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RESEARCH ARTICLE

Design of Knölker-type Catalysts for the Anomeric Oxidation of Unprotected Mono- and Disaccharides

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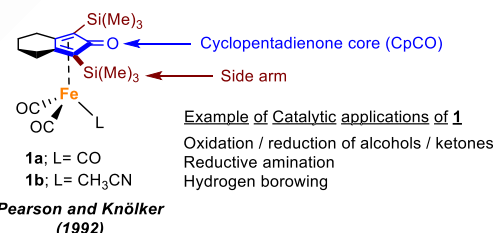
Abstract: Knölker complexes have been recently used to perform the catalytic C1-oxidation of unprotected sugars into sugar lactones. This oxidation method remained limited by the stability of the catalyst with the polyhydroxylated substrates. Our objective is now to overcome these limitations and extend this method to more challenging substrates such as disaccharides. We proposed in this paper two original designs of Knölker-type complexes conceived to promote secondary H-bond interactions with the OH groups of the substrates to stabilise the system and favour the transformation. In total, 8 novel pre-catalysts were synthesised, fully characterised and applied in the anomeric oxidation of several sugar derivatives. Two of these new complexes proved to be more efficient than the Knölker complex for the oxidation of disaccharides. Moreover, a preliminary DFT study revealed the presence of H-bonds interactions between the substrate and the oxygen atom on the ligand arm of the best complexes suggesting a beneficial role of this heteroatom on the catalytic efficiency.

Introduction

The evolution of organic synthesis toward more sustainability has stimulated the development of eco-friendly methodologies such as catalytic transformations using earth-abundant first-row transition metals (e.g. Mn, Fe, Co, Ni etc.).^[1-5] Among these metals, iron is gaining particular interest in different fields of catalysis^[6-8] due to its availability, relatively low toxicity^[9] as well as adjustable Lewis acidity driven by a high range of formal oxidation states (-II to +VI).^[10] In this context, cyclopentadienone iron complexes represent a class of catalysts that cannot be overlooked due to their robustness, straightforward synthesis and performance in several catalytic transformations, such as hydrogenation/oxidation of ketone/alcohols, alkylation of ketones or more complex redox cascades such as reductive amination and hydrogen borrowing

processes.^[11-13] Although cyclopentadienone iron complexes have been described in the 1950s,^[14-22] pioneered applications in catalysis were first reported by Casey *et al.* in 2007 with the catalytic hydrogenation of aryl ketones and imines^[23] using the trimethylsilane (TMS) substituted cyclopentadienone complex **1a**; introduced by independent works of Pearson^[24] and Knölker^[25] in 1992 (**Figure 1a**) and commonly, recognized as Knölker pre-catalyst.

a) Knölker pre-catalyst : a versatile cyclopentadienone iron complex



b) Previous work in our team : Chemo-selective C1-oxidation of unprotected sugars

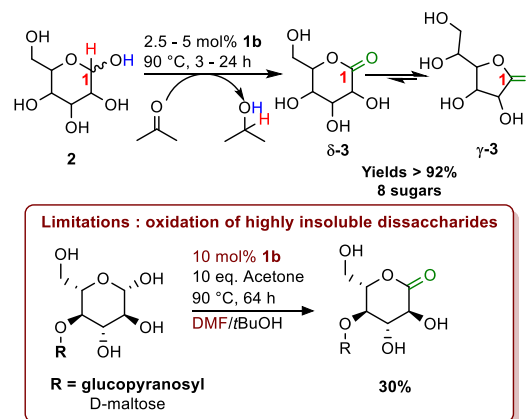


Figure 1. Knölker complex (a) and our previous results (b)

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We have recently described an innovative catalytic hydrogen transfer methodology for the chemoselective oxidation of the anomeric position of **unprotected sugars** into corresponding sugar lactones using the Knölker complexes **1a** and **1b** as catalysts in the presence of acetone as a formal hydrogen acceptor (**Figure 1b**).^[26] Catalytic transformations of **fully unprotected sugars** are still rare but represent a challenge as such methodologies could provide a sustainable way to exploit sugars from biomass.

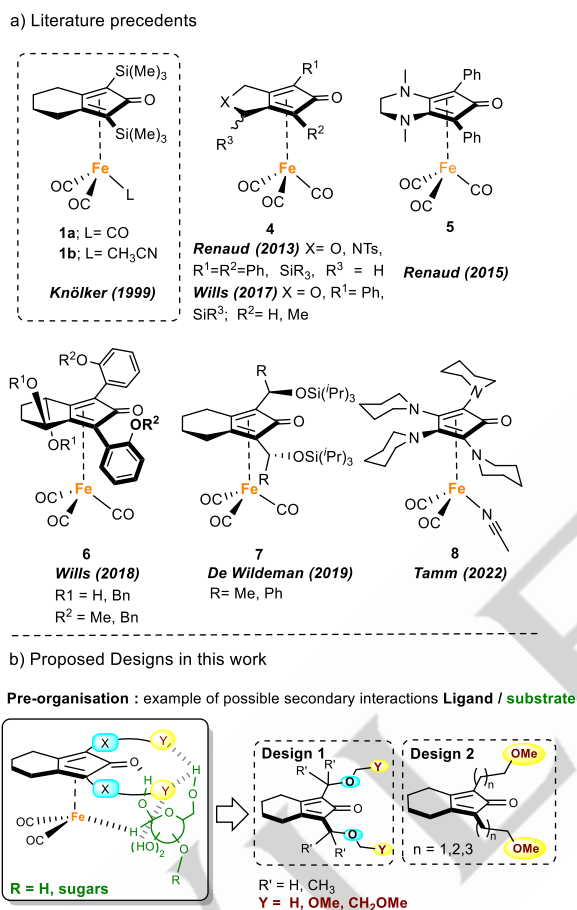


Figure 2. (a) Selected literature examples of Knölker complexes designs bearing heteroatom either on the backbone or side-arms; (b) Proposed designs of complexes.

While this approach was successful in yielding sugar lactones from various pentoses and hexoses, its efficiency toward disaccharides remained limited by the catalyst instability in the presence of such substrates. Indeed, the degradation of the catalyst seemed closely related to the nature of the substrate as the Knölker complexes (**1a & 1b**) were reported to tolerate harsher conditions (toluene 130°C or *t*BuOH 110°C).^[12] To address this limitation, our goal was to develop a novel design of Knölker-type complex. We hypothesized that by promoting secondary interactions between the catalyst and the OH groups of the substrates, we could pre-organise and stabilize the system.

To favour such interactions, we propose to add alkyl side-arms featuring heteroatoms (oxygen), on the CpCO. (**Designs 1 & 2, Figure 2b**). These types of modifications on the Knölker complexes have not been reported to date. In the literature, Knölker-type complexes with heteroatoms on the cyclohexyl backbone were found with diverse modifications often on the backbone. For example, Renaud *et al.* reported **4**^[28] and **5**^[29] (**Figure 2a**) with heteroatoms (N, O) on the backbone ring. Wills *et al.* in 2017, reported a chiral version of Renaud's catalyst (**Figure 2a**) and used them in the asymmetric hydrogenation of ketones.^[30–32] A few other contemporary chiral Knölker-type complexes are also reported with heteroatoms on their chiral backbones; such as (*R*)-BINOL derivatives,^[33–35] biotinyl^[36] *etc.* There have been very few designs (chiral and achiral) with **heteroatom added on the side arm of the cyclopentadienone with applications in catalysis**. In 2018, Wills *et al.* described chiral complexes **6** with OR₁ (R₁ = H or Bn) groups on the 2,5-positions of the cyclopentadienone in addition to *ortho*-substituted phenyl ring on the side-arms (**Figure 2a**) to amplify the steric hindrance and induce more asymmetry.^[32] In 2019, De Wildeman *et al.* proposed a C₂-symmetrical complex **7** with a bulky OTIPS group on the side chain close to the carbonyl group of the CpCO core (**Figure 2a**) for the reduction of ketone and imines.^[37] More recently, Tamm *et al.* reported the synthesis of complex tetraaminocyclopentadienone complex **8** (**Figure 2a**) presenting higher activity than other Knölker-type complexes for the reduction of ketone using low-pressure hydrogen gas (3 bar).^[38] Complexes **7** and **8** were tested for the reduction (asymmetric or non-asymmetric respectively) of ketones and imines using transfer hydrogenation or direct hydrogenation strategies.^[37,38] It is noteworthy that to the best of our knowledge, no Knölker-type complex bearing alkyl-OR side chain was used in oxidation transformation.

In this study, we will present two novel designs of Knölker-type complexes featuring selected alkyl-OR side arms. **Design 1** is based on a C(R₁)₂OR₂ with a **fixed oxygen atom on the γ -position of the C=O moiety (Figure 2b)**. In **Design 2**, the oxygen atom will be placed gradually further away from the CpCO scaffold and the influence of its position on the chain will be studied in catalysis. These catalysts were chosen as easily accessible candidates which can potentially promote secondary interactions with the substrates and potentially lead to higher efficiency. In the key step of the sequence, the aldol is described to proceed via the simultaneous transfer of both hydrogens on the oxygen and the iron atom of the catalyst.^[39,40] We should note here that before the oxidation, the iron atom will display an electron gap conferring to the iron a Lewis acid behaviour. In this context, the substrate will tend to interact by its oxygen atom's free lone pair with the catalyst, impacting the reactivity. Indeed, this type of interaction will put the substrate in the lower part of the catalyst in a stable state far from the transition state involved in the reaction. Our working hypothesis relies on the prediction that the secondary interactions created with the substrate would help to place the substrate in the upper part of the catalyst (toward the CpCO) and therefore would help to place the CH bond of the carbon atom that undergoes the oxidation to point toward the iron atom of the catalyst (**Figure 2b**). Their catalytic activities in the anomeric oxidation of unprotected sugars and

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disaccharides will be presented and compared with complexes **1a** and **1b** to evaluate the influence of the oxygen atom on the catalytic activity.

Results and Discussion

Synthesis of complexes

Designs 1 & 2 are derived from the traditional Knölker complex **1a** and will be synthesized following an analogous route starting from a symmetrical diyne. Syntheses and characterisations of the different diynes required for the preparation of the complexes are fully described in the Supporting Information. Complexes from **Design 1** are obtained via a [2+2+1] cycloaddition of the diyne **9** on iron pentacarbonyl.^[30,31,41,42] The reaction is performed at 130 °C in toluene for 24 hours.

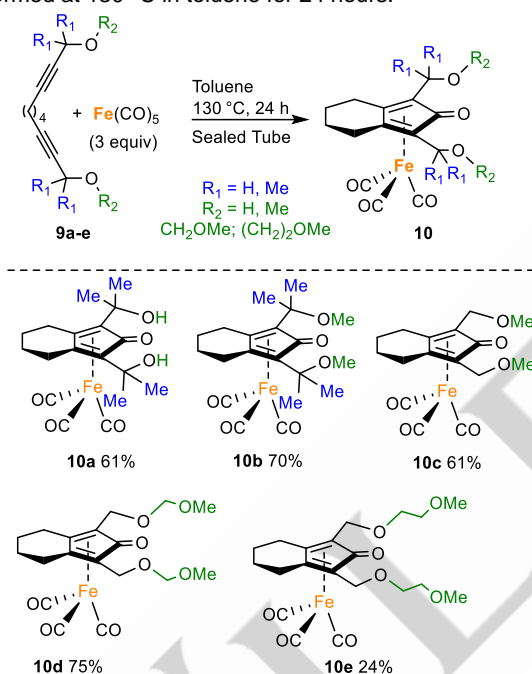


Figure 3. Synthesis of complexes derived from **Design 1**

The complexes **10a** to **10d** were obtained in moderate yields as yellow to dark-orange solids. These yields are consistent with those one usually obtained for the preparation of Knölker-type complexes. In contrast, complex **10e** was isolated pure in only 24% yields as a viscous liquid at room temperature. Complexes based on **Design 2** were prepared following a similar route from the diyne **11**. Good yields of complexes were obtained in DME.

As observed with complex **10f**, the complex with the longest side chain **10h** exhibits a lower melting point and was isolated as a thick liquid at room temperature in a lower yield. Complexes **10a** – **10h** were fully characterised (see SI). For each complex, ¹³C{¹H} NMR, exhibited a carbonyl signal between 208 – 210 ppm and a CpCO moiety between 170 – 172 ppm. No

significant differences were observed in NMR between the complex of **Design 1** and **2** in terms of the chemical shift of C=O and carbonyl groups. However, compared to the classical Knölker complex **1a** (C=O: 183 ppm), we observed a significant shielding of the carbonyl signal of the CpCO with a chemical shift standing more in the range of complex **7** (C=O: 170 ppm) (**Figure 1**).

Infrared spectra of complexes **10b**–**10h** revealed stretching frequencies of the carbonyl ligands between 1966 – 2070 cm⁻¹ and around 1626 -1640 cm⁻¹ for the C=O. These values are close to the frequencies observed for complex **7** which exhibits bands at 1980 and 2070 cm⁻¹ for the carbonyl ligands and a band at 1630 cm⁻¹ for the cyclopentadienone C=O. Complex **10a** exhibits a significantly low C=O stretching frequency at 1556 cm⁻¹ revealing hydrogen bonding between the free hydroxyl groups and the C=O moiety. These interactions are expected to decrease the electronic density around the C=O, lowering the CO bond order and provoking the shift of the stretching frequencies toward smaller values.^[43]

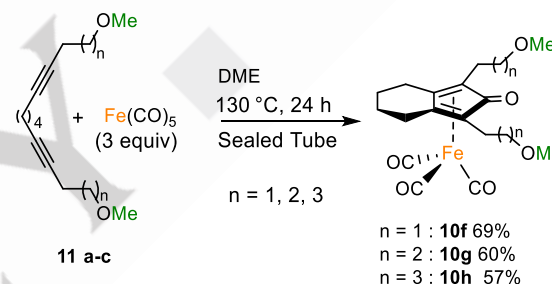


Figure 4. Synthesis of complexes derived from **Design 2**

Complexes were crystallised by slow diffusion of cyclohexane into a saturated solution of complexes in dichloromethane and the solid-state structure was determined by X-ray crystallography. For viscous/liquid compounds at room temperature (*i. e.* **10e**, **10h**) the crystallisation was successful at – 20°C. For **10a**–**h** (**Design 1 & 2**), the common structural features agree with the Knölker complex^[25] and hitherto reported cyclopentadienyl iron tricarbonyl complexes^[24,38,44–47] with a piano stool geometry. As previously observed in the classical Knölker complexes, the distances between the iron and common carbon atoms of the CpCO, C(6) and C(7) [Fe–C 2.068–2.095 Å] are shorter (~0.03 Å) than the distances between the metal and carbon atoms C(5) and C(8) [Fe–C 2.092–2.126 Å]. The iron–C(4) bond distance is also longer [Fe–C 2.331–2.421 Å] highlighting the bending arrangement of that carbonyl carbon with a torsion angle of 18–20.5° and validates the η⁴ coordination of the diene of the CpCO and is consistent with its envelope shape.

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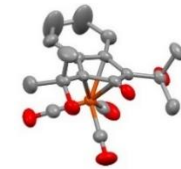
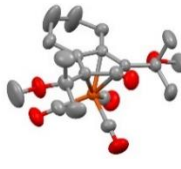
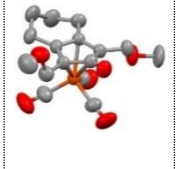
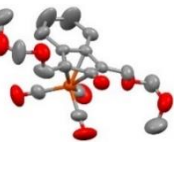
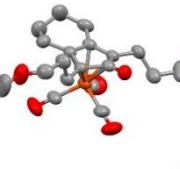
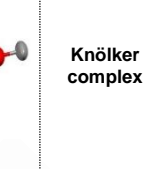
						
	10a	10b	10c	10d	10g	1a
CCDC Number	2190166	2329684	2329685	2329686	2329688	1230422 ^[25]
Fe(1)-C(4)	2.331(4)	2.421(5)	2.377(4)	2.382(4)	2.407(5)	2.397
Fe(1)-C(5)	2.114(4)	2.102(5)	2.106(4)	2.102(4)	2.126(4)	2.134(7)
Fe(1)-C(8)	2.109(4)	2.110(6)	2.090(4)	2.092(4)	2.115(6)	2.104(6)
Fe(1)-C(6)	2.084(4)	2.083(6)	2.086(4)	2.095(4)	2.084(4)	2.099(6)
Fe(1)-C(7)	2.083(3)	2.089(6)	2.068(4)	2.079(5)	2.074(5)	2.126(7)
C(4)-C(5)	1.460(6)	1.479(9)	1.475(5)	1.488(7)	1.478(8)	1.51(1)
C(4)-C(8)	1.462(6)	1.486(9)	1.463(5)	1.472(5)	1.485(5)	1.51(1)
C(5)-C(6)	1.446(6)	1.435(9)	1.428(5)	1.426(6)	1.419(5)	1.44(1)
C(7)-C(8)	1.426(6)	1.441(9)	1.426(5)	1.433(6)	1.436(7)	1.44(1)
C(6)-C(7)	1.435(6)	1.414(9)	1.421(5)	1.425(7)	1.419(7)	1.44(1)
C(4)-O(4)	1.253(6)	1.229(8)	1.227(5)	1.232(5)	1.231(6)	1.216(8)
C(5)-C(alk)	1.510(6)	1.499(9)	1.489(5)	1.476(7)	1.492(7)	1.887 (C-Si)
C(8)-C(alk)	1.529(6)	1.500(1)	1.486(5)	1.535(9)	1.485(8)	1.878 (C-Si)
C(5)-C(4)-C(8)	106.0(3)	103.3(5)	103.2(3)	102.7(4)	103.9(4)	103.4(5)

Table 1. Molecular views, Selected bond lengths (Å) and bond angle of new complexes and comparison with **1a**

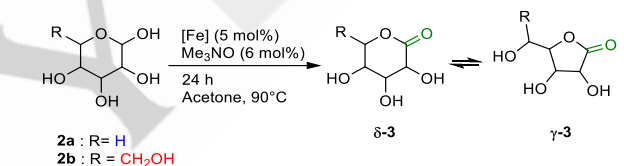
As expected, the bond distances between the CpCO core and the C-alkyl chain (1.476-1.529 Å) are shorter than the CpC-Si bond distances (1.877-1.886 Å) in the Knölker complex **1a**.^[25]

Application in catalysis

All these new complexes were initially tested on our benchmark C1-oxidation of monosaccharides and the results were compared to the performance of the traditional Knölker catalyst under the same conditions. Catalytic experiments were initially optimized on D-xylose (pentose) and D-glucose (hexose) with 5 mol% of complexes, in acetone, at 90 °C (**Table 2**). After 24 hours the yield of lactones was determined by ¹H NMR using an internal standard.

Both D-xylose and D-glucose were quantitatively converted by the Knölker complex (TMS) (**Entries 1 & 12**). Similarly, D-xylose was fully converted under these conditions with every newly synthesized complex (**Entries 2 – 11**). Complexes **10d** and **10h** were successfully tested at lower catalyst loading (2.5 mol%, **Entries 10 & 11**) with complete conversion of the xylose into xylolactones, highlighting a catalytic activity comparable to the Knölker **1a** and **1b** with pentoses. Decreasing the catalyst loading to 1.25 mol% resulted in a slight yield erosion with complex **10d** while the traditional Knölker **1a** and complex **10h** exhibited full conversion of the substrate (**Entries 12, 13 & 14**). The oxidation of D-glucose proved more challenging. When sterically constrained complexes **10a** and **10b** (**Entries 16 – 17**) were employed, the yields of lactones were limited to 33% and 22% respectively, while replacing the gem-dimethyl groups with hydrogens led to a significant yield increase (**Entries 18, 19 & 20**). We envisioned that the steric hindrance (**10a & 10b**) limits the accessibility of the C=O moiety involved in the proton transfer leading to poor catalytic activity.

Table 2. Catalytic oxidation of the anomeric position of unprotected sugars



Entry	Substrate	Pre-Catalyst (5 mol%)	% Yield (δ + γ lactones)
1		1a	> 98
2		10a	>98
3		10b	>98
4		10c	>98
5		10d	>98
6		10e	>98
7		10f	>98
8		10g	>98
9	2a R = H	10h	>98
10		10d (2.5 mol%)	>98
11		10h (2.5 mol%)	>98
12		1a (1.25 mol%)	>98
13		10d (1.25 mol%)	70
14		10h (1.25 mol%)	>98
15		1a	>98
16		10a	33
17		10b	22
18		10c	80
19		10d	>98
20	2b R = CH ₂ OH	10e	66
21		10f	74
22		10g	77
23		10h	92
24		10h (2.5 mol%)	54
25		10d (2.5 mol%)	58
26		1a (2.5 mol%)	60

Yields of lactones were determined by ¹H NMR using 1-bromo-4-nitrobenzene as an internal standard.

Moreover, the presence of hydrogen bonding (**10a**) in agreement with the IR observations discussed above could lower the Lewis basicity of the oxygen atom in C=O linkage, and be detrimental too.^[29]

Conversely, the presence of an additional heteroatom (oxygen) on the chain proved beneficial with the quantitative formation of lactones (**Entry 19**). In agreement with our working hypothesis, this oxygen atom would control the approach of the sugars and favour the transformation.

The optimal distance of the oxygen atom leading to the best catalytic activity was reached in complex (**10d**) as lower yields of lactones were observed when complex (**10e**) was employed as a catalyst (**Entries 19 & 20**).

Complexes based on **Design 2 (alkyl-OME)** with a distant oxygen atom were also effective for the oxidation of D-glucose with yields ranging between 74 – 92% (**Entries 21 – 23**). For these complexes, the activity of the catalysts seemed related to the number of carbons in the chain with an optimal efficiency obtained with complex **10h**. Noteworthy, complexes **10d** and **10h** proved as active as the Knölker complex **1a**, at lower catalyst loading (2.5 mol%) with 58% and 54% yields of lactone obtained respectively (**Entries 24 - 26**).

The complexes from both **Designs 1 and 2**, exhibiting the best activity with D-xylose and D-glucose (*i. e.* **10d & 10h**) were also tested on other pentoses and hexoses (**Figure 5**). Using a catalyst loading of 5 mol% (**10d**, **10h** or **1a**) resulted in the complete conversion of every pentoses and deoxy-hexoses into their respective lactones. The difference in reactivity between the complexes appeared when the catalyst loading was decreased to 1.25 mol%. Indeed, the Knölker catalyst allowed the conversion of each substrate into their lactones with yields above 87% while with catalysts **10d** and **10h** some substrates were not efficiently oxidised (e. g. L-arabinose). Interestingly, it was also possible to discriminate the efficiency of **10d** and **10h** with higher yields of lactones often observed with **10h**.

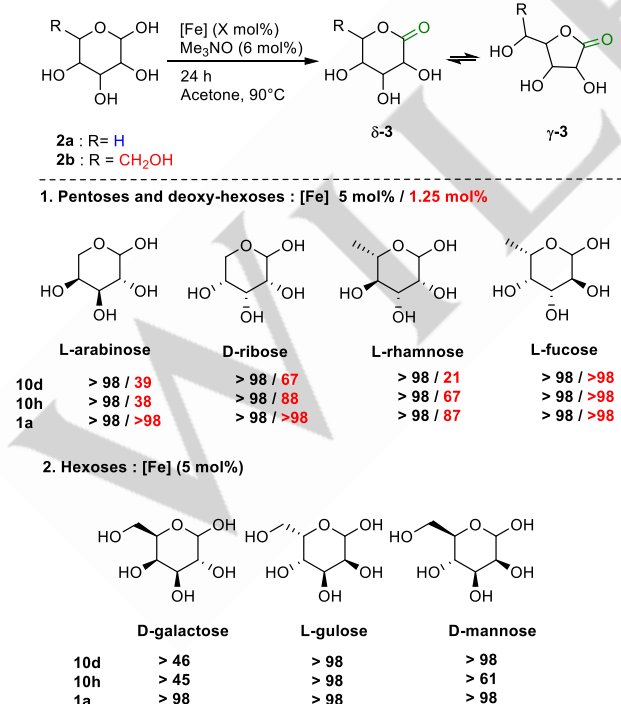


Figure 5: Monosaccharides scope. Yields of lactones were determined by ¹H NMR using 1-bromo-4-nitrobenzene as an internal standard.

Similarly, to the Knölker catalyst, D-mannose and L-gulose were quantitatively oxidized with both complexes **10d** and **10h** under the reaction condition. In contrast, D-galactose was not fully converted with moderate yields of 46% and 45% of galactolactone for **10d** and **10h**, respectively. The yield discrepancy observed between the substrates potentially suggests a potential preference of the catalyst **10d** or **10h** for some stereochemistry of sugars.

The complexes **10d** and **10h** were finally tested on the more challenging C1-oxidation of di-saccharides and their performance was compared to **1b** (in comparison to our previous study)²⁶ and **1a** (**Table 3**). The low solubility of disaccharides in *tert*-butanol at high temperatures compelled us to use DMF as a co-solvent, in the presence of 10 equivalents of acetone as acceptor, leading to the rapid degradation of the TMS-complex **1b** (10 mol%) and limited conversion with only 30% yield of lactone obtained at 90°C and 59% yield at 110°C (**Entries 1 & 2**). The discrepancy in performance between the two temperatures could likely be explained by the difference in solubility observed. To avoid the use of highly hazardous DMF, a solvent screening was performed and a mixture of *tert*-butanol and acetone (7:3) was selected as the best medium. When the reaction was carried out at 110 °C with 10 mol% or 5 mol% of catalyst **1b**, the lactone was obtained in 70% and 35% yields respectively after 72 hours (**Entries 3 & 4**). As previously observed in the literature, using tricarbonyl pre-catalyst **1a** in the presence of trimethylamine N-oxide led to similar results with only 43% of lactone observed (**Entry 5**).

Table 3. C1-oxidation of D-maltose

Entry	Catalyst (mol%)	Solvent	T°C (Time h)	% Yield 3c
1 ^{a,b}	1b (10)	<i>t</i> BuOH:DMF (80:20)	90 (64)	30
2 ^a	1b (10)	<i>t</i> BuOH:DMF (80:20)	110°C (72)	59
3	1b (10)	<i>t</i> BuOH:acetone (70:30)	110 (72)	70
4	1b (5)	<i>t</i> BuOH:acetone (70:30)	110 (72)	35
5	1a ^c (5)	<i>t</i> BuOH:acetone (70:30)	110 (72)	43
6	10d ^c (5)	<i>t</i> BuOH:acetone (70:30)	110 (72)	63
7	10h ^c (5)	<i>t</i> BuOH:acetone (70:30)	110 (72)	66

Yields of lactones were determined by ¹H NMR using 1-bromo-4-nitrobenzene as an internal standard. ^a 10 equiv. acetone; ^b *t*BuOH:DMF (80:20), 10 eq. acetone, 5 mol% **1b**, 90 °C, 24 h;^c 6 mol% of Me₃NO was added to activate *in situ* the pre-catalyst.

Novel complexes **10d** and **10h** were finally tested under these conditions. In contrast to complex **1**, the lactones were obtained in 66 % and 63% using only 5 mol% of pre-catalyst **10e** and **10h** respectively. These two pre-catalysts proved significantly more active than the traditional Knölker complex **1**, validating the role of the oxygen atom in our newly designed catalysts. Attempts to oxidize D-cellobiose and D-lactose remained unsuccessful due to

the extremely poor solubility of these two disaccharides under the reaction conditions.

Preliminary theoretical investigations

To provide some elements to rationalize our hypothesis concerning the existence of hydrogen bonds existing between the oxygenated arms of the catalyst and the substrate, we modeled the transition state involved during the oxidation of glucose in the presence of the catalyst **10h**. Transition state calculations were performed at the M06/def2-SVP level using the nudge elastic band implementation of ORCA. The 3D structure of the transition state **ts_glu_10h** highlights the presence of two hydrogen bonds; one with the primary alcohol (CH₂OH) of the sugar on one side and one with the secondary alcohol in α position of the anomeric carbon on the other side. Interestingly, on the CH₂OH side, the oxygenated side-arm of the catalyst is fully extended justifying simultaneously the shape and size of the catalyst arms. In addition, these side-arms contribute to placing the substrate in a conformation close to the transition state which presents the anomeric CH bond toward the iron atom of the catalyst.

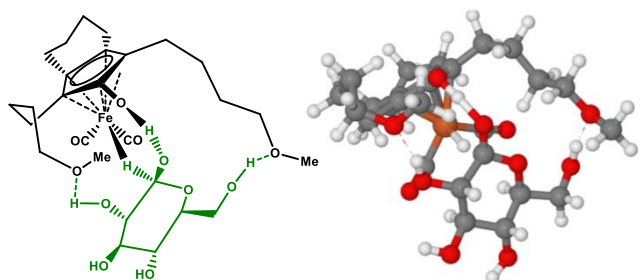


Figure 6: 3D structure of **ts_glu_10h**.

Conclusion

We report in this study 2 innovative designs of Knölker-type complexes featuring alkyl-OR side-arms on the cyclopentadienone core.

These designs aim to promote interactions with the OH groups of polyfunctional compounds and favour the reactivity of the catalyst. Eight original complexes were prepared, fully characterized and tested in the oxidation of sugar lactols into lactones. Despite the absence of a silicon atom in these catalysts and the possible electronic side-effects, each complex allowed full conversion of D-xylose into xylolactone in quantitative yields similar to the Knölker catalyst. The oxidation of D-glucose was more difficult but two new complexes were at least as efficient as the Knölker complex with high yields of lactones observed. A range of monosaccharides was then oxidized with these most active complexes and their performances were compared to the results obtained with the traditional Knölker complex. Pentoses and deoxysugars were fully converted affording quantitative yields of lactones using 5 mol% of both catalysts and exhibiting the same activity as the Knölker complex. At lower catalyst loading (1.25 mol%), the results with the newly designed catalysts were dependent on the substrates. Indeed, L-fucose and D-ribose were converted in good yields while L-arabinose was partially oxidized.

A difference in reactivity was also noticeable between the two designs introduced in favour of **Design 2** in most of the examples. Hexoses such as D-mannose and L-gulose were quantitatively oxidized into their lactones in the presence of 5 mol% of the iron catalyst. However, D-galactose proved more difficult to oxidise with our newly designed complexes.

These two pre-catalysts were then tested on more challenging substrates such as D-maltose as we previously reported major limitations with the Knölker complex for their oxidation. Our study revealed that these newly developed complexes exhibited superior performance compared to the classical Knölker complex at lower catalyst loading (5 mol% versus 10 mol%) and afforded the D-maltose corresponding lactone in good yields. Moreover, early results obtained in our theoretical investigations revealed H-bonding interactions between the substrate and the oxygen atom of the arm in complex **10h**. Even though it is difficult to exclude that the catalytic efficiency could be influenced by the steric effect of our bulky substrate,^[47] our preliminary DFT calculations highlighted the beneficial effect of the oxygen atoms on the alkyl-side arms of the catalyst and underscored the efficiency of our design. Current work in our laboratory focuses now on following our theoretical investigations to improve further the catalyst design for the oxidation of polyfunctional substrates.

Experimental section

General considerations: All the chemicals were used as received. Reagent grade THF and toluene were purchased from Fisher Scientific and were distilled on sodium benzophenone or solid CaH₂, respectively. Distilled solvents were vacuum-degassed and stored under argon with molecular sieves (4Å). Reagent-grade acetone and *tert*-butanol from Acros were degassed by argon bubbling.

General procedure for the synthesis of complex 10a – 10e (Design 1): A mixture of diyne **9** (1 equiv.) and Fe(CO)₅ (3 equiv.) in toluene (1 mL for each 25 mg of starting material) under argon was refluxed in a sealed tube for 24 hours. The resulting suspension was evaporated and the crude was purified by flash chromatography using a gradient of cyclohexane-EtOAc as eluent.

Complex 10a was synthesized starting from the diyne **9a** (0.175 g, 0.79 mmol), Fe(CO)₅ (0.47 mL, 2.37 mmol) and toluene (7 mL). **10a** was obtained as a yellow solid in 61% yields (0.187 g) after purification by flash chromatography using EtOAc-cyclohexane (1:4). **Melting Point (°C):** 168-171; **¹H NMR (δ, ppm, 300 MHz, CDCl₃):** 4.87 (broad s, 2H, OH), 2.76 (d, AB system, *J*_F = 17.1 Hz, 2H, CH₂), 2.52 (d, AB system, *J*_F = 17.1 Hz, 2H, CH₂), 1.78 (m, 4H, CH₂), 1.60 (s, 6H, CH₃), 1.43 (s, 6H, CH₃); **¹³C{¹H} NMR (δ, ppm, 75 MHz, CDCl₃):** 208.8 (s, Fe-C=O), 171.4 (s, C=O), 99.0 (s, quat C=C), 91.2 (s, quat C=C), 70.6 (s, quat C), 30.7 (s, CH₃), 29.2 (s, CH₃), 23.5 (s, CH₂), 22.1 (s, CH₂); **IR (ATR, ν_{co}, cm⁻¹):** 2070, 2000 (Fe-C≡O); 1556 (Cp-C=O). **HRMS (ESI+):** 391.0834 (calcd. for C₁₈H₂₃O₆Fe [M+H]) 391.0844).

Complex 10b was synthesized using the diyne **9b** (0.124g, 0.52 mmol), Fe(CO)₅ (0.2 mL, 2.49 mmol) and toluene (6 mL). **10b** was obtained as a pale-yellow solid in 70% yield (0.145 g) after purification by flash chromatography using EtOAc-cyclohexane

(1:9). **Melting Point (°C):** 142-144; **¹H NMR (δ, ppm, 300 MHz, CDCl₃):** 3.17 (s, 6H, OCH₃), 2.91 (d, AB system, *J*₁ = 17.7 Hz, 2H, CH₂), 2.49 (d, AB system, *J*₁ = 17.8 Hz, 2H, CH₂), 1.70 (m, 4H, CH₂), 1.62 (s, 6H, CH₃), 1.43 (s, 6H, CH₃); **¹³C{¹H} NMR (δ, ppm, 75 MHz, CDCl₃):** 209.8 (s, Fe-C=O), 170.9 (s, C=O), 100.8 (s, quat C=C), 89.0 (s, quat C=C), 74.4 (s, quat C), 47.5 (s, OCH₃), 24.9 (s, CH₃), 24.3 (s, CH₂), 22.6 (s, CH₂), 22.5 (s, CH₃); **IR (ATR, ν_{co}, cm⁻¹):** 2056, 1981 (Fe-C≡O); 1626 (Cp-C=O); **HRMS (ESI+):** 419.1177 (calcd. for C₂₀H₂₇O₆Fe [M+H] 419.1157).

Complex 10c was synthesized using the diyne **9c** (0.231 g, 3.58 mmol), Fe(CO)₅ (0.5 mL, 3.58 mmol) and toluene (9 mL) and obtained as a brownish orange solid in 61% (0.26 g) yield after purification by flash chromatography using EtOAc-Cyclohexane (4:1). **Melting Point (°C):** 51-54 ; **¹H NMR (δ, ppm, 300 MHz, CDCl₃):** 4.01 (d, AB system, *J*₁ = 11.4 Hz, 2H, OCH₂), 3.89 (d, AB system, *J*₁ = 11.5 Hz, 2H, OCH₂), 3.36 (s, 6H, OCH₃), 2.53 (m, 4H, CH₂), 1.78 (s, 4H, CH₂) ; **¹³C{¹H} NMR (δ, ppm, 75 MHz, CDCl₃):** 208.2 (s, Fe-C=O), 170.5 (s, C=O), 102.3 (s, quat C=C), 77.8 (s, quat C=C), 64.0 (s, OCH₂), 59.1 (s, OCH₃), 21.9 (s, CH₂), 21.6 (s, CH₂) ; **IR (ATR, ν_{co}, cm⁻¹):** 2065, 2006, 1966 (Fe-C≡O); 1637 (Cp-C=O) ; **HRMS (ESI+):** 363.0526 (calcd. for C₁₆H₁₉O₆Fe [M+H] 419.1157 363.0531).

Complex 10d was synthesized starting from the diyne **9d** (0.3 g, 1.2 mmol), Fe(CO)₅ (0.48 mL, 3.6 mmol) in toluene (12 mL). **10d** was obtained as a yellow solid in 75% yield (0.38 g) after purification by flash chromatography using a gradient of EtOAc-cyclohexane (80-100%). **Melting Point (°C):** ≤ 40; **¹H NMR (δ, ppm, 300 MHz, CDCl₃):** 4.70 (d, AB system, *J*₁ = 5.6 Hz, 2H, OCH₂), 4.66 (d, AB system, *J*₁ = 5.6 Hz, 2H, OCH₂), 4.18 (d, AB system, *J*₁ = 11.4 Hz, 2H, OCH₂), 4.08 (d, AB system, *J*₁ = 11.5 Hz, 2H, OCH₂), 3.39 (s, 6H, OCH₃), 2.60 (m, 4H, CH₂), 1.85 (s, 4H, CH₂); **¹³C{¹H} NMR (δ, ppm, 75 MHz, CDCl₃):** 208.2 (s, Fe-C=O), 170.7 (s, C=O), 102.1 (s, quat C=C), 96.8 (s, OCH₂O), 77.7 (s, quat C=C), 59.0 (s, OCH₂), 55.6 (s, OCH₃), 22.1 (s, CH₂), 21.7 (s, CH₂); **IR (ATR, ν_{co}, cm⁻¹):** 2056, 2008, 1984 (Fe-C≡O); 1641 (Cp-C=O); **HRMS (ESI+):** 423.0725 (calcd. for C₁₈H₂₃O₈Fe [M+H] 423.0742).

Complex 10e was synthesized from the diyne **9e** (0.42 g, 1.51 mmol), Fe(CO)₅ (0.6 mL, 4.53 mmol) in toluene (17 mL). **10e** was obtained as a dark brown viscous liquid in 24% yield (0.154 g) after purification by chromatography using a gradient of EtOAc-cyclohexane (80-100%). **Melting Point (°C):** ≤ 40; **¹H NMR (δ, ppm, 300 MHz, CDCl₃):** 4.16 (d, AB system, *J*₁ = 11.7 Hz, 2H, OCH₂), 4.01 (d, AB system, *J*₁ = 11.7 Hz, 2H, OCH₂), 3.69-3.66 (m, AB system, 4H, OCH₂), 3.53-3.50 (m, AB system, 4H, OCH₂), 3.34 (s, 6H, OCH₃), 2.58 (m, 4H, CH₂), 1.81 (s, 4H, CH₂); **¹³C{¹H} NMR (δ, ppm, 75 MHz, CDCl₃):** 208.2 (s, Fe-C=O), 170.6 (s, C=O), 102.7 (s, quat C=C), 77.8 (s, quat C=C), 71.9 (s, OCH₂), 70.4 (s, OCH₂), 62.6 (s, OCH₂Cp), 59.0 (s, OCH₃), 22.0 (s, CH₂), 21.7 (s, CH₂); **IR (ATR, ν_{co}, cm⁻¹):** 2064, 1986 (Fe-C≡O); 1638 (Cp-C=O); **HRMS (ESI+):** 451.1047 calcd. for C₂₀H₂₇O₈Fe [M+H] 451.1055).

General procedure for the synthesis of complex 10f – 10h (Design 2): A mixture of diynes **11** (1 equiv.) and Fe(CO)₅ (3 equiv.) in DME (1 mL for each 25 mg of starting material) under argon was refluxed in a sealed tube for 24 hours. The resulting dark green suspension was evaporated and the crude mixture

was purified by flash chromatography using a gradient of cyclohexane-EtOAc as eluent.

Complex 10f was synthesized from the diyne **11a** (0.364 g, 1.64 mmol), Fe(CO)₅ (0.64 mL, 4.92 mmol) in DME (15 mL). **10f** was obtained as a low melting point brownish orange solid in 69% yield (0.44 g) after purification by flash chromatography using EtOAc-cyclohexane (4:1). **Melting Point (°C):** ≤ 40; **¹H NMR (δ, ppm, 300 MHz, CDCl₃):** 3.69-3.62 (td, AB system, *J*₁ = 9.0 Hz, *J*₂ = 6.8 Hz, 2H, OCH₂), 3.55-3.48 (td, AB system, *J*₁ = 9.1 Hz, *J*₂ = 6.3 Hz, 2H, OCH₂), 3.33 (s, 6H, OCH₃), 2.53 (m, 4H, CH₂), 2.35 (t, *J*₁ = 6.5 Hz, 4H, CH₂), 1.81 (s, 4H, CH₂); **¹³C{¹H} NMR (δ, ppm, 75 MHz, CDCl₃):** 209.2 (s, Fe-C=O), 171.5 (s, C=O), 102.1 (s, quat C=C), 79.8 (s, quat C=C), 71.2 (s, OCH₂), 58.6 (s, OCH₃), 24.4 (s, CH₂), 22.1 (s, CH₂), 21.7 (s, CH₂); **IR (ATR, ν_{co}, cm⁻¹):** 2054, 1974 (Fe-C≡O); 1627 (Cp-C=O) ; **HRMS (ESI+):** 391.0836 (calcd. for C₁₈H₂₃O₆Fe [M+H] 391.0844).

Complex 10g was synthesized from the diyne **11b** (0.17 g, 0.68 mmol), Fe(CO)₅ (0.27 mL, 2.04 mmol) in DME (7 mL) and obtained as a low melting point brownish orange solid in 60% yield (0.17 g) after purification by flash chromatography using EtOAc-cyclohexane (4:1); **Melting Point (°C):** ≤ 40 ; **¹H NMR (δ, ppm, 300 MHz, CDCl₃):** 3.44 (t, *J*₁ = 6.1 Hz, 4H, OCH₂), 3.33 (s, 6H, OCH₃), 2.56-2.42 (m, 4H, CH₂), 2.29-2.19 (m, AB system, 2H, CH₂), 2.12-2.02 (m, AB system, 2H, CH₂), 1.97-1.73 (m, 4H, CH₂), 1.83 (s, 4H, CH₂) ; **¹³C NMR (δ, ppm, 75 MHz, CDCl₃):** 209.4 (s, Fe-C=O), 171.4 (s, C=O), 101.3 (s, quat C=C), 83.2 (s, quat C=C), 72.5 (s, OCH₃), 58.6 (s, OCH₂), 29.7 (s, CH₂), 22.2 (s, CH₂), 21.6 (s, CH₂), 21.0 (s, CH₂) ; **IR (ATR, ν_{co}, cm⁻¹):** 2046, 1970 (Fe-C≡O); 1638, 1613, 1584 (Cp-C=O) ; **HRMS (ESI+):** 419.1146 (calcd. for C₂₀H₂₇O₆Fe [M+H] 419.1157).

Complex 10h was synthesized from the diyne **11c** (0.3 g, 1.1 mmol), Fe(CO)₅ (0.9 mL, 6.57 mmol) and DME (12.5 mL). **10h** was obtained as an orange viscous liquid in 57 % yield (0.23 g) after purification by flash chromatography using EtOAc-cyclohexane (4:1). **Melting Point (°C):** ≤ 40 ; **¹H NMR (δ, ppm, 300 MHz, CDCl₃):** 3.38 (dt, *J*₁ = 5.7 Hz, *J*₂ = 1.8 Hz, 4H, OCH₂), 3.30 (s, 6H, OCH₃), 2.53-2.40 (m, 4H, CH₂), 2.27-2.17 (m, AB system, 2H, CH₂), 1.98-1.89 (m, AB system, 2H, CH₂), 1.81 (s, 4H, CH₂), 1.65-1.49 (m, 8H; 4H, CH₂ + 4H, CH₂) ; **¹³C{¹H} NMR (δ, ppm, 75 MHz, CDCl₃):** 209.4 (s, Fe-C=O), 171.2 (s, C=O), 101.2 (s, quat C=C), 83.4 (s, quat C=C), 72.6 (s, OCH₃), 58.7 (s, OCH₂), 30.1 (s, CH₂), 26.5 (s, CH₂), 24.1 (s, CH₂), 22.1 (s, CH₂), 21.6 (s, CH₂); **IR (ATR, ν_{co}, cm⁻¹):** 2052, 1971 (Fe-C≡O); 1637 (Cp-C=O); **HRMS (ESI+):** 447.1451 (calcd. for C₂₂H₃₁O₆Fe [M+H] 447.1470).

General Procedure for the oxidation of hexoses and pentoses: In a sealed tube containing a hexose or a pentose (50 mg, X mmol), the pre-catalyst **10** (5 mol%) and Me₃NO (6 mol%) under Argon atmosphere, acetone (0.8 mL) was added and degassed with argon for 2-3 min. The reaction was stirred at 90°C for 24 hours. Then, the crude mixture was evaporated under reduced pressure and 1-bromo-4-nitrobenzene (1 equiv.) was added as the internal standard. A sample for ¹H NMR was prepared in DMSO-D₆ after filtration through a PTFE filter (0.2 μm). Yield of sugars lactones and ratios of 1,5-δ- and 1,4-γ-lactones (δ-3 and γ-3) were determined from the ¹H NMR spectrum.

General procedure for the catalytic oxidation of disaccharides:

Solvent-acceptor mix (0.8 mL) was degassed with argon for 15 min in a sealed tube after the addition of disaccharides (D-maltose, 50 mg, 0.146 mmol) catalyst **1a**, **1b**, **10d** or **10h** (5 or 10 mol%). When catalyst **1a** was used, Me₃NO was added (1.2 X 5 mol%). The reaction was stirred at 110°C for 72 hours before the addition of 1-bromo-4-nitrobenzene (1 equiv.) as an internal standard and evaporation to dryness. The yield of lactone was determined by ¹H NMR in DMSO-d₆, after filtration through a PTFE filter (0.2 μm).

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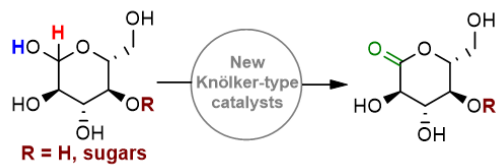
Keywords: Homogeneous Catalysis • Ligand design • oxidation • sugars derivatives • iron catalyst •

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RESEARCH ARTICLE

Entry for the Table of Contents

- 2 novel catalyst designs : 8 Knölker-type complexes
- Catalytic Application : C1-oxidation of sugars derivatives



Higher efficiency than the Knölker on the oxidation of disaccharides

Designed to promote secondary H-bond interactions

