclohexyl group on the same side of the carbonyl ligand.

The ^{1}H NMR analysis of **3** (acetone-d_6) revealed the presence of two species in equimolar ratio, with signals close to each other. We hypothesize that the two species correspond to the cis form (the chemical shift values of the Cp rings strictly match those related to the cis isomer of **2a**), existing as two diastereoisomers due to the chirality of the diiron core associated with the presence of a stereocenter on the five-membered carbamate cycle. A similar feature was previously observed upon tethering enantiopure sugar scaffolds to a vinyliminium ligand bridging coordinated to the [$Fe_2Cp_2(CO)_2$] core [66].

The coordinated amine moiety in **2–4** manifests itself with a high field ^{1}H NMR signal falling in the interval from −0.80 to −2.98 ppm. As a comparison, this signal occurs at −0.94 ppm in **3** and at 2.28 ppm in uncoordinated **NH_2^{OX}**. The N-bound methylene moiety is significantly shielded in **2–3** with respect to the corresponding amines; for instance, it has been detected at 2.35 and 2.17 ppm (two isomers) in the ^{1}H NMR spectrum of **3** (to be compared with δ = 3.24 ppm in free **NH_2^{OX}**). Conversely, the resonances due to the oxazolidinone ring do not undergo an appreciable shift on coordination to the iron center.

In the ^{13}C NMR spectra of **2–3**, the signals due to the aminocarbyne carbon have been found in the 332.9–330.8 ppm range [24,67,68], while those of the terminal and bridging CO ligands are at 214.5–212.2 ppm and 270.8–268.5 ppm, respectively. This feature confirms that the amine coordination to iron does not affect the $Fe_2Cp_2(CO)_2$ framework and the aminocarbyne moiety [24,25].

2.2. Behavior in Aqueous Solutions

In view of possible aqueous applications of the novel diiron complexes **2a–c** and **3**, and especially in the biological field, we assessed their behavior in aqueous media by means of well-established spectroscopic methods (see Table 1 and Experimental for details). First, we determined the solubility of the complexes in D_2O by ^{1}H NMR spectroscopy using dimethylsulfone ($DMSO_2$) as an internal standard. All complexes were fairly soluble, with solubility values ranging from 9.6 mM (**2c**) to 0.47 mM (**3**); as a relevant reference, note that the estimated water solubility of the leading metal drug cisplatin is 8.4 mM [69]. The water stability was ascertained by ^{1}H NMR analyses on CD_3OD-D_2O mixtures stored at 37 °C ($DMSO_2$ as internal standard), and a similar study was performed in a deuterated cell culture medium (DMEM-d) mixed with CD_3OD. The results shown in Table 1 show the fair inertness of **2a–c**, with a variable amount (17–45%) of the starting material recovered after 72 h; the stability of **2a** (with a Me_2N substituted carbyne) appears slightly better and was also tested in the absence of methanol, leading to similar results. NMR spectra did not suggest the formation of new organo-iron species, thus it is presumable that the

decomposition of **2a–c** proceeds *slowly* with extensive disassembly of the organometallic structure, as previously described for similar compounds [28,34]. In contrast, complex **3** showed markedly less stability in the aqueous media, and extensive decomposition with formation of a mixture of unidentified products including the precipitation of a solid that was observed after ca. 24 h. This decomposition, which could not be quantified, is presumably associated with the relative steric hindrance of the oxazolidinone moiety, favoring the replacement of the amine ligand by one solvent molecule and triggering the degradation process [34].

Table 1. Solubility of diiron amine complexes in D_2O (based on ^1H NMR spectroscopy, $DMSO_2$ as internal standard). Residual % of complex in aqueous media after 72 h at 37 °C, and solvent (D_2O or DMEM-d) over CD_3OD ratio.

Complex	Solubility/mol·L^{-}	% Stability D_2O/CD_3OD	% Stability DMEM-d/CD_3OD	Solvent/CD_3OD Ratio
2a	$2.0{\cdot}10^{-3}$	45	45	2
		49	29	∞
2b	$0.2{\cdot}10^{-3}$	29	≈10	2
2c	$9.6{\cdot}10^{-3}$	19	17	2
3	$4.7{\cdot}10^{-4}$	≈0	≈0	2

3. Experimental Section

3.1. Materials and Methods

Reactants and solvents were purchased from Alfa Aesar, Merck, Strem or TCI Chemicals, and were of the highest purity available. Diiron complexes **1a–b** [26,27] and (2-bromo-1-phenylethyl)dimethylsulfonium bromide [70] were prepared according to published procedures. Reactions were conducted under N_2 atmosphere using standard Schlenk techniques and monitored by means of liquid IR spectroscopy. Products were stored under N_2 once isolated. Dichloromethane and tetrahydrofuran were dried with the solvent purification system mBraun MB SPS5, while acetonitrile was used as received. Chromatography separations were carried out on columns of deactivated alumina (Merck, 4% *w*/*w* water). IR spectra of solutions were recorded using a CaF_2 liquid transmission cell (2300–1500 cm^{-1}) on a Perkin Elmer Spectrum 100 FT-IR spectrometer. IR spectra were processed with Spectragryph software [71]. The ^1H and ^{13}C NMR spectra were recorded at 298 K on a Jeol JNM-ECZ500R instrument equipped with a Royal HFX Broadband probe. Chemical shifts (expressed in parts per million) are referenced to the residual solvent peaks [72]. NMR spectra were assigned with the assistance of ^1H-^{13}C (*gs*-HSQC and *gs*-HMBC) correlation experiments [73]. NMR signals due to secondary isomeric forms (where it is possible to detect them) are italicized. Elemental analyses were performed on a Vario MICRO cube instrument (Elementar).

3.2. Synthesis and Characterization of Diiron Aminocarbyne Complexes with Primary Amines

General procedure. A solution of **1a–b** (ca 0.2 mmol) in MeCN (15 mL) was treated with $Me_3NO{\cdot}2H_2O$ (1.1 eq.), and the resulting mixture was stirred for 1 h, allowing the outflow of the produced gas. The conversion of the starting material into the acetonitrile adducts, $\mathbf{1a^{NCMe}}$ and $\mathbf{1b^{NCMe}}$, was checked by IR spectroscopy, as is routine for this type of reaction [42]. Volatiles were removed under vacuum, thus affording a brown residue. This solid was dissolved in CH_2Cl_2 (ca. 10 mL), the selected amine (ca. 5 eq.) was added, and this solution was stirred overnight at room temperature. The crude reaction mixture was filtered on a celite pad, and the filtrated solution was evaporated under reduced pressure. The residue was suspended in Et_2O (15 mL) for 1 h, then the liquid was eliminated. The resulting dark-brown powder was dried under vacuum. All products are soluble in

acetonitrile, acetone, dichloromethane and tetrahydrofuran, and manifested hygroscopic behavior; thus, they were conserved under N_2 atmosphere.

$[Fe_2Cp_2(\kappa N\text{-}NH_2CH_2CH_2OH)(CO)(\mu\text{-}CO)\{\mu\text{-}CN(Me)_2\}]CF_3SO_3$, **2a** (Figure 1).

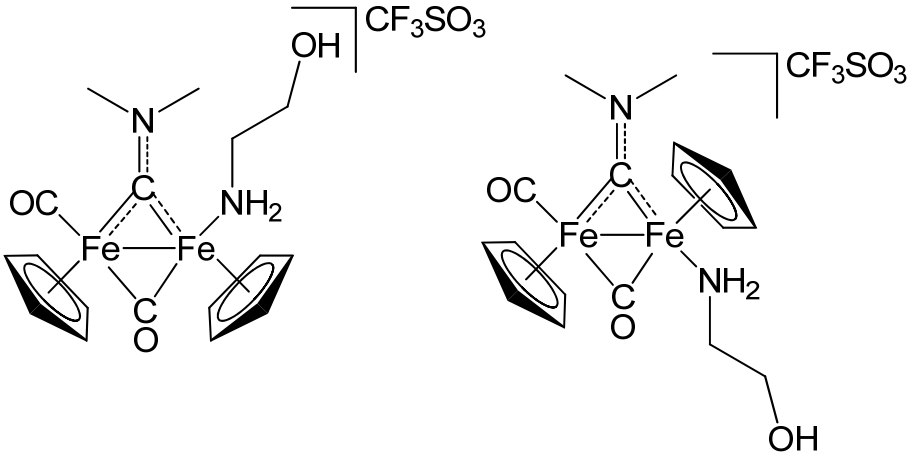


Figure 1. Structure of **2a** (**left**: cis isomer; **right**: trans isomer).

From **1a** (49 mg, 0.092 mmol) and $NH_2CH_2CH_2OH$ (17 μL, 0.28 mmol). Brown solid, yield 47 mg (91%). Anal. calcd. for $C_{18}H_{23}F_3Fe_2N_2O_6S$: C, 38.32; H, 4.11; N, 4.97; S, 5.68. Found: C, 38.62; H, 4.24; N, 4.76; S, 5.44. IR (CH_2Cl_2): $\tilde{\upsilon}/cm^{-1}$ = 1973vs (CO), 1798s (μ-CO), 1573m (μ-CN). ^{1}H-NMR (acetone-d_6): δ/ppm = *5.21*, 5.12, 4.97, *4.82* (s, 10 H, Cp); *4.80*, 4.73, *4.40*, 4.35 (s, 6 H, NMe_2); 3.18 (m, 2 H, OCH_2); *2.32*, 2.17 (m, 2 H, NCH_2); 1.73, *1.45* (m, 1 H, NH); *−0.80*, −1.12 (m, 1 H, NH). $^{13}C\{^1H\}$-NMR (acetone-d_6): δ/ppm = *332.9*, 331.6 (μ-CN); 270.4, *268.3* (μ-CO); 214.0, *212.7* (CO); *89.8*, 89.3, *88.7*, 87.2 (Cp); 61.3, *61.2* (OCH_2); 54.5, *53.9*, 52.8, *52.7* (NMe_2); *52.8*, 51.3 (NCH_2). Cis/trans ratio = 4.

$[Fe_2Cp_2(\kappa N\text{-}NH_2CH_2CH_2OH)(CO)(\mu\text{-}CO)\{\mu\text{-}CN(Me)(Cy)\}]CF_3SO_3$, **2b** (Figure 2).

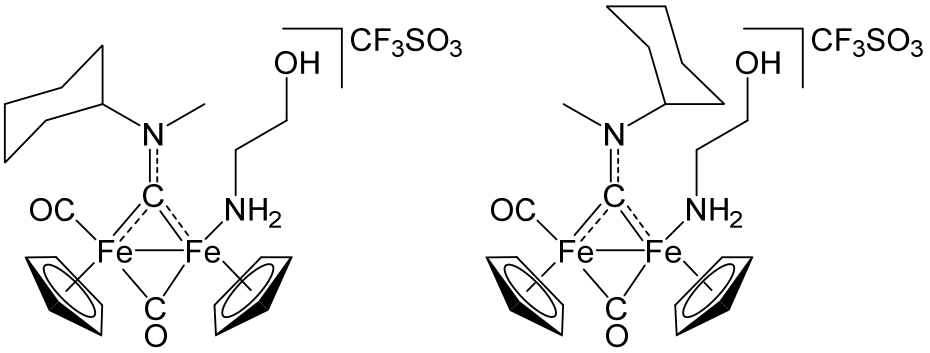


Figure 2. Structure of **2b** (**left**: α isomer; **right**: β isomer).

From **1b** (130 mg, 0.217 mmol) and $NH_2CH_2CH_2OH$ (65 μL, 1.1 mmol). Brown solid, yield 129 mg (95%). Anal. calcd. for $C_{23}H_{31}F_3Fe_2N_2O_6S$: C, 43.69; H, 4.94; N, 4.43; S, 5.07. Found: C, 43.46; H, 5.03; N, 4.36; S, 5.14. IR (CH_2Cl_2): $\tilde{\upsilon}/cm^{-1}$ = 1970vs (CO), 1799s (μ-CO), 1532w (μ-CN). ^{1}H NMR ($CDCl_3$): δ/ppm = *5.66*, 4.80* (m, 1 H, CH^{Cy}); *4.85*, 4.83, *4.80*, 4.79 (s, 10 H, Cp); 4.50, *4.09* (s, 3 H, NMe); 3.60, 3.39–3.32 (m, 2 H, OCH_2); 3.20–3.13, 2.84 (m, 2 H, NCH_2); 2.43–2.35 (m, 1 H, NH); 2.31–2.28, 2.20–2.11, 1.57–1.45, 1.41, 1.29 (m, 10 H, CH_2^{Cy}); *−1.92*, −2.14 (m, 1 H, NH). *Overlapped with Cp resonance. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ/ppm = *331.1*, 330.5 (μ-CN); *268.5*, 268.1 (μ-CO); 212.6, *212.4* (CO); 120.5 (q, $^1J_{CF}$ = 320 Hz, CF_3); *88.1*, 87.9, 86.7, *86.6* (Cp); 78.4, *75.3* (CH^{Cy}); *61.0*, 60.8 (OCH_2); 50.7, *49.7* (NCH_2); *46.4*, 45.1 (NMe); 33.0, 32.6, 31.8, 31.6, 31.1, 31, 30.8, 26.1, 26, 25.5, 25.3, 25.1, 24.5 (CH_2^{Cy}). α/β ratio = 2.

$[Fe_2Cp_2(\kappa N\text{-}NH_2CH_2CH_2OMe)(CO)(\mu\text{-}CO)\{\mu\text{-}CN(Me)(Cy)\}]CF_3SO_3$, **2c** (Figure 3).

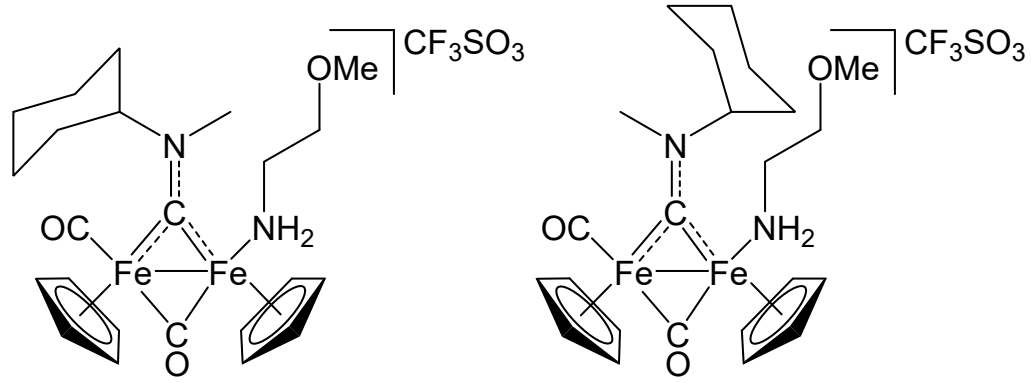


Figure 3. Structure of **2c** (**left**: α isomer; **right**: β isomer).

From **1b** (130 mg, 0.217 mmol) and $NH_2CH_2CH_2OCH_3$ (94 μL, 1.1 mmol). Brown solid, yield 113 mg (81%). Anal. calcd. for $C_{24}H_{33}F_3Fe_2N_2O_6S$: C, 44.60; H, 5.15; N, 4.33; S, 4.96. Found: C, 44.32; H, 5.24; N, 4.42; S, 5.03. IR (CH_2Cl_2): $\tilde{\upsilon}/cm^{-1}$ = 1971vs (CO), 1799s (μ-CO), 1532w (μ-CN). ^{1}H NMR ($CDCl_3$): δ/ppm = *5.66*, 4.80* (m, 1 H, CH^{Cy}); 4.84–4.82 (s, 10 H, Cp); 4.48, *4.08* (s, 3 H, NMe); 3.02, *3.00* (s, 3 H, OMe); 2.37–2.30, 2.18–2.11, 2.07–1.99, 1.93–1.87, 1.85–1.81, 1.78–1.73, 1.55–1.49, 1.44–1.33 (m, 15 H, CH_2^{Cy} + NCH_2 + OCH_2 + NH); *−2.13*, −2.22 (m, 1 H, NH). *Overlapped with Cp resonance. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ/ppm = *330.8*, 330.4 (μ-CN); *268.7*, 268.5 (μ-CO); 212.2, *212.1* (CO); 120.6 (q, $^1J_{CF}$ = 320 Hz, CF_3); *88.2*, 87.9, 87.7, *86.6* (Cp); 78.2, *75.1* (CH^{Cy}); *70.8*, 70.7 (OCH_2); *58.6*, 58.3 (OMe); 47.9, *47.5* (NCH_2); *46.2*, 45.0 (NMe); 32.9, 32.7, 31.5, 31.2, 26.1, 26, 25.4, 25.3, 25.1, 24.2 (CH_2^{Cy}). α/β ratio = 2.

3.3. Synthesis of Diiron Aminocarbyne Complex with Oxazolidinone–Amine

3.3.1. Synthesis and Characterization of 3-(2-Aminoethyl)-5-phenyloxazolidin-2-one (**NH_2^{OX}**, Figure 4) [61]

The title compound was prepared using a slight modification of the literature procedure, which avoids chromatographic purification, affording a purer product. A round bottom flask (volume = 100 mL) containing 30 mL of H_2O was evacuated and then filled with CO_2. Ethylenediamine (2.05 mL, 30.7 mmol) was added. The mixture was stirred until gas absorption ceased, and then (2-bromo-1-phenylethyl)dimethylsulfonium bromide (1.000 g, 3.066 mmol) was added. A balloon (volume ≈ 1 L) filled with CO_2 was connected to the flask, and the mixture was stirred for 48 h under a constant pressure of CO_2. Formation of an oily phase occurred; this oil was extracted with dichloromethane (3 × 20 mL) and the organic phase was collected. The solvent was eliminated under reduced pressure, affording a colorless/pale-yellow oil. Yield: 226 mg (36%). ^{1}H NMR ($CDCl_3$): δ = 7.41–7.29 (m, 5 H, C_6H_4); 5.40 (t, $^3J_{HH}$ = 8.2 Hz, 1 H, CH); 3.89, 3.33 (t, $^3J_{HH}$ = 8.3 Hz, 2 H, CH_2); 3.33, 3.17 (m, 2 H, $NC\underline{H_2}CH_2$); 2.78 (t, $^3J_{HH}$ = 6.2 Hz, 2 H, $NCH_2C\underline{H_2}$); 2.28 (s, 2 H, NH_2).

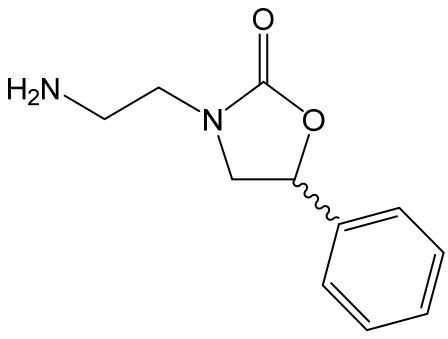


Figure 4. Structure of **NH_2^{OX}**.

3.3.2. Synthesis and Characterization of
$[Fe_2Cp_2\{\kappa N\text{-}NH_2{}^{OX}\}(CO)(\mu\text{-}CO)\{\mu\text{-}CN(Me)_2\}]CF_3SO_3$, **3** (Figure 5)

A solution of **1a** (135 mg, 0.255 mmol) in THF (8 mL) was treated with $\mathbf{NH_2{}^{OX}}$ (91 mg, 0.44 mmol) and then $Me_3NO{\cdot}2H_2O$ (56 mg, 0.51 mmol). The resulting mixture was left stirring for 4 h, allowing for the outflow of produced gas. Volatiles were then removed under vacuum, and the brown residue was washed with diethyl ether (20 mL) and then with ethyl acetate/hexane 2:1 (*v*/*v*). The solid obtained was dissolved in a small volume of CH_2Cl_2 and this solution was filtered through a celite pad. The solvent was removed under vacuum, affording a brown solid. Yield 166 mg (96%). IR (CH_2Cl_2): $\tilde{\upsilon}/cm^{-1}$ = 1973vs (CO), 1797s (μ-CO), 1751vs (C=O), 1575m (μ-CN). ^{1}H-NMR (acetone-d_6): δ/ppm = 7.49–7.33 (m, 5 H, Ph); 5.47, *5.35* (s, 1 H, CH); 5.14, *5.12*, 4.99, *4.98* (s, 10 H, Cp); 4.69, *4.68*, 4.33, *4.32* (s, 6 H, NMe_2); 3.91, *3.85*, 3.31, *3.29* (m, 2 H, CH_2); 3.17–2.90 (m, 2 H, $NCH_2\underline{CH_2}$); 2.84 (m, 1 H, NH)*; 2.35, *2.17* (m, 2 H, $N\underline{CH_2}CH_2$); −0.94 (m, 1 H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ/ppm = 331.5, 331.4 (μ-CN); 270.8, *270.5* (μ-CO); 214.5, *214.3* (CO); 159.0, 159.0 (C=O); 139.9, *139.7* (ipso-Ph); 129.6, *129.6*, 129.5, *129.5*, 126.9, *126.8* (Ph); 122.2 (q, $^1J_{CF}$ = 323 Hz, CF_3); 89.5, *89.4*, 87.2, *87.2* (Cp); 75.6, *75.6* (CH); 54.5, *54.5*, 52.8, *52.8* (NMe_2); 53.1, *53.0* (CH_2); 47.2, 46.8 ($N\underline{C}H_2CH_2$); 46.2, 46.1 ($NCH_2\underline{C}H_2$). Diastereoisomer ratio = 1. *Overlapped with H_2O signal.

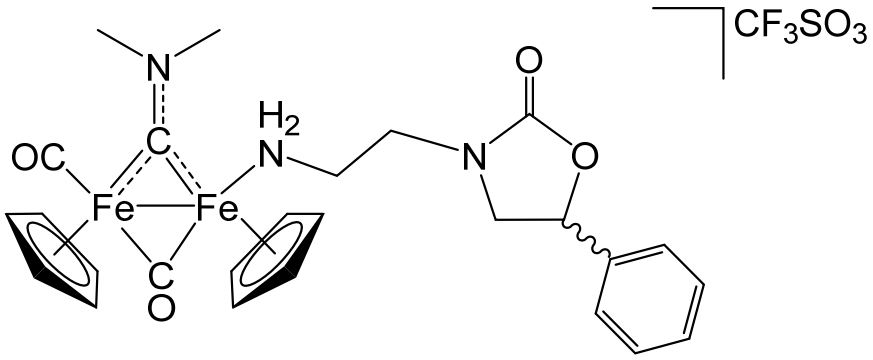


Figure 5. Structure of **3**.

3.4. Synthesis of Diiron Aminocarbyne Complexes with Diethylamine

$[Fe_2Cp_2(NHEt_2)(CO)(\mu\text{-}CO)\{\mu\text{-}CN(Me)_2\}]CF_3SO_3$, **4a** (Figure 6).

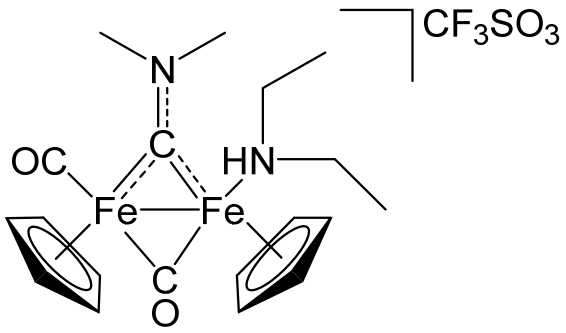


Figure 6. Structure of **4a**.

The title compound was prepared using a procedure analogous to that described for the synthesis of **3**, from **1a** (38 mg, 0.071 mmol), TMNO (12 mg, 0.11 mmol) and $NHEt_2$ (0.040 mL, 0.36 mmol). Dark-brown solid, yield 28 mg. **4a** was obtained in admixture with other by-products and could not be purified due to its instability. IR (CH_2Cl_2): $\tilde{\upsilon}/cm^{-1}$ = 1978vs (CO), 1800s (μ-CO), 1577w (μ-CN). ^{1}H NMR (acetone-d_6): δ/ppm = 5.12,

4.96 (s, 10 H, Cp); 4.69, 4.34 (s, 6 H, NMe_2); 1.43, 1.29 (m, 4 H, NCH_2); 0.87, 0.70 (t, $^3J_{HH}$ = 6.9 Hz, 6 H, CH_3); −1.20 (m, 1 H, NH).

$[Fe_2Cp_2(NHEt_2)(CO)(\mu\text{-}CO)\{\mu\text{-}CN(Me)_2\}]CF_3SO_3$, **4b** (Figure 7).

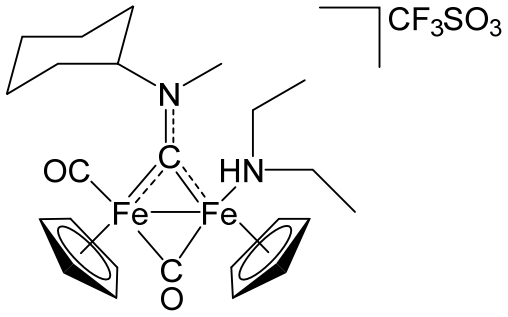


Figure 7. Structure of **4b**.

The title compound was prepared using a procedure analogous to that described for the synthesis of **3**, from **1b** (120 mg, 0.200 mmol), TMNO (44 mg, 0.400 mmol) and $NHEt_2$ (0.12 mL, 1.0 mmol). Dark-brown solid, yield 70 mg. **4b** was obtained in admixture with other by-products and could not be purified due to its instability. IR (THF): $\tilde{\upsilon}/cm^{-1}$ = 1963vs (CO), 1799s (μ-CO), 1534w (μ-CN). ^1H NMR ($CDCl_3$): δ/ppm = 4.91, 4.86 (s, 10 H, Cp); 4.62 (s, 3 H, NMe); 1.43–1.28 (m, 4H, NCH_2); 0.79, 0.56 (t, $^3J_{HH}$ = 6.9 Hz, 6 H, CH_3); -2.97 (t, 1 H, NH).

3.5. Behavior of the Diiron Complexes in Aqueous Media

3.5.1. Solubility in D_2O

A suspension of the selected diiron complex (3–5 mg) in a D_2O solution (0.7 mL) containing dimethylsulfone ($DMSO_2$) as internal standard ($4.64 \cdot 10^{-3}$ M) was vigorously stirred at room temperature for 1 h. The saturated solution was filtered over celite, transferred into an NMR tube and analyzed by ^1H NMR (delay time = 4s; number of scans = 25). The concentration of the saturated solution (=solubility) was calculated by the relative integral with respect to $DMSO_2$ (δ/ppm = 3.16, s).

3.5.2. Stability in Aqueous Solutions

The selected diiron complex (ca. 5 mg) was dissolved in a CD_3OD/D_2O solution (ca. 0.8 mL) containing $DMSO_2$ ($4.64 \cdot 10^{-3}$ M). The mixture was stirred for 30 min, filtered over celite and transferred into an NMR tube. The solution ($C_{Fe} = 6 \cdot 10^{-3}$ M) was analyzed by ^1H NMR (delay time = 4 s; number of scans = 25, see Table S1) and then heated at 37 °C for 72 h. After cooling to room temperature, the final solution was separated from a brown solid using filtration over celite, and the ^1H NMR spectrum was recorded. The residual amount of the starting material in the solution (% with respect to the initial spectrum) was calculated by the relative integral with respect to $DMSO_2$ as an internal standard. The same procedure was adopted for studying the stability in cell culture medium by dissolving the selected diiron complex (3–5 mg) in the CD_3OD/DMEM-d solution containing $DMSO_2$ ($4.64 \cdot 10^{-3}$ M) as an internal standard [74]. Deuterated cell culture medium (DMEM-d) was prepared by dissolving powdered DMEM (D2902, Merck) in D_2O according to the manufacturer's instructions.

4. Conclusions

Diiron aminocarbyne complexes based on the $[Fe_2Cp_2(CO)_x]$ scaffold represent a versatile class of organometallics, to which structural diversity may be supplied using different strategies. Here, we describe the synthesis of new derivatives containing terminal amine ligands, showing that the synthesis reaction, via a dissociative substitution mechanism, is straightforward for primary alkyl-amines and tolerates heteroatom functions on the amine substituent. Remarkably, through this approach, we report a rare example of conjugation

of a biologically relevant cyclic carbamate with an organo-diiron core. The new cationic complexes display sufficient water solubility, and those complexes with small alkyl substituents manifest a fair inertness in aqueous media under pseudo-physiological conditions, thus justifying the reported synthetic strategy for the future development of water-tolerant homogeneous catalysts and drug candidates. In contrast, steric factors appear to be crucial in that bulkier amine substituents may lead to labile coordination in aqueous media, while secondary amines do not form stable adducts.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/inorganics11030091/s1. NMR spectra of diiron complexes. Figure S1: ^{1}H NMR spectrum (401 MHz, acetone-d6) of **2a** (integration refers to the major isomer); Figure S2: ^{13}C{^{1}H} NMR spectrum (101 MHz, acetone-d6) of **2a**; Figure S3: ^{1}H NMR spectrum (401 MHz, CDCl3) of **2b** (integration refers to the major isomer); Figure S4: ^{13}C{^{1}H} NMR spectrum (101 MHz, CDCl3) of **2b**; Figure S5: ^{1}H NMR spectrum (401 MHz, CDCl3) of **2c** (integration refers to the major isomer); Figure S6: ^{13}C{^{1}H} NMR spectrum (101 MHz, CDCl3) of **2c**; Figure S7: ^{1}H NMR spectrum (401 MHz, CDCl3) of $\mathbf{NH_2^{OX}}$. Figure S8. ^{1}H NMR spectrum (401 MHz, acetone-d6) of **3**; Figure S9. ^{13}C{^{1}H} NMR spectrum (101 MHz, acetone-d6) of **3**; Figure S10. ^{1}H NMR spectrum (401 MHz, acetone-d6) of **4a** (integration refers to the major isomer); Figure S11. ^{1}H NMR spectrum (401 MHz, CDCl3) of **4b** (integration refers to the major isomer).

Author Contributions: C.S. and S.S. performed the synthesis and the spectroscopic characterization of the complexes; G.B. performed the synthesis of the organic reagent; L.B. gave assistance with the characterization of the complexes; L.B., G.P. and F.M. procured funding; F.M. supervised the work and wrote the manuscript with the assistance of the other authors. All authors have read and agreed to the published version of the manuscript.

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References

1. Wenger, O.S. Is Iron the New Ruthenium? *Chem. Eur. J.* **2019**, *25*, 6043–6052. [CrossRef] [PubMed]
2. Bresciani, G.; Zacchini, S.; Marchetti, F.; Pampaloni, G. Non-precious metal carbamates as catalysts for the aziridine/CO_2 coupling reaction under mild conditions. *Dalton Trans.* **2021**, *50*, 5351–5359. [CrossRef]
3. Bisz, E.; Szostak, M. Iron-Catalyzed C–O Bond Activation: Opportunity for Sustainable Catalysis. *ChemSusChem* **2017**, *10*, 3964–3981. [CrossRef] [PubMed]
4. Enthaler, S.; Junge, K.; Beller, M. Sustainable Metal Catalysis with Iron: From Rust to a Rising Star? *Angew. Chem. Int. Ed.* **2008**, *47*, 3317–3321. [CrossRef] [PubMed]
5. Coufourier, S.; Gaignard Gaillard, Q.; Lohier, J.-F.; Poater, A.; Gaillard, S.; Renaud, J.-L. Hydrogenation of CO_2, Hydrogenocarbonate, and Carbonate to Formate in Water using Phosphine Free Bifunctional Iron Complexes. *ACS Catal.* **2020**, *10*, 2108–2116. [CrossRef]
6. van Beek, C.B.; van Leest, N.P.; Lutz, M.; de Vos, S.D.; Klein Gebbink, R.J.M.; de Bruin, B.; Broere, D.L.J. Combining metal-metal cooperativity, metal-ligand cooperativity and chemical non-innocence in diiron carbonyl complexes. *Chem. Sci.* **2022**, *13*, 2094–2104. [CrossRef]
7. Govindarajan, R.; Deolka, S.; Khusnutdinova, J.R. Heterometallic bond activation enabled by unsymmetrical ligand scaffolds: Bridging the opposites. *Chem. Sci.* **2022**, *13*, 14008–14031. [CrossRef]
8. Ritleng, V.; Chetcuti, M.J. Hydrocarbyl Ligand Transformations on Heterobimetallic Complexes. *Chem. Rev.* **2007**, *107*, 797−858. [CrossRef]
9. Desnoyer, A.N.; Nicolay, A.; Rios, P.; Ziegler, M.S.; Don Tilley, T. Bimetallics in a Nutshell: Complexes Supported by Chelating Naphthyridine-Based Ligands. *Acc. Chem. Res.* **2020**, *53*, 1944–1956. [CrossRef]
10. Tsurugi, H.; Laskar, P.; Yamamoto, K.; Mashima, K. Bonding and structural features of metal-metal bonded homo—And hetero-dinuclear complexes supported by unsaturated hydrocarbon ligands. *J. Organomet. Chem.* **2018**, *869*, 251–263. [CrossRef]
11. Busetto, L.; Maitlis, P.M.; Zanotti, V. Bridging vinylalkylidene transition metal complexes. *Coord. Chem. Rev.* **2010**, *254*, 470–486. [CrossRef]

12. Swanson, K.D.; Ortillo, D.O.; Broderick, J.B.; Peters, J.W. [FeFe]-Hydrogenase. In *Encyclopedia of Inorganic and Bioinorganic Chemistry*, 2nd ed.; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2011.
13. Lubitz, W.; Ogata, H.; Rüdiger, O.; Reijerse, E. Hydrogenases. *Chem. Rev.* **2014**, *114*, 4081–4148. [CrossRef] [PubMed]
14. Kleinhaus, J.T.; Wittkamp, F.; Yadav, S.; Siegmund, D.; Apfel, U.-P. [FeFe]-Hydrogenases: Maturation and reactivity of enzymatic systems and overview of biomimetic models. *Chem. Soc. Rev.* **2021**, *50*, 1668–1784. [CrossRef] [PubMed]
15. Gee, L.B.; Pelmenschikov, V.; Wang, H.; Mishra, N.; Liu, Y.-C.; Yoda, Y.; Tamasaku, K.; Chiang, M.-H.; Cramer, S.P. Vibrational characterization of a diiron bridging hydride complex—A model for hydrogen catalysis. *Chem. Sci.* **2020**, *11*, 5487–5493. [CrossRef] [PubMed]
16. Gao, S.; Liu, Y.; Shao, Y.; Jiang, D.; Duan, Q. Iron carbonyl compounds with aromatic dithiolate bridges as organometallic mimics of [FeFe] hydrogenases. *Coord. Chem. Rev.* **2020**, *402*, 213081. [CrossRef]
17. Li, Y.; Rauchfuss, T.B. Synthesis of Diiron(I) Dithiolato Carbonyl Complexes. *Chem. Rev.* **2016**, *116*, 7043–7077. [CrossRef]
18. Mazzoni, R.; Salmi, M.; Zanotti, V. C-C Bond Formation in Diiron Complexes. *Chem. Eur. J.* **2012**, *18*, 10174–10194. [CrossRef]
19. Busetto, L.; Zanotti, V. Carbene ligands in diiron complexes. *J. Organomet. Chem.* **2005**, *690*, 5430–5440. [CrossRef]
20. Chen, J.; Wang, R. Remarkable reactions of cationic carbyne complexes of manganese, rhenium, and diiron with carbonylmetal anions. *Coord. Chem. Rev.* **2002**, *231*, 109–149. [CrossRef]
21. Casey, C.P.; Austin, E.A. Photochemical Reactions of Diiron p-Alkenylidene Complexes with Hydrogen, Trialkylsilanes, and Diazo Compounds: Cleavage to Alkenes, Vinylsilanes, and Allenes. *J. Am. Chem. Soc.* **1988**, *110*, 7106–7113. [CrossRef]
22. Murshid, N.; El-Temtamy, A.; Wang, X. Synthesis and solution behaviour of metal-carbonyl amphiphiles with an Fp ($CpFe(CO)_2$) junction. *J. Organomet. Chem.* **2017**, *851*, 40–45. [CrossRef]
23. García, M.E.; García-Vivó, D.; Ramos, A.; Ruiz, M.A. Phosphinidene-bridged binuclear complexes. *Coord. Chem. Rev.* **2017**, *330*, 1–36. [CrossRef]
24. Biancalana, L.; Marchetti, F. Aminocarbyne ligands in organometallic chemistry. *Coord. Chem. Rev.* **2021**, *449*, 214203. [CrossRef]
25. Marchetti, F. Constructing Organometallic Architectures from Aminoalkylidyne Diiron Complexes. *Eur. J. Inorg. Chem.* **2018**, *2018*, 3987–4003. [CrossRef]
26. Agonigi, G.; Bortoluzzi, M.; Marchetti, F.; Pampaloni, G.; Zacchini, S.; Zanotti, V. Regioselective Nucleophilic Additions to Diiron Carbonyl Complexes Containing a Bridging Aminocarbyne Ligand: A Synthetic, Crystallographic and DFT Study. *Eur. J. Inorg. Chem.* **2018**, *2018*, 960–971. [CrossRef]
27. Biancalana, L.; De Franco, M.; Ciancaleoni, G.; Zacchini, S.; Pampaloni, G.; Gandin, V.; Marchetti, F. Easily Available and Amphiphilic Diiron Cyclopentadienyl Complexes Exhibit In Vitro Anticancer Activity in 2D and 3D Human Cancer Cells via Redox Modulation Triggered by CO Release. *Chem. Eur. J.* **2021**, *27*, 10169–10185. [CrossRef] [PubMed]
28. Rocco, D.; Batchelor, L.K.; Agonigi, G.; Braccini, S.; Chiellini, F.; Schoch, S.; Biver, T.; Funaioli, T.; Zacchini, S.; Biancalana, L.; et al. Anticancer Potential of Diiron Vinyliminium Complexes. *Chem. Eur. J.* **2019**, *25*, 14801–14816. [CrossRef]
29. Biancalana, L.; Kubeil, M.; Schoch, S.; Zacchini, S.; Marchetti, F. Switching on Cytotoxicity of Water-Soluble Diiron Organometallics by UV Irradiation. *Inorg. Chem.* **2022**, *61*, 7897–7909. [CrossRef]
30. Arrigoni, F.; Bertini, L.; De Gioia, L.; Cingolani, A.; Mazzoni, R.; Zanotti, V.; Zampella, G. Mechanistic Insight into Electrocatalytic H_2 Production by $[Fe_2(CN)\{\mu\text{-}CN(Me)_2\}(\mu\text{-}CO)(CO)(Cp)_2]$: Effects of Dithiolate Replacement in [FeFe] Hydrogenase Models. *Inorg. Chem.* **2017**, *56*, 13852–13864. [CrossRef]
31. Mazzoni, R.; Gabiccini, A.; Cesari, C.; Zanotti, V.; Gualandi, I.; Tonelli, D. Diiron Complexes Bearing Bridging Hydrocarbyl Ligands as Electrocatalysts for Proton Reduction. *Organometallics* **2015**, *34*, 3228−3235. [CrossRef]
32. Bresciani, G.; Biancalana, L.; Zacchini, S.; Pampaloni, G.; Ciancaleoni, G.; Marchetti, F. Diiron Bis-Cyclopentadienyl Complexes as Transfer Hydrogenation Catalysts: The Key Role of the Bridging Aminocarbyne Ligand. *Appl. Organomet. Chem.* **2023**, *37*, e6990. [CrossRef]
33. Bresciani, G.; Schoch, S.; Biancalana, L.; Zacchini, S.; Bortoluzzi, M.; Pampaloni, G.; Marchetti, F. Cyanide-alkene competition in a diiron complex and isolation of a multisite (cyano)alkylidene—Alkene species. *Dalton Trans.* **2022**, *51*, 1936–1945. [CrossRef] [PubMed]
34. Agonigi, G.; Biancalana, L.; Lupo, M.G.; Montopoli, M.; Ferri, N.; Zacchini, S.; Binacchi, F.; Biver, T.; Campanella, B.; Pampaloni, G.; et al. Exploring the Anticancer Potential of Diiron Bis-cyclopentadienyl Complexes with Bridging Hydrocarbyl Ligands: Behavior in Aqueous Media and In Vitro Cytotoxicity. *Organometallics* **2020**, *39*, 645–657. [CrossRef]
35. Boss, K.; Dowling, C.; Manning, A.R. Preparation, spectra and structure of $[Fe_2(\eta^5\text{-}C_5H_5)_2(L)(CN)(\mu\text{-}CO)\{\mu\text{-}CN(R')R\}]$, $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)(CN)\{\mu\text{-}CNMe_2\}_2]^+$ and $[Fe_2(\eta^5\text{-}C_5H_5)_2(CN)_2\{\mu\text{-}CNMe_2\}_2]$ zwitterions (L = CO or organoisocyanide) and their reactions with alkyl and protic electrophiles. *J. Organomet. Chem.* **1996**, *509*, 197–207. [CrossRef]
36. Marchetti, F.; Zacchini, S.; Zanotti, V. Coupling of Isocyanide and μ-Aminocarbyne Ligands in Diiron Complexes Promoted by Hydride Addition. *Organometallics* **2014**, *33*, 3990–3997. [CrossRef]
37. Busetto, L.; Marchetti, F.; Zacchini, S.; Zanotti, V. Diiron and diruthenium aminocarbyne complexes containing pseudohalides: Stereochemistry and reactivity. *Inorg. Chim. Acta* **2005**, *358*, 1204–1216. [CrossRef]
38. Howell, J.A.S.; Rowan, A.J. Synthesis and fluxional character of complexes of the type $[M_2(cp)_2(CO)_3(CNR)]$(M = Fe or Ru, Cp =η-C_5H_5). *J. Chem. Soc. Dalton Trans.* **1980**, 503–510. [CrossRef]
39. Adams, R.D.; Cotton, F.A. On the Pathway of Bridge-Terminal Ligand Exchange in Some Binuclear Metal Carbonyls. *J. Am. Chem. Soc.* **1973**, *95*, 6589–6594. [CrossRef]

40. Biancalana, L.; Ciancaleoni, G.; Zacchini, S.; Pampaloni, G.; Marchetti, F. Carbonyl-isocyanide mono-substitution in $[Fe_2Cp_2(CO)_4]$: A re-visitation. *Inorg. Chim. Acta* **2020**, *517*, 120181. [CrossRef]
41. Luh, T.-Y. Trimethylamine N-Oxide-A Versatile Reagent for Organometallic Chemistry. *Coord. Chem. Rev.* **1984**, *60*, 255–276. [CrossRef]
42. Albano, V.G.; Busetto, L.; Monari, M.; Zanotti, V. Reactions of acetonitrile di-iron μ-aminocarbyne complexes; synthesis and structure of $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}H)(CO)_2(Cp)_2]$. *J. Organomet. Chem.* **2000**, *606*, 163–168. [CrossRef]
43. Bresciani, G.; Boni, S.; Zacchini, S.; Pampaloni, G.; Bortoluzzi, M.; Marchetti, F. Alkyne–alkenyl coupling at a diruthenium complex. *Dalton Trans.* **2022**, *51*, 15703–15715. [CrossRef]
44. Bresciani, G.; Zacchini, S.; Pampaloni, G.; Marchetti, F. Carbon-Carbon Bond Coupling of Vinyl Molecules with an Allenyl Ligand at a Diruthenium Complex. *Organometallics* **2022**, *41*, 1006–1014. [CrossRef]
45. Bresciani, G.; Zacchini, S.; Pampaloni, G.; Bortoluzzi, M.; Marchetti, F. η^6-Coordinated ruthenabenzenes from three-component assembly on a diruthenium μ-allenyl scaffold. *Dalton Trans.* **2022**, *51*, 8390–8400. [CrossRef] [PubMed]
46. Bresciani, G.; Biancalana, L.; Pampaloni, G.; Zacchini, S.; Ciancaleoni, G.; Marchetti, F. A Comprehensive Analysis of the Metal–Nitrile Bonding in an Organo-Diiron System. *Molecules* **2021**, *26*, 7088. [CrossRef] [PubMed]
47. Kufelnicki, A.; Tomyn, S.V.; Nedelkov, R.V.; Haukka, M.; Jaciubek-Rosinska, J.; Pajak, M.; Jaszczak, J.; Swiatek, M.; Fritsky, I.O. Synthesis of cobalt(III) complexes with novel open chain oxime ligands and metal–ligand coordination in aqueous solution. *Inorg. Chim. Acta* **2010**, *363*, 2996–3003. [CrossRef]
48. Dahlenburg, L.; Treffert, H.; Farr, C.; Heinemann, F.W.; Zahl, A. Rhodium(I) Complexes Containing β-Amino Alcohol and 1,2-Diamine Ligands: Syntheses, Structures, and Catalytic Applications. *Eur. J. Inorg. Chem.* **2007**, 1738–1751. [CrossRef]
49. Bortoluzzi, M.; Bresciani, G.; Marchetti, F.; Pampaloni, G.; Zacchini, S. $MoCl_5$ as an effective chlorinating agent towards α-amino acids: Synthesis of α-ammonium-acylchloride salts and α-amino-acylchloride complexes. *Dalton Trans.* **2015**, *44*, 10030–10037. [CrossRef] [PubMed]
50. Niemi, T.; Repo, T. Antibiotics from Carbon Dioxide: Sustainable Pathways to Pharmaceutically Relevant Cyclic Carbamates. *Eur. J. Org. Chem.* **2019**, 1180–1188. [CrossRef]
51. Jadhavar, P.S.; Vaja, M.D.; Dhameliya, T.M.; Chakraborti, A.K. Oxazolidinones as Anti-tubercular Agents: Discovery, Development and Future Perspectives. *Curr. Med. Chem.* **2015**, *22*, 4379–4397. [CrossRef]
52. Zhao, Q.; Xin, L.; Liu, Y.; Liang, C.; Li, J.; Jian, Y.; Li, H.; Shi, Z.; Liu, H.; Cao, W. Current Landscape and Future Perspective of Oxazolidinone Scaffolds Containing Antibacterial Drugs. *J. Med. Chem.* **2021**, *64*, 10557–10580. [CrossRef]
53. Xie, Y.; Lu, C.; Zhao, B.; Wang, Q.; Yao, Y. Cycloaddition of Aziridine with CO_2/CS_2 Catalyzed by Amidato Divalent Lanthanide Complexes. *J. Org. Chem.* **2019**, *84*, 1951−1958. [CrossRef] [PubMed]
54. Sengoden, M.; North, A.C. Whitwood. *ChemSusChem* **2019**, *12*, 3296–3303. [CrossRef] [PubMed]
55. Bresciani, G.; Bortoluzzi, M.; Pampaloni, G.; Marchetti, F. Diethylammonium iodide as catalyst for the metal-free synthesis of 5-aryl-2-oxazolidinones from aziridines and carbon dioxide. *Org. Biomol. Chem.* **2021**, *19*, 4152–4161. [CrossRef] [PubMed]
56. Sonzini, P.; Damiano, C.; Intrieri, D.; Manca, G.; Gallo, E. A Metal-Free Synthesis of N-Aryl Oxazolidin-2-Ones by the One-Pot Reaction of Carbon Dioxide with N-Aryl Aziridines. *Adv. Synth. Catal.* **2020**, *362*, 2961–2969. [CrossRef]
57. Bresciani, G.; Bortoluzzi, M.; Ghelarducci, C.; Marchetti, F.; Pampaloni, G. Synthesis of a-alkylidene cyclic carbonates via CO_2 fixation under ambient conditions promoted by an easily available silver carbamate. *N. J. Chem.* **2021**, *45*, 4340–4346. [CrossRef]
58. Bresciani, G.; Busto, N.; Ceccherini, V.; Bortoluzzi, M.; Pampaloni, G.; Garcia, B.; Marchetti, F. Screening the biological properties of transition metal carbamates reveals gold(I) and silver(I) complexes as potent cytotoxic and antimicrobial agents. *J. Inorg. Biochem.* **2022**, *227*, 111667. [CrossRef]
59. Biancalana, L.; Bresciani, G.; Chiappe, C.; Marchetti, F.; Pampaloni, G.; Pomelli, C.S. Modifying bis(triflimide) ionic liquids by dissolving early transition metal carbamates. *Phys. Chem. Chem. Phys.* **2018**, *20*, 5057—5066. [CrossRef]
60. Bortoluzzi, M.; Bresciani, G.; Marchetti, F.; Pampaloni, G.; Zacchini, S. Synthesis and structural characterization of mixed halide–N,N-diethylcarbamates of group 4 metals, including a case of unusual tetrahydrofuran activation. *New J. Chem.* **2017**, *41*, 1781–1789. [CrossRef]
61. Bresciani, G.; Antico, E.; Ciancaleoni, G.; Zacchini, S.; Pampaloni, G.; Marchetti, F. Bypassing the Inertness of Aziridine/CO_2 Systems to Access 5-Aryl-2-Oxazolidinones: Catalyst-Free Synthesis Under Ambient Conditions. *ChemSusChem* **2020**, *13*, 5586–5594. [CrossRef]
62. Bresciani, G.; Zacchini, S.; Famlonga, L.; Pampaloni, G.; Marchetti, F. Trapping carbamates of α-Amino acids: One-Pot and catalyst-free synthesis of 5-Aryl-2-Oxazolidinonyl derivatives. *J. CO2 Util.* **2021**, *47*, 101495. [CrossRef]
63. Busetto, L.; Marchetti, F.; Zacchini, S.; Zanotti, V.; Zoli, E. Diiron-aminocarbyne complexes with amine or imine ligands: C–N coupling between imine and aminocarbyne ligands promoted by tolylacetylide addition to $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)(NH{=}CPh_2)(Cp)_2][SO_3CF_3]$. *J. Organomet. Chem.* **2005**, *690*, 348–357. [CrossRef]
64. Labinger, J.A. Does cyclopentadienyl iron dicarbonyl dimer have a metal–metal bond? Who's asking? *Inorg. Chim. Acta* **2015**, *424*, 14–19. [CrossRef]
65. Frenking, G.; Frohlich, N. The Nature of the Bonding in Transition-Metal Compounds. *Chem. Rev.* **2000**, *100*, 717–774. [CrossRef] [PubMed]
66. Schoch, S.; Iacopini, D.; Dalla Pozza, M.; Di Pietro, S.; Degano, I.; Gasser, G.; Di Bussolo, V.; Marchetti, F. Tethering Carbohydrates to the Vinyliminium Ligand of Antiproliferative Organometallic Diiron Complexes. *Organometallics* **2022**, *41*, 514–526. [CrossRef]

67. Marchetti, F. Alkylidyne and Alkylidene Complexes of Iron. In *Comprehensive Organometallic Chemistry IV*; Parkin, G., Meyer, K., O'Hare, D., Eds.; Elsevier: Kidlington, UK, 2022; Volume 7, pp. 210–257. [CrossRef]
68. Zhou, X.; Barton, B.E.; Chambers, G.M.; Rauchfuss, T.B. Preparation and Protonation of $Fe_2(pdt)(CNR)_6$, Electron-Rich Analogues of $Fe_2(pdt)(CO)_6$. *Inorg. Chem.* **2016**, *55*, 3401−3412. [CrossRef]
69. Dasari, S.; Tchounwou, P.B. Cisplatin in cancer therapy: Molecular mechanisms of action. *Eur. J. Pharmacol.* **2014**, *740*, 364–378. [CrossRef]
70. Matlock, J.V.; Fritz, S.P.; Harrison, S.A.; Coe, D.M.; McGarrigle, E.M.; Aggarwal, V.K. Synthesis of α-substituted vinylsulfonium salts and their application as annulation reagents in the formation of epoxide-and cyclopropane-fused heterocycles. *J. Org. Chem.* **2014**, *79*, 10226–10239. [CrossRef]
71. Menges, F. Spectragryph-Optical Spectroscopy Software, Version 1.2.5, 2016–2017. Available online: http://www.effemm2.de/spectragryph (accessed on 29 January 2023).
72. Fulmer, G.R.; Miller, A.J.M.; Sherden, N.H.; Gottlieb, H.E.; Nudelman, A.; Stoltz, B.M.; Bercaw, J.E.; Goldberg, K.I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29*, 2176–2179. [CrossRef]
73. Willker, W.; Leibfritz, D.; Kerssebaum, R.; Bermel, W. Gradient selection in inverse heteronuclear correlation spectroscopy. *Magn. Reson. Chem.* **1993**, *31*, 287–292. [CrossRef]
74. Rundlöf, T.; Mathiasson, M.; Bekiroglu, S.; Hakkarainen, B.; Bowden, T.; Arvidsson, T. Survey and qualification of internal standards for quantification by ^{1}H NMR spectroscopy. *J. Pharm. Biomed. Anal.* **2010**, *52*, 645–651. [CrossRef] [PubMed]